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Provisional Publication Schedule for 1969

In the interests of rapid publication it has been found necessary to schedule 5 volumes for appearance in 1969. Since monthly publication will be maintained, this implies that 2 of the volumes will each consist of three issues, while 3 of the volumes will each consist of only 2 issues. The following provisional schedule applies:

Vol. **44,** No. **1**	January 1969	
Vol. **44,** No. **2**	February 1969	**(completing Vol. 44)**
Vol. **45,** No. **1**	March 1969	
Vol. **45,** No. **2**	April 1969	
Vol. **45,** No. **3**	May 1969	**(completing Vol. 45)**
Vol. **46,** No. **1**	June 1969	
Vol. **46,** No. **2**	July 1969	**(completing Vol. 46)**
Vol. **47,** No. **1**	August 1969	
Vol. **47,** No. **2**	September 1969	
Vol. **47,** No. **3**	October 1969	**(completing Vol. 47)**
Vol. **48,** No. **1**	November 1969	
Vol. **48,** No. **2**	December 1969	**(completing Vol. 48)**

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PROF. PHILIP W. WEST,
Coates Chemical Laboratories,
College of Chemistry and Physics,
Louisiana State University,
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La. 70803 (U.S.A.)

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Department of Chemistry,
The University,
P.O. Box 363
Birmingham 15 (Great Britain)

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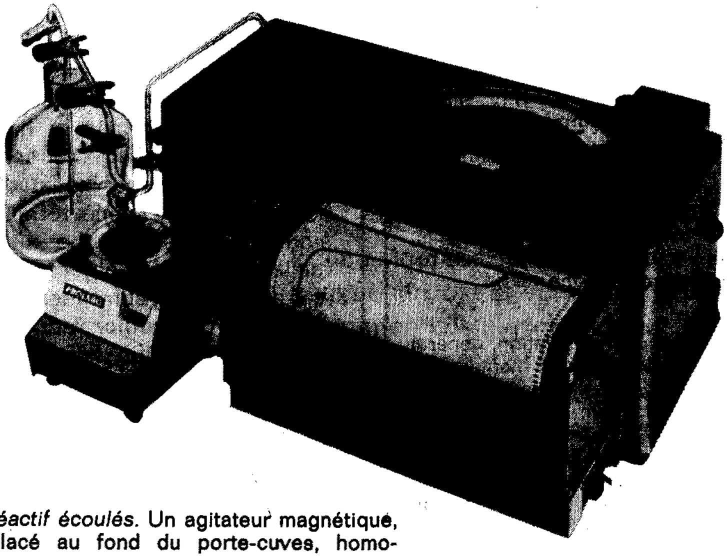
SPECTROPHOTOMETRE

Jean et Constant **à enregistreur**

Domaine de longueurs d'ondes 375 à 1100 mm

La Société PROLABO a mis au point, en collaboration avec le Commissariat à l'Energie Atomique, un dispositif d'enregistrement adapté au spectrophotomètre Jean et Constant. L'instrument fonctionne automatiquement. Il enregistre les variations de densité optique d'un échantillon à une *longueur d'ondes fixe* choisie à l'avance.
Ce nouveau spectrophotomètre peut tout d'abord servir à faire des *mesures automatiques* en série, en passant successivement des échantillons divers, soit dans des cuves distinctes introduites les unes après les autres dans l'appareil, soit dans une cuve à circulation. Toutes les cuves et les porte-cuves normaux peuvent être utilisés, ce qui permet d'effectuer automatiquement toutes les mesures habituellement pratiquées avec l'appareil manuel classique. L'instrument peut encore servir à faire des titrages photométriques dans un bécher, en le reliant à une burette à moteur synchronisé avec le déroulement du papier enregistreur: la courbe enregistrée donne alors la *densité optique du milieu réactionnel en fonction des volumes de réactif écoulés.* Un agitateur magnétique, placé au fond du porte-cuves, homogénéise le contenu du vase à réaction sans interférer dans le faisceau lumineux. Sont justiciables de la méthode de titrage photométrique toutes les réactions qui s'accompagnent d'un changement de coloration de l'élément à doser, du réactif de titrage, ou encore d'un indicateur coloré. La détermination du point d'équivalence sur la courbe enregistrée est très précise. Cette méthode est précieuse en *complexométrie,* où les indicateurs colorés donnent des virages apparemment indistincts. Les éléments couramment dosés sont le calcium, le magnésium, le fer, l'aluminium, le cuivre, le zinc, le titane, les sulfates, fluorures, chlorures, etc.



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THE CHEMISTRY OF TITANIUM AND VANADIUM

AN INTRODUCTION TO THE CHEMISTRY OF THE EARLY TRANSITION ELEMENTS

by R. J. H. CLARK, University College, London (Great Britain)

Monograph 11 in the series Topics in Inorganic and General Chemistry edited by P. L. Robinson

With the development of techniques for handling air-sensitive materials, many aspects of the chemistry of titanium and vanadium have developed very rapidly, most noticeably in the last ten years. This is the first book to summarise and critically assess these developments, and to point to likely areas for further research. The chemistry of these two elements is in many ways very similar and the comparisons drawn within this book help to focus attention on the similarities.
The book is devoted to the preparations, properties and structures of the various compounds of titanium and vanadium. Many possible avenues for further research are indicated in the text.

Contents: 1. Discovery, isolation, general and elementary properties of titanium and vanadium. 2. Halides and oxyhalides. 3. Complexes of titanium (IV), vanadium (IV) and (V). 4. Complexes of tervalent titanium and vanadium. 5. Complexes of titanium and vanadium in the oxidation states two, and lower. 6. Spectra and magnetism of titanium and vanadium complexes. 7. Metal oxo species. 8. Organometallic compounds. 9. Oxides, sulphides and other binary compounds. 10. Other topics. Appendix. Subject index.

5½ x 8½", xi + 327 pages, 67 tables,
35 illus., 1055 lit.refs., 1968
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THE *ODD* BOOK OF DATA

by **R. HOUWINK**
Wassenaar, The Netherlands

6 x 9", ix + 105 pages, 28 diagrams, 6 tables,
1965, reprinted 1966,
Dfl. 12.50, 30s., US$5.00

This intriguing and often amusing volume attempts to put science in perspective. Although Man claims to be Nature's most accomplished observer he nevertheless falls sadly short in one important respect - he cannot fully appreciate the enormity of his own discoveries. To grasp the scale of the natural phenomena his studies reveal he must evolve some form of expression which relates the intangible to familiar every day objects. To this end, and by precise yet frequently surprising examples, the author reduces the most advanced scientific data to terms which are sure to fascinate every reader.

Of interest to: Scientists in all disciplines and at all levels; all laymen interested in the world in which they live.

Contents: Introduction. Acknowledgements The Universe. The Earth. Physics. Atoms and Molecules. Botany. Biology. Mankind. Sense organs. Energy. Some technical facts. Science and education. Economy. Transport and communication. Oddly enough. References. Basic numerical data.

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 44, No. 2, February 1969

A CRITICAL REVIEW OF ELECTROANALYTICAL METHODS FOR THE NOBLE METALS

This review deals with the published electroanalytical methods of polarography, coulometry, amperometry, potentiometry and electrogravimetry. For polarography, the period covered is subsequent to June 1958. For potentiometry, the reports included are in general those published after a previous review on titrimetric methods. The remaining electroanalytical methods for the noble metals have only recently received significant attention; the review of these methods, as well as the others, covers the chemical abstracts up to January 1968.

During the past decade polarographic methods have taken an important place in industrial laboratories dealing with noble metals; such methods remain largely confined to simple systems although there has occasionally been some integration with other analytical techniques to allow application to complex noble metal systems. Coulometry and amperometry seem to find little application in laboratories concerned with determination of noble metals, possibly because of a lack of analytical emphasis in the reported researches. The review should make clear the paucity of industrial interest in electrogravimetric methods.

F. E. Beamish,
Anal. Chim. Acta, 44 (1969) 253–286

STUDIES IN THE TETRAARYLBORATES

PART IV. THE PREPARATION AND REAGENT PROPERTIES OF SODIUM TETRAKIS (*m*-TRIFLUOROMETHYLPHENYL)BORATE

Sodium tetrakis (*m*-trifluoromethylphenyl)borate has been synthesized and shown to be a highly selective reagent for cesium ion even in the presence of other alkali metal ions. Equivalent amounts of rubidium or potassium do not interfere.

M. Meisters, C. E. Moore and F. P. Cassaretto,
Anal. Chim. Acta, 44 (1969) 287–291

THE DETERMINATION OF SODIUM AND POTASSIUM AFTER SEPARATION FROM EACH OTHER AND OTHER IONS BY MEANS OF AMMONIUM PHOSPHOMOLYBDATE AND OTHER ION EXCHANGERS

The separation of sodium and potassium by means of ammonium molybdophosphate (AMP) cation-exchange columns is described. Up to 0.1 meq of potassium can be separated quantitatively from amounts up to 50 meq of sodium on a small (4 g AMP) column. With as much as 0.25 meq of potassium, quantitative separation can be effected by the successive use of two small columns. By a combination of this separation with conventional ion-exchange methods, sodium and potassium can be determined individually in the presence of varous other cations.

C. J. Coetzee and E. F. C. H. Rohwer,
Anal. Chim. Acta, 44 (1969) 293–299

CONCENTRATION AND DETERMINATION OF TRACES OF METAL IONS

A procedure for the preconcentration and determination of Ag^+, Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} is presented. The conditions for the simultaneous extraction of all these metal ions with dithizone in ethyl propionate are described. The metal dithizonates are very stable in ethyl propionate and the chelate–solvent system enhances the sensitivity for the atomic absorption method used for the determination. With 10:1 aqueous–organic solvent ratios, the sensitivities for 1% absorption of the signal range from 0.001 μg/ml for Cd^{2+} and Zn^{2+}, to 0.004 μg/ml for Pb^{2+}. Interference effects of 38 diverse ions and compounds were studied and their tolerance levels are given. The resulting procedure is very sensitive and selective.

S. L. Sachdev and P. W. West,
Anal. Chim. Acta, 44 (1969) 301–307

COMPLEX FORMATION IN THE COPPER(II)–TARTARIC ACID SYSTEM

Copper(II) complexes with (+)-, (−)-, and (±)-isomeric forms of tartaric acid have been investigated by a polarographic method. At pH 2–5 only one complex species was found: monotartaratocopper(II), with a stability constant of $10^{3.2}$. No difference between the isomeric tartaric acids was found as far as their complexing abilities are concerned.

Vl. Simeon, K. Voloder and O. A. Weber,
Anal. Chim. Acta, 44 (1969) 309–313

STUDIES OF URANIUM(VI) COMPLEXES OF OXINE IN CHLOROFORM

The solubilities and absorption spectra of uranium(VI)–oxine complexes in chloroform were studied. The solubility of the 1:2 complex in chloroform was found to be $3.99 \cdot 10^{-4}$ *M*. In chloroform containing ethanol, the 1:2 complex decomposed: $3UO_2Ox_2 + C_2H_5OH \rightarrow (UO_2Ox_2)_2HOx + UO_2Ox \cdot OH_5C_2$. The solubilities of the 1:3 complex in chloroform and chloroform containing ethanol were $8.35 \cdot 10^{-4}$ *M* and $9.86 \cdot 10^{-4}$ *M*, respectively. The presence of a 1:4 complex, $UO_2Ox_2 \cdot 2HOx$, was suggested by the decrease in the solubility of the 1:3 complex with increasing amount of oxine in chloroform. The presence of the 1:4 complex was also supported by the spectral change of a solution containing the 1:3 complex when oxine was added to the solution. The absorption spectra of the 1:2, 2:5, and 1:4 complexes are given.

S. Ōki,
Anal. Chim. Acta, 44 (1969) 315–322

SOURCES OF ERROR IN THE USE OF ARSONIUM REAGENTS

PART I. COMPOSITIONS AND THERMAL STABILITIES OF SOME TETRAPHENYL- AND TRIPHENYLMETHYL-ARSONIUM SALTS

A search has been made for sources of error in the use of arsonium salts as reagents. Compositions, thermogravimetric curves and hydrate vapor pressures have been measured for a variety of tetraphenylarsonium and triphenylmethylarsonium salts and triphenylarsine oxide. Some of the salts are hygroscopic and form hydrates. Tetraphenylarsonium salts are more stable to heat than triphenylmethylarsonium salts. Some published data on these compounds are incorrect.

K. W. Loach,
Anal. Chim. Acta, 44 (1969) 323–332

SPECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM WITH CHROME AZUROL S

The well-known determination of beryllium with chrome azurol S may be carried out at pH 4.9 ± 0.1 (pyridine or acetate), at pH 6.7 ± 0.2 (TRIS buffer), at pH 10.0 ± 0.2 in aqueous medium, or at pH 6.5 ± 0.4 (hexamethylenetetramine) in the presence of polyvinyl alcohol. These conditions correspond to the sole presence of three particular complexes of beryllium with chrome azurol S. In presence of polyvinyl alcohol, the sensitivity reaches 1.75 ng Be/ml for an absorbance of 0.01 at 6.15 nm. EDTA, Ca–EDTA and Ca–CDTA are effective masking agents in the different procedures.

L. SOMMER AND V. KUBÁŇ,
Anal. Chim. Acta, 44 (1969) 333–344

SPECTROPHOTOMETRIC DETERMINATION OF MAGNESIUM WITH CHROMOTROPE 2R

APPLICATION TO ZINC AND ALUMINUM ALLOYS

Chromotrope 2R forms a pink complex ($\lambda_{max}=570$ nm) with magnesium in aqueous acetone medium at pH 10.8; down to 0.01 p.p.m. of magnesium can be determined spectrophotometrically. The method is sensitive ($\varepsilon=37{,}000$) and relatively selective. The colour is formed immediately, and is stable for 90 min. Zinc (200 mg), aluminum (10 mg), iron(III) (20 mg), manganese (1.5 mg), copper (1 mg), lead (0.7 mg), cadmium (1 mg), tin (0.5 mg), and nickel (0.02 mg) do not interfere in the presence of triethanolamine and many other metals can be tolerated; large amounts of beryllium interfere. The method is applicable to the direct determination of magnesium (0.01–4%) in zinc and aluminum alloy die castings.

S. SHIBATA, A. UCHIUMI, S. SASAKI AND K. GOTO,
Anal. Chim. Acta, 44 (1969) 345–352

THE DETERMINATION OF VANADIUM IN SILICATE MATERIALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

A method was developed for the determination of vanadium down to 5 p.p.m. in silicate materials on the basis of a 1-g sample. The absorption of the vanadium was measured after aspiration of a solution of the vanadium–cupferron complex in *n*-butyl acetate. Vanadium (V) was extracted, after oxidation with potassium periodate, from an aqueous solution containing 5% (v/v) of sulphuric acid and 50 mg of molybdenum (as molybdate), to avoid serious interference by other elements. Sodium phosphate was added to mask any iron, which can be tolerated in amounts up to 200 mg in the aqueous solution being extracted.

D. C. G. PEARTON, J. D. TAYLOR, P. K. FAURE AND T. W. STEEL
Anal. Chim. Acta, 44 (1969) 353–359

ANALYTICAL APPLICATIONS OF THE PHOSPHATASE ENZYME SYSTEM

DETERMINATION OF BISMUTH, BERYLLIUM AND PESTICIDES

A fluorimetric method is described for the determination of bismuth and beryllium, and the pesticides methyl parathion, Aldrin and Heptachlor. The procedure is based on the inhibition of acid and alkaline phosphatase by these substances. The substrate umbelliferone phosphate is used, which is cleaved by phosphatase to the highly fluorescent umbelliferone ($\lambda_{ex}=346$ nm at pH 5, and $\lambda_{ex} = 365$ nm at pH 8; $\lambda_{em} = 450$ nm). Beryllium (0.01–0.30 µg/ml), bismuth (1–70 µg/ml), Aldrin (5–100 µg/ml) and Heptachlor (50–700 µg/ml) inhibit the hydrolysis catalyzed by alkaline phosphatase, and methyl parathion (5–500 µg/ml) that catalyzed by acid phosphatase, causing a decrease in the slopes of the fluorescence–time curves. This decrease is a direct measure of the concentration of inhibitor.

4-Methylumbelliferone nonanoate was found to be a good substrate for acid phosphatase in the presence of large amounts of phosphate (1.0 *M*). As little as 0.00006 units of acid phosphatase can be assayed with an accuracy and precision of 2%.

G. G. GUILBAULT, M. H. SADAR AND M. ZIMMER,
Anal. Chim. Acta, 44 (1969) 361–367

AN AUTOMATED COULOMETRIC TITRATOR AND ITS APPLICATION TO THE DETERMINATION OF WATER

An automated coulometric titrator and its successful application to the determination of water *via* a Karl Fischer-type reaction is described. Coulometric *in situ* generation of the highly moisture-sensitive Karl Fischer reagent is used to determine accurately the water content of a variety of compounds. The titrator is applicable to all levels of water, from hydrocarbons containing a few parts-per-million water to samples consisting of pure water.

J. L. HOYT,
Anal. Chim. Acta, 44 (1969) 369–375

THE DETERMINATION OF STABILITY CONSTANTS FROM CONTINUOUS VARIATION DATA

A method for the determination of stability constants of complexes in solution is described. It is based on the method of continuous variation and on computer calculated values of the maximum complex concentrations for different total molar concentrations. The measurements are carried out in cells of different light paths, and the molar concentration sum is chosen so that the product of the light path and the concentration sum is constant. The method can be used to differentiate between monomeric and dimeric complexes A_mB_n, with $m = n$.

K. S. KLAUSEN,
Anal. Chim. Acta, 44 (1969) 377–384

FLUORESCENCE AND METALLIC VALENCY STATES

PART I. DETERMINATION OF SILVER WITH OXINE-5-SULPHONIC ACID

Small amounts (0.1–10 µg) of silver can be determined by measurement of the fluorescent intensity (at 485 nm) obtained on addition of persulphate to aqueous solutions (pH 1.5–3.5) containing mum complex concentrations for different total molar concentrations. silver(I) and oxine-5-sulphonic acid. Fluorescence intensity is linear from 12.5 p.p.b. to 5 p.p.m. and most metal ions do not interfere; 1 p.p.m. of copper, mercury or palladium causes fluorescence quenching whilst similar amounts of zirconium and hafnium form strongly fluorescent chelates and cause high results. The reaction involves formation of silver(III) which then reacts with the oxine-5-sulphonic acid to give the fluorescent product.

D. E. RYAN AND B. K. PAL,
Anal. Chim. Acta, 44 (1969) 385–389

THE QUANTITATIVE ANALYSIS OF HYDRAZINE MIXTURES BY PROTON MAGNETIC RESONANCE SPECTROMETRY

The application of proton magnetic resonance spectrometry to the quantitative analysis of binary and ternary mixtures of hydrazine, monomethylhydrazine, and asymmetrical dimethylhydrazine is described. The methyl absorptions and the amine exchange absorption serve as reciprocating internal reference standards. The integrated absorptions, corrected statistically to area per proton, are used in simultaneous equations. The solution of the equations yields the analytical result expressed as mole fraction. Twenty seven hydrazine mixtures were analyzed; the average deviation in mole fraction was less than 0.01.

J. C. MacDonald,
Anal. Chim. Acta, 44 (1969) 391–395

FLUORIMETRIC DETERMINATION OF OXALATE ION

A very selective, simple, sensitive fluorimetric method for the determination of oxalate ion is described. The method is based on the quenching by oxalate of the fluorescence of a 1:1 zirconium–flavonol chelate in dilute sulfuric acid solution. The fluorescence is measured at 460 nm. A linear calibration curve is obtained for 0–10 μg of oxalate ion; there are very few interferences.

D. A. Britton and J. C. Guyon,
Anal. Chim. Acta, 44 (1969) 397–401

AN IMPROVED FLUORIMETRIC DETERMINATION OF HISTAMINE BY STABILIZING THE *o*-PHTHALALDEHYDE REAGENT

An improved fluorimetric determination of histamine based on the formation of a fluorophore between histamine and *o*-phthalaldehyde (OPT) is obtained if conditions are maintained anhydrous during recrystallization of the OPT and for the preparation and storage of the OPT solution in *p*-xylene. The increased precision of the method is reflected by a relative standard deviation of 0.007, for 37 aliquots of a *p*-xylene solution of OPT removed over a 2-week period. The calibration curve is linear above 10 ng of histamine, at which lower limit the fluorescence intensity of the fluorophore is almost twice that of the blank.

M. Yusem, W. E. Delaney, M. A. Lindberg and E. M. Fashing.
Anal. Chim. Acta, 44 (1969) 403–409

PRECISION POLAROGRAPHY BY TIME-INTEGRATION OF THE DIFFUSION CURRENT

A new method of measuring the polarographic limiting current is described, based on integrating it over a precisely known time interval which includes 50 or more mercury drops. The averaging effect of integration minimizes the influence of small random variations in the factors which govern the diffusion current and is conducive to high precision. The electrical instrumentation, which produces the time integral as a direct readout, is relatively simple, and all components are available commercially as complete units whose assembly requires only interconnection. Provided that the correction for any preceding diffusion currents is smaller than the one being measured, and by comparison with a standard solution, substances present at concentrations of 1–10 m*M* are determinable with a precision and accuracy of the order of ± 0.1%.

J. J. Lingane,
Anal. Chim. Acta, 44 (1969) 411–424

ANODIC STRIPPING SQUARE-WAVE VOLTAMMETRIC DETERMINATION OF LEAD IN HIGH-PURITY BISMUTH

Anodic stripping voltammetry of lead with a mercury-plated platinum electrode and the square-wave technique is described. In combination with anion-exchange separation in nitric and hydrochloric acid media, this method is applicable to the determination of down to 0.01 p.p.m. of lead in high-purity bismuth. The error is about ±5% at the 0.6 p.p.m. level.

A. Mizuike, T. Miwa and S. Oki,
Anal. Chim. Acta, 44 (1969) 425–430.

SIMULTANEOUS DETERMINATION OF STRONTIUM AND BARIUM BY NEUTRON ACTIVATION ANALYSIS WITH A Ge(Li) DETECTOR

A method is described for the simultaneous determinations of strontium and barium in rock samples by neutron activation analysis with a Ge(Li) detector after chemical group-separation. The re-activation technique was employed to obtain the chemical yields for both elements without any additional chemical treatment. The values obtained for several geochemical standard rocks (G-1, W-1, G-2, GSP-1, AGV-1 and BCR-1) are in reasonable agreement with previously published data.

H. Higuchi and K. Tomura,
H. Takahashi and N. Onuma and H. Hamaguchi,
Anal. Chim. Acta, 44 (1969) 431–436

THE DETERMINATION OF MOLYBDENUM BY ATOMIC ABSORPTION SPECTROSCOPY

(Short Communication)

T. V. Ramakrishna, P. W. West and J. W. Robinson,
Anal. Chim. Acta, 44 (1969) 437–439

SPECIFIC MICRODETERMINATION OF VANADIUM(V) ON THE RING OVEN

(Short Communication)

E. Jungreis and P. W. West,
Anal. Chim. Acta, 44 (1969) 440–442

DERIVATIVES OF SALICYLKETONES.

PART III. THE DETERMINATION OF PALLADIUM WITH N,N′-BIS(*o*-AMINOACETOPHENONE) ETHYLENEDIIMINE

(Short Communication; in German)

V. E. Uhlemann and M. Plath,
Anal. Chim. Acta, 44 (1969) 442–444

THE ANALYSIS OF INORGANIC SILICEOUS MATERIALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY AND THE HYDROFLUORIC ACID DECOMPOSITION TECHNIQUE.

PART IV. THE ANALYSIS OF CEMENTS, CLINKERS, RAW MIXES AND SILICEOUS LIMESTONES

(Short Communication)

F. J. Langmyhr and P. E. Paus,
Anal. Chim. Acta, 44 (1969) 445–446

SUPPLEMENTARY INTERPRETATIONS OF THE NMR SPECTRA OF PHOSPHORUS PESTICIDES

(Short Communication)

L. H. Keith and A. L. Alford,
Anal. Chim. Acta, 44 (1969) 447–448

SPECTROPHOTOMETRIC DETERMINATION OF PHENOLIC HYDROXYL GROUPS WITH TITANIUM(IV) CHLORIDE AS REAGENT

(Short Communication)

D. R. Jacob,
Anal. Chim. Acta, 44 (1969) 449–451

ANALYSIS OF MICRON-SIZED PARTICLES: DETECTION OF IRON

(Short Communication)

J. P. Lodge, Jr. and M. P. Lodge,
Anal. Chim. Acta, 44 (1969) 452

EFFECT OF TRIS BUFFER ON THE BIURET REACTION

(Short Communication)

L. E. Stewart, J. W. Thomas and G. E. Hull,
Anal. Chim. Acta, 44 (1969) 453–456

THE PREPARATION OF ELECTRODELESS DISCHARGE TUBES FOR SOME ALKALI AND ALKALINE EARTH ELEMENTS

(Short Communication)

K. M. Aldous, R. M. Dagnall and T. S. West,
Anal. Chim. Acta, 44 (1969) 457–460.

THE SEPARATION OF IRON FROM RUTHENIUM BY ISOPROPYL ETHER EXTRACTION

(Short Communication)

L. W. Potts and P. J. Lingane,
Anal. Chim. Acta, 44 (1969) 460–461.

PHOTOMETRIC DETERMINATION OF TRACES OF PYRIDINE BY REACTION WITH CYANOGEN BROMIDE AND 4,4′-DIAMINOSTILBENE-2,2′-DISULPHONIC ACID

(Short Communication)

J. Fuentes-Duchemin and E. Casassas,
Anal. Chim. Acta, 44 (1969) 462–466

A HIGHLY SENSITIVE MICROCHEMICAL REACTION FOR IRON PARTICLES

(Short Communication)

O. Vittori A.,
Anal. Chim. Acta, 44 (1969) 466–467

SEPARATION OF RHENIUM FROM MOLYBDENUM, TUNGSTEN, CHROMIUM, VANADIUM, SELENIUM, TELLURIUM AND OSMIUM BY EXTRACTION WITH ACETYLACETONE FROM ALKALINE SOLUTION

(Short Communication)

V. YATIRAJAM AND L. R. KAKKAR,
Anal. Chim. Acta, 44 (1969) 468–471

THE EXTRACTION OF GALLIUM WITH CUPFERRON

(Short Communication)

K. G. VADASDI,
Anal. Chim. Acta, 44 (1969) 471–472

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REVIEW

A CRITICAL REVIEW OF ELECTROANALYTICAL METHODS FOR THE NOBLE METALS

F. E. BEAMISH
Department of Chemistry, University of Toronto, Toronto 5, Ontario (Canada)

(Received June 21st, 1968)

With this presentation the author has completed a series of reviews of analytical methods for the noble metals which include the major analytical techniques both classical and modern. It is hoped that the reviews may contribute toward effective approaches to the separation and determination of noble metals. In general, naturally occurring materials present complex problems of separation, and the competent noble metal analyst will wish to select the most profitable set of separational and determinative procedures.

High specialization in a specific technique is not conducive to the most effective analytical approach. Nevertheless, in many instances, the specialist has contributed analytical advances of great value and the well-informed analytical chemist should have an adequate knowledge of at least the identity and something of the applicability of the new techniques. From these points of view, the compilation entitled *Trace Characterization, Chemical and Physical,* which deals in good detail with the most recently developed analytical approaches to determinations, is to be recommended. In the case of *Electrochemical Methods,* LAITINEN[1] has provided an excellent discussion of the analytical advantages and limitations of one of the useful specialized analytical fields.

In a previous review dealing with polarographic methods[2] and covering the period up to June 1958, the present author stated that "few detailed procedures have been recorded for the determination of any platinum metal ...". Since that time many excellent polarographic procedures for noble metals, present in relatively simple and in some complex noble metal systems, have been recorded, most of which have emanated from Russian or Czechoslovakian laboratories. Most of these recorded polarographic methods deal with determinations of gold, rhodium and ruthenium. In a reference to the progress of polarographic methods for ruthenium, which applies equally to all of the noble metals, AVTOKRATOVA[3] stated that "the slow rate of acceptance of the polarographic methods in analytical chemistry of ruthenium is apparently due to insufficient knowledge of the chemistry of ruthenium, to contradictory data on the chemical behaviour of its various compounds, and also to the fact that the compounds of platinum metals are reduced without the application of external potential difference". In the case of ruthenium SAWYER *et al.*[4] stated that "the absence of an easily purified and isolatable compound has helped prevent the development of reliable analytical methods". In this connection, it may be stated that along with the increased interest in polarographic methods there has been, during the past five years, a considerable interest in electrochemical researches which are concerned with general problems of solution composition and instability constants of noble metal compounds. Indeed, the greater effort has been expended toward this end. It should be noted that insofar as the growing importance of polarographic methods for the noble metal is concerned, there is some evidence that industrial laboratories now favour its replacement by atomic absorption techniques. It is encouraging to note that a good proportion of the proposed electroanalytical methods were applied by their authors to practical situations and indeed, some of these could serve as models of this practice and are worthy of emulation by authors of other analytical techniques.

Analytical applications of electroanalytical techniques such as amperometry and coulometry to noble metals have received relatively little attention by researchers. PSHENITSYN *et al.*[5] stated that "the amperometric titration method is no less accurate and sensitive than the polarographic method, and is simpler, while the apparatus is more readily available". In any case, the numbers of new methods included in this review for polarography, coulometry and amperometry are respectively 70, 21 and 17.

In the present review potentiometric methods for the noble metals recorded in abstracts since the author's review of titrimetric methods[6] are discussed. It is hoped that those few which were inadvertently omitted in the above review have been recovered. Some few publications dealing with the gravimetric electro-deposition of the noble metals are also included in the present review. Unless otherwise stated, all potentials mentioned in this review are referred to the saturated calomel electrode.

POLAROGRAPHIC METHODS

Gold

To determine traces of gold of the order of 0.05 troy ounce per ton in cyanide solutions, TUCKER[7] concentrated by the anion-exchange resin IRA-400 in chloride form. For larger proportions the author used the classical lead acetate–zinc collection. The stripped solution of the anion exchanger or the ethyl acetate–gold extraction from the sponge treatment were polarographed over the range −0.2 to −1.0 V after the addition of sodium hydroxide and gelatin to the gold extract.

Oscillographic polarography with a vibrating electrode was used by VRTILKOVA AND KALYODO[8] to determine gold along with mercury and silver in 10 *M* nitric acid. Large amounts of iron, copper, lead and zinc did not interfere.

The polarographic behaviour of ions with sodium fluoride as the supporting electrolyte was discussed by WEST *et al.*[9]. Among the various metals examined, gold was found to give a wave from the anodic dissolution of mercury when present as gold(III). The wave started at a voltage of 0. In the case of iridium an irreversible wave was obtained at −1.4 V and the limiting current was poorly defined. Rhodium gave two poorly defined waves.

One of the first attempts to find suitably stable complexes of gold for the adaptation of the dropping mercury electrode was recorded by SANIGAR[10] who used a potassium nitrate solution of potassium tetracyanoaurate. About one decade later

HERMAN[11] examined the application of a solution of gold(I) and (II) complexes in alkali hydroxides and cyanides. He was interested in the application of the method to the determination of gold in ores, bullion, etc., but aside from a few suggested and very general methods of approach little information of analytical significance was recorded and the authors statement that "methods are given by which gold might be polarographically estimated in ores and alloys" must be very loosely interpreted.

LINHART[12,13] rejected as insensitive HERMAN's[11] polarographic method for the determination of gold in alloys in amounts of 200 μg or less. The preferred method for silver alloys which contained gold in the ratio of 1:3, *e.g.* an assay bead, involved dissolution in nitric acid to isolate metallic gold. The latter was dissolved in *aqua regia* and the solution evaporated to a thick syrup at 60° or less. Nitric acid was then removed as usual with hydrochloric acid. Sodium hydroxide was then added to the solution at 20°, to 2.5 N followed by gelatin. Standard gold solutions (0.025 mg/ml) were similarly prepared and both solutions were polarographed after a 5-min period of bubbling with hydrogen. As would be expected colloidal gold solutions were formed at high concentration of gold. The limit of accuracy up to concentrations of $5 \cdot 10^{-3}\%$ of gold in silver was $\pm 1.7\%$. The time of an analysis was 1.5 h. It would be interesting to know the extent to which this method is applied, if at all, in assay laboratories. The instability of $Au(OH)_4^-$ in basic media is not an encouraging feature. However, LINHART found that the complex remained undecomposed for 2 h, even when in contact with mercury.

A study of the reaction of gold at a rotating platinum microdisc electrode was made by BARDIN AND TEMYANKO[14] who also examined its analytical application to the determination of gold. The electrode was a platinum wire fused into a glass tube the bottom of which, along with the wire, were polished. The anode was a platinum plate, the reference electrode being saturated calomel and mercury. The electrode was rotated at 800 r.p.m. Two diffusion-controlled waves occurred with a supporting electrolyte of sodium nitrate or potassium chloride. The first break, at +0.6 V, resulted from a reduction of gold(III) to gold; the second from a reduction of hydrogen ions. Oxygen did not interfere. A variety of supporting electrolytes proved equally effective for gold reduction and detailed differences were described. The reproducibility of results depended on the state of the surface of the microdisc. Three or more preliminary successive polarograms were necessary to precondition the electrode, and after a large number of determinations the electrode required polishing or treatment with *aqua regia*. Average accuracy was ± 2–3%. The range of concentration was 0.6–40 μg/ml.

The polarographic determination of gold in the presence of platinum and palladium at a rotating microdisc electrode was also described by BARDIN *et al.*[15]. The three metals in solution were treated with mercury(I) chloride, the filtered precipitate was heated to remove the mercury and the residue was dissolved in *aqua regia*. Nitric acid was removed as usual by heating with hydrochloric acid, sodium bromide was added and the acidity adjusted to 2 N in hydrochloric acid. The wave height was proportional to the gold content over the range of 0.2–20 μg/ml. At concentrations greater than 10 μg/ml, the precision was 3%; at lower concentrations, 5–7%. At a clean platinum electrode gold and platinum may be precipitated simultaneously but in the presence of N sodium bromide and 2 N sodium chloride gold may be determined selectively, even in the presence of gold, platinum and palladium ratios of 1:20–25:25–30.

In 1 N hydrochloric acid or sodium chloride the ratios permitted were 1:10:5. These three platinum metals are those most commonly associated in relatively large proportions, and the above method, preferably with a more efficient precipitant, could be applied for the polarographic analysis of assay beads.

The characteristics of the polarographic determination of gold(III) on solid electrodes were discussed by KABANOVA[16]. Gold or platinum disc cathodes rotated at 1,000–15,000 r.p.m. were used along with a platinized platinum wire. The electrolyzed solution of gold chloride in hydrochloric acid was treated with ethylenediamine tartrate; polarograms were taken at pH 4 and 25° in a purified nitrogen atmosphere. The half-wave potential was -0.07 V. The limiting current was measured at -0.2 V. The lowest concentration of gold applicable was 10^{-6} M gold. There was a linear relationship between the limiting current caused by reduction of gold(III) and the square root of the angular rotation speed of the electrode, and also between the limiting current and the gold concentration at constant rotation speed. The relationships remained linear for gold concentrations of $4\cdot10^{6}$–$4\cdot10^{-4}$ M gold(III). In the case of the platinum electrode the reproducibility of the polarographic waves was significantly less than that for the gold electrode. The potential for the reduction of gold was about -0.1 V and the supporting electrolyte current was higher for platinum than for gold. The author preferred the gold electrode or a platinum electrode which had been gilded for an extended time before use.

The polarography of metals at a graphite electrode was discussed by BRAININA *et al.*[17]. An oscillographic polarograph was used with the graphite indicator electrode and a saturated calomel electrode as reference. Oxygen was removed by nitrogen and during electrodeposition the solutions were magnetically stirred or a rotating electrode was used. Some 16 metals including gold could be determined. The authors stated that "the graphite electrode may be successfully used in the cathodic and anodic (film) polarography of a large number of metals, enabling the metal ions to be determined over an extremely wide range of concentrations ...". In the case of gold this range is 1–10^{-3} μg/ml. With gold the electrolytes were hydrochloric acid or potassium nitrate; the half-wave potentials were respectively $+0.5$ and $+0.75$ V. For dropping analysis the potential of deposition was -0.2 V in both cases and the potentials of the subsequent electrooxidation current peak were 0.5 and 0.85 V in the respective supporting electrolytes for a gold concentration of 10^{-4}–10^{-5} g/l.

An interesting polarographic method for gold and silver was developed by ADAM AND DOLEZAL[18]. The determination was indirect and involved the oxidation of Tiron by gold or silver to form the metal and a quinoid compound, the latter forming a polarographically reversible system with the product obtained by reduction at the mercury cathode. The authors present an explanation for the reaction and suggest reaction products. In the presence of excess of iodine the height of the polarographic wave of the quinoid-reduced system was directly proportional to the concentration of the added gold(III) or silver at pH 9.5–10. At higher pH the oxidation of Tiron proceeded to a higher state and the product was inactive. Below pH 9.5 the reaction was not quantitative. The method is applicable to complex materials only after the separation of silver or gold.

In a study of the factors which improved the analytical application of the rotating platinum electrode, FERRET AND PHILLIPS[19] described modifications which allowed greater precision for solutions of metals; among other metals the authors obtained a direct relationship between the diffusion current and the concentration of gold.

Polarograms of $[Au(en)_2]Cl_3$ and $[Au(en)(en\text{-}H)]Br_2$ with 0.1 *M* potassium chloride as a supporting electrolyte and a dropping mercury electrode were studied by BLOCK AND BAILAR[20]. No analytical applications were recorded.

Palladium

The complex of palladium with the disodium salt of EDTA was used by EZERSKAYA AND FILIMONOVA[21] for a polarographic determination. The complex H_4PdYCl_2 formed at pH 3–4 in the presence of sodium chloride. The solution for polarography was formed by mixing H_2PdCl_4 with solutions of disodium-EDTA, sodium chloride, sodium hydroxide and gelatin. Nitrogen was used to displace oxygen and polarography was carried out from +0.1 to −0.3 V with a dropping mercury electrode. Because EDTA formed an anodic wave continuous with the cathodic wave of the palladium complex, the height of the wave was measured from the abscissa to the limiting current plateau. The optimum concentration of palladium was 20–60 μg/ml. To avoid interferences from other platinum metals, the solution at pH 5–7 was boiled before polarography. Copper and iron interfered.

The EDTA complex with palladium was also used by RALEA AND VICOL-UNGUREANU[22] for the polarographic determination of 10–100 μg of palladium per ml at −1.3 V. The electrolyte contained sodium hydroxide, potassium chloride, gelatin and EDTA in 1:1 ethanol:water.

For the polarographic determination of palladium POPEL AND TREBELEVA[23] used ammonia and chloride ion electrolytes. The reductions were irreversible and the waves well-defined. Gelatin was added to eliminate the polarographic maximum. Variations of the electrolyte constituents resulted in changes of $E_{\frac{1}{2}}$ of 40–60 mV. The height of the palladium wave reached a constant value after about 100 h, although polarograms were recorded after 30 h. There was no interference from copper or silver and the error of determination was 2%. Obviously, better analytical methods are available.

Pyridine and γ-picoline previously used for the polarographic determination of rhodium[24] have been similarly used by PANTANI[25] for 0.1–5 m*M* of palladium. With an electrolyte containing potassium chloride and pyridine or α, β or γ-picoline, waves were produced in the neighbourhood of −0.3 V. There was no interference from iridium(IV), platinum(II) or (IV), and gold(III). Rhodium(III) interfered. At concentrations of palladium to pyridine of 1:10 a second wave occurred with the electrolyte.

Platinum

The application of a revolving platinum microdisc electrode for the polarographic determination of platinum was described by TEMYANKO *et al.*[26]. In particular the authors discussed the contrast in the results from base electrolytes of nitric acid and sodium nitrate and those from hydrochloric acid and sodium chloride. In the former case, when the concentration of the nitrates was increased by addition of nitric acid, only the second wave corresponding to the reduction of hydrogen ion increased in height. The sodium chloride electrolyte provided a different polarogram: high proportions of sodium chloride lowered the height of the platinum wave and the hydrogen wave disappeared. Bromides and iodides increased this tendency. Under precise conditions reproducible platinum waves with heights proportional to the platinum concentration were produced.

In 1932 SLENDYK AND HERASYMENKO[27] described a polarographic method for platinum concentrations of 0.02–0.2 μg/ml. The method was based on the catalytic wave in 2 M hydrochloric acid, the height of which was proportional to the platinum concentration. The authors used the method to determine platinum in palladium.

The adsorption and reduction of tetrachloroplatinate(II) ion at the dropping mercury electrode was examined by LAITINEN AND ONSTOTT[28]. It was shown that the ion must be adsorbed on the dropping mercury electrode to be reduced at potentials more positive than about 1 V. In 1 M potassium chloride solution the platinate ion showed a normal irreversible reduction wave whose half-wave potential was -1.35 V. No analytical applications were described.

A mixture of ethylenediamine tartrate and thiocyanate was used by BERAN AND DOLEZAL[29] for the polarographic determination of $4 \cdot 10^{-5}$–$3 \cdot 10^{-3}$ M platinum. The complex $Pt[(en)(CNS)_2]$ required 12 h for its complete formation. There were interferences from iron, copper, cerium, tellurium, palladium and gold. Errors were about 4%. The method has little to recommend it except perhaps the wide range of application.

SCARANO[30] used the dropping and pool mercury electrodes to study the behaviour of hexachloroplatinate(IV) in saturated sodium chloride solutions. Two half-waves were obtained, the first resulting from the formation of mercury(II) and the deposition of platinum on the mercury electrode, and the second wave resulting from the discharge of non-reduced $HPtCl_6^-$ ion. The total height of the two waves was proportional to the platinum concentration.

Rhodium

A polarographic method for rhodium was described by SEIFERT AND SIMEK[31]. The method involved dissolution of the alloy in *aqua regia*, treatment with sodium chloride and hydrochloric acid, and evaporation to remove nitrates. Rhodium was then precipitated to form a hydrated dioxide which was dissolved in hydrochloric acid. After evaporation, the red solution of the oxide together with gelatin and hydrochloric acid was added to a calibrated flask and an aliquot was polarographed over the range -0.1 V to -0.6 V. Analytical waves were formed in phosphate, sulphate and ammonium thiocyanate, as well as in hydrochloric acid solutions. A list of half-wave potentials in these base electrolytes in the presence of gelatin was recorded. The yellow modification of rhodium solutions did not form waves. The results were compared with data obtained by hydrolytic precipitation. It may be noted that the precision obtained by the latter method leaves something to be desired.

The polarography and coulometry of perchlorates of rhodium and the *aquo* and chloride complexes of rhodium(III) were investigated by VAN LOON AND PAGE[32]. Controlled-potential electrolysis of the dissolved species $Rh(H_2O)_6^{3+}$ was carried out. The solution, prepared by a repeated fuming of the hexachloride of rhodium with perchloric acid, was added to sodium perchlorate and the pH adjusted to 1 or 2.1; the rhodium was then coulometrically determined at -0.55 V. The results on about 7 mg were very satisfactory. The reference electrode and the counter electrode were in a separate compartment of the cell connected by an agar salt bridge which was

1 *M* in sodium nitrate. In the case of chloride media, the authors applied polarographic examination to solutions of the hexachloride in 6 *M*, 0.4 *M* and 0.1 *M* hydrochloric acid. The dissolved constituents formed as a result of the detailed treatments were respectively $RhCl_6^{3-}$, an average composition of $[RhCl_{3.5}(H_2O)_{2.5}]^{0.5-}$, and an overall composition of $RhCl_3(H_2O)_3$. Equilibrium in the 0.4 *M* solution could be established by heating the freshly diluted rhodium solution for 1 h at 100° and cooling. Presumably, the rhodium constituent in the 0.1 *M* solution remained unchanged over a 2-week period.

Controlled-potential electrolysis of the various pink solutions of rhodium produced precise values for about 1–15 mg of rhodium. The author's comments on the conversion of the *aquo*chloride complexes to the chloride form have some analytical interest. From recent researches by the present author, it has become apparent that complete conversion of the perchlorate of rhodium to the chloride form is not accomplished by repeated fuming to dryness before and after the addition of hydrochloric acid. The one treatment that has so far proved successful involves precipitation as the hydrated oxide formed at pH 10 and subsequent treatments with hydrochloric acid. VAN LOON AND PAGE's coulometric determinations at −0.2 V after fuming perchloric solutions, diluting and heating for several hours with a large excess of sodium chloride, showed about 75% of rhodium(III) in an easily reduced form. In those cases where the fumed sample was diluted and the acidity adjusted to pH 2.5 before the excess of chloride was added, the coulometric determination was quantitative. If it is a fact that the net result of the above treatment suffices to produce 100% conversion to the anionic chloride complex, the method would be of very considerable value in certain analytical separations. The present author cannot accept this interpretation without more convincing data. In any case the authors state that "the coulometry in perchlorate media is not suitable for quantitative work because of the large background corrections". In the case of chloride media "analytical polarography can only be done when strict attention is paid to reproducing the solution constituents and to stabilizing the system by heating". For coulometry, in contrast to polarography "it is not essential to have a reproducible distribution of rhodium among the chloride complexes".

A polarographic and spectrophotometric investigation of rhodium(III) bromocomplexes was made by COZZI AND PANTANI[33]. While no analytical applications were described, some of the data will be useful where quantitative ion-exchange separations are involved and could prove of value for the development of electrochemical and spectrophotometric methods of determination. These authors[34] also recorded a similar investigation of the rhodium chloride complexes at pH values close to 0. Basic complexes were therefore not considered in detail. The authors' data support the previous finding that the red form of the chloride behaves like an anion, the yellow form being mainly cationic; furthermore that the yellow form was more typical in solutions of low chloride concentration and the red form characteristic of high chloride ion concentration.

A polarographic determination of rhodium in the presence of iridium and the absence of platinum was recorded by PANTANI AND DESIDERI[35]. Evidence for the non-interference of iridium was not particularly convincing and consisted solely in the statement that "from several polarograms of mixtures of rhodium and iridium, the latter being present up to 8 times the amount of the former, it was found possible to determine rhodium with a 2–3% error". Because of the importance of methods of determining rhodium or iridium in their mixed solutions, this claim would be more acceptable had it been accompanied by results comparable to those provided for the simultaneous polarographic determination of rhodium and palladium. The method for rhodium involved deoxygenation with nitrogen, a temperature of 25°, and heating the rhodium solution with an excess of thiourea. A well-shaped step occurred at -0.4 V. The authors examined the effects of various supporting electrolytes, the effect of excess of thiourea, and the use of gelatin as a maximum suppressor. Using the diffusion current constant in 0.2 M thiourea solution, the authors estimated that the process was a 3-electron reduction. This was confirmed by millicoulometry. The rhodium–thiourea solution showed no spectrophotometric maximum absorption apart from the thiourea itself. Rhodium and palladium in milligram amounts could be determined simultaneously.

PANTANI[24] continued his investigations of the polarographic behaviour of rhodium with pyridine and recorded the successful use of the γ-picoline–rhodium complex as an analytical reagent for rhodium in the presence of iridium. The pyridine–rhodium complex showed a cathodic step at about -0.4 V which was poorly developed above 0.4 mM of rhodium. The γ-picoline complex showed a well-defined step in the range of -0.4–0.5 V for rhodium concentrations up to 4 mM. The limiting current was proportional to the rhodium concentration and the recorded data indicated good separations in the presence of 2 mg of rhodium with 22 mg of iridium contained in 25 ml of 1 M γ-picoline solution. Information on the electrode process was included and emphasized the ageing effects on the dissolved rhodium complexes. The electrode process seemed to involve a 2-electron reduction.

Applying oscillographic polarography, BERAN AND DOLEZAL[36] were able to determine rhodium in the presence of platinum, palladium and gold. In rhodium solutions which were 0.1 M in hydrochloric acid and 0.6 M in sodium chloride, a sharp peak appeared in the anodic part of the curve, the length of which was found to be proportional to rhodium concentrations of 0.5–25 µg in 20 ml of solution and hence analytically suitable. The results could be obtained from a calibration curve or by the use of a suitable standard sample. The data obtained in the presence of milligram amounts of platinum, palladium or gold and 2–19 µg of rhodium indicated errors of ±9%.

The oscillopolarographic determination of rhodium in inorganic acid solutions was described by NEEB AND HORSTMANN[37]. Rhodium (1–3 µg/ml) could be determined from the length of the incision which appeared on the anodic part of the wave. The authors discussed the various factors which influenced the length of the incision, such as instrumental components, external variables and solution composition. A circuit which allowed low a.c. frequencies increased the sensitivity toward rhodium to 5–50 ng/ml. The dropping mercury electrode was used and the capillary was treated with silicone. The reference electrode in hydrochloric acid was silver–silver chloride, and in sulphuric or perchloric acids an S.C.E. was used with a diaphragm. The investigation of the degree of interferences from associated platinum metals was extended beyond that described by BERAN *et al.*[36,38,39] special emphasis being placed on a method of separating iridium by an extraction of its complex with 3,4-dichlorobenzyltriphenylphosphonium chloride or by a precipitation as hexachloroiridate. However, the rhodium method could be used in a hydrochloric acid solution of iridium containing up to $10^{-2}\%$ of rhodium. Palladium, platinum, and osmium could be removed, as in the case of iridium, by extraction by chloroform of the corresponding phosphonium salts. Excess of organic material must be destroyed before rhodium is determined. The authors recorded the degree of tolerance for the platinum metals. Relative standard deviations for the determination of 0.5–1 µg/ml of rhodium varied from 2.83 to 4.75%.

Ethylenediaminetetraacetic acid, previously used spectrophotometrically for rhodium, was applied to its polarographic determination by EZERSKAYA AND FILIMONOVA[40]. Iridium forms no complex with EDTA and is reduced to chloroiridite which forms a complex only in strongly alkaline media. There was interference from relatively large proportions of platinum, palladium, ruthenium and associated base metals. The authors suggested that iridium could first be determined in hydrochloric acid solution by the method of PSHENITSYN *et al.*[5] followed by their rhodium method; this suggestion was not supported by data but one may hope that it will be achieved. The EDTA complex with rhodium in solution at pH 6–7, in the presence of excess of sodium chloride and heated for 10 min, formed an equilibrium mixture of two complexonates and an *aquo*hydroxy rhodium compound. Measurements were made in the absence of oxygen with a dropping mercury electrode. The reduction wave at rhodium concentrations of 0.8–1.0 mM was convenient for measuring; at higher concentrations maxima appeared which could be suppressed by gelatin, methyl red, or bromocresol purple, although excess of these lowered the waveheight and shifted the wave to more negative potentials. The diffusion current of the complexonate at pH 6.4 was used over the range of $3 \cdot 10^{-2}$–1 mM rhodium; the precision was 1.5–2.5%. Below $3 \cdot 10^{-2}$ mM appreciable deviation appeared. In the present author's opinion, spectrophotometric procedures are preferable.

PSHENITSYN AND EZERSKAYA[41] stated that polarographic determinations of rhodium could be made through the complex with Trilon B in ratios of >5:1 and at pH 6.5–7, after boiling for 10–15 min. The complex was stable and was reduced at a dropping mercury electrode at −1.0 to −1.1 V. The accuracy for 2–400 µg/ml was 3–4%. Iridium could be present in ratios of 10 to 1% rhodium. There was interference from platinum, palladium and ruthenium present in ratios of 0.1:1 or less. Lead did not interfere except in ratios of over 100:1.

Studies of the polarographic behaviour of rhodium with oxalates[42] and the thiocyanates[43] have been recorded. While these are not analytical papers, data of analytical significance can be derived from the discussions; acceptable methods for rhodium remain at a premium.

For the polarographic determination of iridium (1–450 µg/ml), EZERSKAYA AND PSHENITSYN[44] reduced iridium(IV) to iridium(III) in hydrochloric acid solutions containing 1 to 450 ng/ml. There was no interference from rhodium, palladium and mercury(II). The errors were about 5%.

Ruthenium

Early efforts to obtain data which could be used to determine ruthenium polarographically met with little success. In 1945 WILLIS[45], using a variety of supporting electrolytes and a dropping mercury electrode, found no reduction waves for ruthenium(III) or (IV). Later, investigators[46,47] recorded half-wave potentials for ruthenium(VI), (VII) and (VIII). RECHNITZ AND GOODKIN[48] recently recorded a review of polarographic publications dealing with the properties of ruthenium(III) and (IV) in acid solution. New advances in oxidation–reduction methods for determining ruthenium were discussed by MACDONALD[49]. Although many reports contain potentially useful analytical data, relatively few have been applied to produce polarographic methods.

The polarography of ruthenium salts was studied by PSHENITSYN AND EZERSKAYA[50,51] with a view to the analytical application of $K_2[RuCl_5(H_2O)]$ and to discovering the identity of the oxidized product. The pentachloro*aquo*ruthenate(III) was oxidized at +1.0 V to give a well-defined wave with an $E_{\frac{1}{2}}$ value of 0.70 V. Either stationary or rotating platinum electrodes could be used and at the applied potential used there was no reduction of other platinum metals except iridium. The authors dealt with the techniques used to identify the oxidized product as potassium hexachlororuthenate(III) and the method of preparing the complex was included. The procedure involved the hydrogen peroxide reduction of $K_4[Ru_2OCl_{10}]$ to $K_2[RuCl_5(H_2O)]$ and then oxidation with peroxide and the chlorine formed *in situ* to form the hexachloro complex which was separated by evaporation. Earlier similar methods used by other authors generally contained $K_4[Ru_2OCl_{10}]$ as an impurity. The authors discussed conditions which encouraged instability of the hexachlororuthenate with reference to polarographic methods. The relative ease of reduction of $K_2[RuCl_6]$ allowed the development of an amperometric determination of ruthenium. PSHENITSYN AND EZERSKAYA[41] also described methods for the determination of ruthenium and rhodium. The method of preparing potassium hexachlororuthenate(III) was again described. A solution of the salt (Ru< 0.1 mg) in 1:1 hydrochloric acid was polarographed from +0.9 to +0.5 V within 45 min of preparation. For concentrations of 0.1–1 mg of ruthenium, the solution remained stable for several hours. The method was applicable over the range of 1–200 μg Ru/ml. There was no interference from dissolved oxygen, rhodium, palladium, osmium, copper, nickel, tellurium or selenium. Gold and iron(III) interfered only when present in 10:1 proportions. There was interference from iridium, sulphite and chlorine. The last could be removed by boiling for 5 min or less. Longer boiling encouraged reduction to ruthenium(III).

The reduction wave of the hexachlororuthenate(III) was also used for amperometric titration with hydroquinone. The preparation of the solution and the electrodes were similar to those used for the polarography. The cathode potential was −0.5 V. The method was applied to 0.02–2 mg of ruthenium and the interfering elements were those found for the polarographic method. The precision was 1–5%.

PSHENITSYN AND EZERSKAYA[51] recorded a third paper containing much the same method as they had recorded elsewhere[50,41]. They dealt with the comparative usefulness of the polarography of $K_2[RuCl_5(H_2O)]$ and of K_2RuCl_6, the former occurring as a result of the reduction of the latter in a sodium chloride supporting electrolyte at a stationary platinum electrode, and producing a wave over the range 0.5–0.3 V *vs.* NCE. The diffusion current of ruthenium was proportional to the ruthenium concentration to within 1.5–2% over the range of 5–500 μg/ml. The removal of oxygen was essential. The preferred ruthenium complex was K_2RuCl_6 and its preparation from the above chloro*aquo* complex was recorded. With the K_2RuCl_6 complex, a rotating platinum electrode could be used, oxygen did not interfere and the diffusion current was much larger, being proportional to the concentration of ruthenium from 10^{-5}–$5 \cdot 10^{-2}$ *M* with an accuracy of 1–2%. An amperometric titration of K_2RuCl_6 could also be made with hydroquinone or ascorbic acid. The titration curves showed a sharp break at the equivalence point. Determinations of 0.02–2.0 mg of ruthenium in 10 ml could be made with an accuracy of 5%.

Sodium gluconate has been used as the supporting electrolyte for the polarographic determination of ruthenium. SAWYER *et al.*[4] found difficulty in preparing a ruthenium(III)–gluconate system where the dissolved constituents remained constant. Acceptable results were obtained by dissolving the ruthenium(III) sample in hydrochloric acid, adding sodium gluconate to 0.1 *M* gluconate, adjusting to pH 14, diluting, adding the sample to the cell, bubbling oxygen through the system for 15–20 min, deaerating for 5 min with nitrogen and then introducing the dropping mercury electrode and running the polarogram at 25.0° ± 0.10°. The half-wave potential was −0.67 V and the diffusion current constant was 1.18. The average deviation was 2.1% for ruthenium from $1 \cdot 10^{-4}$–$5 \cdot 10^{-3}$ *M*. The procedure permitted a pH range of 12–14.3 and a gluconate concentration range of 0.02–0.20 *M*. There was serious interference from platinum; palladium could be tolerated up to $1 \cdot 10^{-4}$ *M*; iridium and rhodium did not interfere. The authors suggested that the osmium(VI) interference could be removed by a pretreatment of the acid solution with hydrogen peroxide. Statements such as this should be accompanied by experimental evidence, particularly when so little is known concerning the solution composition of ruthenium–peroxide mixtures. In the present author's opinion the proposed method offers few if any advantages over the choice of other ruthenium methods which will apply to the same range of ruthenium concentrations.

For the polarographic determination of ruthenium, GUEBELY[52] used the hydrogen catalytic wave from a dropping mercury electrode for determinations over the range of 0.5–20 µg/ml. The ruthenium was dissolved in sulphuric acid solutions containing potassium sulphate and the polarograms were obtained at 25° with a dropping mercury electrode (drop time 4 sec) and with the oxygen removed by pure nitrogen. The reference electrode was saturated calomel and separation was made through a disc of agar–agar containing potassium sulphate. A single catalytic wave occurred around −1.0 V. The maximum present in higher concentrations could be suppressed by gelatin; it was scarcely discernible at the lower limit of concentration. The height of the wave was proportional to concentrations between $5 \cdot 10^{-10}$–$2 \cdot 10^{-7}$ *M*, measured with the respective precisions of ±10% and ±5%.

About ten years later WANG AND SUNG[53] described the characteristics of the hydrogen catalytic wave from ruthenium produced at −0.6 to −0.7 V in a solution of hydroxylamine at pH 9. The authors discussed the effects on the wave behaviour of the composition of the polarographic solution and the effects of time, temperature, etc. Amounts of ruthenium of the order of 0.5 µg could be determined.

Oxalic acid solutions of ruthenium tetroxide containing 0.006% of thymol and free of oxygen were used by MESARIC AND BRANICA[54] for the polarographic determination of 4–120 µg Ru/ml. The error was 0.7–15%. A well-developed polarographic wave was obtained. The wave remained constant at 0.5 *N* or less of hydrochloric, sulphuric or perchloric acids. Nitric acid or traces of nitrates interfered. The half-wave potential was −0.440 V. In a second paper[55] the authors discussed the use of citrate and tartrate in sodium hydroxide solution. With citric acid the half-wave potential was −0.530 V and with tartrate −0.510 V. Both electrolytes could be used quantitatively for 4–120 μg Ru/ml with relative standard errors of 15–0.8%. Hydrogen was used to remove oxygen and the interferences from acids corresponded to that for oxalic acid.

LOVE AND GREENDALE[56] used the polarograph to determine ruthenium and technetium radionuclides in fission products. The active sample was evaporated to dryness, sodium citrate and sodium hydroxide were added as the supporting electrolyte, and -1.55 V was applied to the D.M.E. Detailed techniques were described for the removal of the ruthenium–mercury amalgam by carbon tetrachloride. The equipment allowed the immediate removal, washing, and dissolution of the mercury followed by the γ-counting of technetium and ruthenium-103 or -106. The authors predicted the successful application of their method to radio-ruthenium in sea water.

A polarographic study of the oxidation states of ruthenium(IV), (VI), (VII) and (VIII) was recorded by SILVERMAN AND LEVY[46]. Half-wave potentials for ruthenate–perruthenate and perruthenate–ruthenium tetroxide were respectively -0.59 and -1.00 V, agreeing with previously recorded data. These values were unaffected by the pH of the cell solution indicating that ruthenium tetroxide in solution exists as a neutral species.

Osmium

An examination of the polarographic characteristics of osmium was made in considerable detail by MEITES[57]. With the dropping mercury electrode strongly acidic solutions were reduced directly to osmium(III). As the pH of the osmium solution increased, a second wave corresponding to osmium(IV) appeared. Above a pH of 5 a third wave appeared possibly indicating the formation of osmium(VI). The author recommended cyanide media for the determination of osmium by polarography or coulometry at controlled potential. Two waves were produced attributed to the successive reductions:

$$\mathrm{Os(VI)} \rightarrow \mathrm{Os(III)} \rightarrow \mathrm{Os(II)}$$

Two-component noble metal systems

The polarographic application of seven amines to the determination of palladium and gold was studied by TOMICEK *et al.*[58]. In the case of palladium all but one of the amines produced well-developed waves suitable for analytical purposes. When maxima appeared these could be suppressed by surface-active agents. Ethylenediamine tartrate was especially suitable for the simultaneous determination of palladium and gold; the $E_{\frac{1}{2}}$ for the former was -0.72 V and for the latter $+0.1$ V. In the case of gold most of the amines were unsatisfactory for analytical purposes. The applicable concentrations of the metals were $2–8 \cdot 10^{-4}$ g of gold or palladium chloride per 10 ml of solution.

The principles involved in the use of the microdisc electrode were discussed by BARDIN *et al.*[59]. The diffusion currents were proportional to the concentration of the solution and the square root of the angular velocity of the electrode. Clearly defined and reproducible waves were obtained for gold and platinum chlorides after the tenth cycle without purifying the electrode surface. The maximum deviation from the mean value did not exceed 3%. Advantages of the microdisc electrode over the wire electrode were discussed by the authors. The experiments showed that the microdisc electrode could be used for polarography in a flow stream. This could have considerable significance where the problem of constant automatic control of composition is being considered.

For the polarographic determination of platinum and palladium in sludges from copper and nickel productions, PATS AND AREF'EVA[60] used solutions containing ammonia, ammonium chloride and sodium thiosulphate. Palladium gave a well-defined wave with no interference from platinum. In the presence of gold and ethylenediamine tartrate, gold could be determined simultaneously with palladium, the waves being separated by 0.6 V. In the presence of sodium chloride and citrate buffer to produce a pH between 7 and 8.5, one could determine platinum with no interference from gold if the latter was present in proportions of less than 7:1. Directions were included for the determination of palladium and platinum in copper and nickel cathode sludges.

Oscillographic polarography was used by BERAN *et al.*[39] for the determination of osmium and ruthenium. The latter in 0.6 M hydrochloric acid and 0.1 M sodium chloride produced a cathodic peak at -1.2 V. The peak height was directly proportional to ruthenium concentrations of $2–40 \cdot 10^{-6}$ g in 5 ml of solution. The determination could be made in the presence of niobium, zirconium, uranium, palladium and osmium. Under the same conditions osmium(IV) produced a break on the cathode branch of the oscillographic curve and 2–25 μg/ml could be determined in the presence of ruthenium. To determine ruthenium in fission products, the sample was dissolved in nitric acid, ruthenium was extracted with tributyl phosphate, and the solution was evaporated in the presence of sulphuric acid and hydroxylamine hydrochloride to white fumes. After dilution with water, barium chloride and sodium chloride were added, the precipitate was allowed to settle and the height of the anodic peak was measured. In another publication[38] the oscillographic behaviour and the determination of ruthenium and osmium were discussed. Methods of preparing the pure salts from the metals were described. Some two dozen electrolytes were studied over ruthenium and osmium(IV) concentrations of $10^{-3}–10^{-4}$ M and a mechanical drop-capillary was used for all measurements. Cyanide and thiocyanate electrolytes were unsatisfactory. For the determination of osmium in the presence of ruthenium, 1 M sodium hydroxide or a mixture of sodium hydroxide and triethanolamine can be used. The polarographic behaviour of the metals in perchloric acid media was discussed in some detail, including the dependence of the ruthenium indentation length upon the concentration of hydrogen and other ions. The influence of anions was also discussed and it was observed that the indentation length increased with the atomic weight of the halogens in perchlorate solution. The oscillographic behaviour of ruthenium and rhodium were compared.

Multicomponent noble metal systems

In a study of the polarography of noble metals, SIMPSON *et al.*[61] noted that earlier investigators had "fostered the impression that the noble metal must be complexed strongly so as to prevent the noble metal ion from reacting spontaneously with the mercury drop". SIMPSON *et al.*[61] believed that the dissolved constituent of the noble metal was much less reactive to the mercury drop and in fact it was only when the noble metal was sufficiently reactive that reasonable diffusion coefficients could be obtained. They[61] recalled the earlier work of ENGLISH[62] who provided a method for the polarographic determination of platinum in organic matter. This was accomplished at pH 7 and the authors were unable to obtain a starting plateau with the use of various complexing reagents. SIMPSON *et al.*[61] described a few inconclusive experiments to indicate the complexities of noble metal solutions and they noted that in the case of palladium, with its increase of the diffusion current with chloride ion concentration that "uncontrolled factors apparently also have an effect, for we observed somewhat different diffusion coefficients for several palladium solutions with the same chloride concentration". The present author has consistently stressed the need to recognize the influence on noble metal solution composition of such factors as pH, temperature, standing time, salt content, etc. Nowhere in the analytical field is this recognition of more importance than in electrochemical methods and particularly in polarography. Here one need only recall the anomalous behaviour of iridium solutions in contact with theoretically favourable reductants.

The application of oscillographic polarography to the determination of noble metals was studied by MAGEE AND BEATTIE[63]. These authors hoped to build their study of polarographic behaviour around the ligand field theory. From the fact that the value of Δ increases for a particular metal over a known set of ligands, it was hoped to find a comparable pattern in the case of the polarographic half-wave potentials and thus to arrive at a systematic approach to the choice of complexing reagent. There was also the intention of developing simple polarographic analytical methods for the noble and related base metals. Half-wave potentials and absorption maxima were determined for a variety of ligands and gold, silver, copper[63]. In all cases, gelatin was added to prevent the occurrence of absorption maxima and nitrogen was used to remove oxygen. Ethanolamine was used for the gold and copper, the former producing a wave at -0.19 V and the latter at -0.42 V. Straight-line curves were obtained from plots of concentration *vs.* peak heights. The concentration range was 10^{-4}–$2 \cdot 10^{-3}$ *M* for each metal. Silver did not interfere because silver chloride formed a water-soluble product on the addition of ethanolamine. The method was applied successfully to 20 mg of dental alloys containing the three metals in solution with ethanolamine, sodium sulphate and gelatin. Synthetic unknowns, containing palladium in addition to the above three metals, could also be analyzed, palladium giving a well-formed wave at -0.78 V. Nickel did not interfere. In a second paper DOUGLAS AND MAGEE[64] proceeded to apply their approach to indicate suitable complexes for the polarographic determination of palladium and rhodium. The fact that Δ increases in the order I^-, Br^-, Cl^-, F^-, SCN^-, H_2O, oxalate, pyridine, ammonia, ethylenediamine, NO_2^-, CN^- for metal ions in their normal valence states formed the basis of their investigation. The ligands used by the authors were Cl^-, SCN^-, pyridine and CN^-, and the polarographic behaviour of these ligands with ruthenium, rhodium, palladium, osmium and iridium was examined. No polarographic waves were formed with these ligands and osmium or iridium. Ruthenium and rhodium formed complexes producing reduction waves with each ligand; palladium only with pyridine, ammonia and cyanide. The polarographic reduction waves of the palladium complex were found to be reversible and increased linearly with the concentrations of palladium, the pyridine complex being particularly suitable for determinations. WILLIS[65] had found earlier that clearly-defined waves were given by rhodium with cyanide, ammonia and thiocyanate and, like REPIN[66], he recommended pyridine as a polarographic reagent for rhodium. WILLIS[65] had also obtained polarographic waves for palladium with the above ligands and claimed that they could be used analytically over a limited range of concentration. RUIS AND MOLERA[67] disagreed and stated that palladium was not reduced from a cyanide solution. WILSON AND DANIELS[68] found that rhodium and iridium interfered with the determination of palladium in ammoniacal solutions. DOUGLAS AND MAGEE[64] applied their data for the determination of rhodium and palladium in alloys using separate aliquots of the solution of the alloy. The latter was dissolved in *aqua regia* and the solution adjusted to pH 5 with sodium hydroxide. Potassium thiocyanate was added, the solution was boiled, then cooled and the volume adjusted to 25.0 ml. The starting potential was −0.3 V and the peak height at −0.6 V was referred to a prepared calibration curve. There was no interference from palladium whose thiocyanate complex was spontaneously reduced by the mercury drop. In the case of palladium the solution of *aqua regia* was diluted, pyridine was added, the reduction was started at −0.2 V and the peak height at −0.4 V was referred to a standardized curve. The procedures were tested with an alloy wire containing rhodium and palladium only. The results compared favorably with those provided by the manufacturer.

MAGEE AND DOUGLAS[69] extended their theoretical approach to recommendations for the polarographic determination of each of the platinum metals. This report is a general summary of their previous reports. The most generally suitable polarographic methods for each of rhodium, iridium and palladium were suggested. These were respectively, $Rh(SCN)_6^{3-}$ with E_P −0.60 V, the catalytic wave of iridium thiocyanate at −1.63 V, and the pyridine, ammonia or cyanide complexes of palladium. In the case of ruthenium it was found that the pyridine–ruthenium complex at 60° gave a reversible reaction and provided a polarogram with two peaks. The double reduction peak was found to have potential use for quantitative analysis. The limit of determination was about 5 μg/ml with good accuracy. The authors suggested polarographic methods for the determination in the presence of each other of mixtures of rhodium, iridium and palladium (A) and of rhodium in the presence of ruthenium, osmium, iridium and palladium (B). These methods (A) were respectively: rhodium was first determined as the thiocyanate complex and then iridium, in which case the determined amount of rhodium was added to correct for the effect of rhodium on the catalytic wave of iridium. Palladium was finally determined as the pyridine complex from a second sample. The authors' statement that "the determination of equal amounts of the metals in the presence of one another and large amounts of iridium in the presence of small amounts of rhodium are equally satisfactory", seems to require experimental investigation. It may be hoped that this latter polarographic determination will receive further attention. The method of determining rhodium and iridium present together is a distinct contribution. With the second mixed solution (B), the authors found three peaks for the thiocyanate solution at −0.5, −0.64 and −0.74 V: the first an adsorption peak for osmium, the second a reduced peak for rhodium, and the third a reduction peak for ruthenium. In the case of palladium the thiocyanate complex provides no wave and is spontaneously reduced at the mercury drop. From calibration curves, rhodium could be determined in the mixed solution and it was found that if the drop time was doubled the precision was increased.

A systematic study of the oscillographic behaviour of noble metals with a wide variety of electrolytes was reported by BERAN AND DOLEZAL[70]. Comparative titration methods were suggested and tables of data for each electrolyte and noble metal in concentrations of 10^{-3}–10^{-5} M were included. For the determination of palladium, rhodium and iridium present together or together with platinum and gold, the authors recommended ethylenediamine sulphate; and for gold a sodium hydroxide solution of $[Au(OH)_4]^-$. In the case of rhodium, a hydrochloric acid medium was particularly useful. The reactions were discussed in good detail and this paper can be examined with profit to the analytical chemist.

In a second paper[71] the authors discussed in further detail oscillographic polarography for the determination of palladium, rhodium and iridium in the absence or presence of gold and platinum, again with ethylenediamine sulphate as the complexing reagent. Characteristic minima on the cathode part of the curve were sufficiently separated to allow simultaneous determinations by comparative titrations for palladium at -1.1 V, rhodium at -0.3 V and iridium at -0.5 V and -1.5 V. The presence of associated noble metals affected the results and it was thus necessary to adjust the standard noble metal solution to a comparable composition. Thus for palladium the minima of the sample and standard, each containing ethylenediamine sulphate, were adjusted to the same value by the slow addition of noble metals standard to a solution containing the complexing reagent. The optimum palladium content was 0.1–1.2 mg/10 ml. For rhodium solution, comparisons could be made with either the cathodic or anodic minimum, the former being more suitable in the presence of platinum, palladium or iridium. The optimum concentrations were 0.025–0.13 mg Rh/10 ml.

In the case of iridium the cathodic minimum at -1.5 V was used for the determination of 0.03–0.2 mg/10 ml. An approach to the simultaneous determination of palladium, rhodium and iridium in the presence of platinum and gold was discussed. Errors were rather large, being ± 4–10%. This comparative titration method offered a wide range of determinations for various combinations of noble metals in solution. Some of these offer useful applications *e.g.* rhodium and iridium in proportions of 1:6, palladium and platinum at ratios of 1:40, etc.

The polarographic behaviour of gold, platinum and palladium in ethylenediamine citrate solution added as an electrolyte and a masking reagent was described by STANKOVIANSKY *et al.*[72]. The half-wave potentials in 0.5 *M* reagent were for gold -0.065 V, for palladium -0.39 V and for platinum $+0.072$ V. The influence of nitrates, chlorides and organic complexing agents on the determination of each metal was described. Gelatin was used to suppress the maxima which appeared with each metal. The authors discussed the conditions which they claimed would allow applications to dental alloys. Accompanying base metals which interfered could be masked by ethylenediamine and 1,2-cyclohexanediaminetetracetic acid. It is unfortunate that the suggestion was not accompanied by experimental verification.

An unusual approach to the polarographic determination of silver, gold and platinum, using the hanging mercury drop, was described by BERGE AND JEROSCHEWSKI[73]. In principle, the method involved a measurement of the reducing effect of the noble metal on the height of the sulphide peak, the decrease in height resulting from the formation of a metal sulphide. The accuracy of an indirect method such as this will depend upon the precision of the peak measurement and, as in all such cases, any imprecision causes relatively high errors for small relative amounts of the constituent. By this method the accuracy will also be affected by any tendency to form complex sulphides, particularly those which are soluble, and this tendency in turn will be a function of the pH and the concentration of the resulting ions. With the platinum metals in a basic medium one may expect complex noble metal sulphides. In the case of gold and platinum strongly acidic solutions were used. In the present author's opinion this indirect approach to the determination will have very restricted applications and much more efficient methods are available. In any case, one would expect a report such as this to include at least a few data from practical applications.

For the oscillographic polarographic determination of about 10–20 μg/ml of palladium, ruthenium and osmium in the presence of about 100–200 μg/ml of platinum, rhodium and iridium, HUBICKI AND MATYSIK[74] used an electrolyte of anhydrous ammonium nitrate and ammonia with the dropping mercury cathode and a graphite anode. The measured indentations were compared with those obtained from aqueous media.

BARDIN *et al.*[75] extended their numerous reports on the use of platinum electrodes for the polarographic determination of noble metals. The microdisc electrode was found advantageous for determinations of platinum, rhodium, palladium, osmium and gold. Diffusion currents and the numbers of electrons involved were determined. The solid electrodes should be cleaned intermittently with emery cloth and filter paper after which the first one or two polarograms should be disregarded. There was a good relationship between the diffusion current and the concentration for all types of solid platinum electrodes. Good waves were given for gold, platinum, palladium and rhodium with sodium nitrate as the supporting electrolyte. In the case of osmium an electrolyte of calcium hydroxide was satisfactory. Except in the case of gold, the removal of oxygen was necessary. In the presence of halogen acids and salts only gold, of the noble metals, provided a diffusion current. For the latter metal amperometric titrations could be made with hydrazine sulphate and the microdisc electrode.

A review of polarographic methods for the noble metals was recorded by PSHENITSYN *et al.*[76]; 62 references were included dealing with pertinent publications up to 1958.

VLCEK in 1956[77] summarized supporting electrolytes and electrode processes previously used for the determination of half-wave potentials of the noble metals.

COULOMETRIC METHODS

Gold

For the coulometric titration of gold, MILLER AND HUME used the mercury complexes of thioglycollic acid[78] and 2-mercaptoethanol[79] to generate the sulfhydryl group. The mercury complex of the ethanol compound was found superior to thioglycollic acid because of the absence of carboxyl group which could lead to side reactions. Both mercury complexes had sufficient water solubility to permit constant-current coulometric generation of its sulfhydryl group. End-point indication could be made potentiometrically with an amalgamated gold wire as the indicator electrode or, in the case of thioglycollic acid, amperometrically at two mercury electrodes. The titration cell of 3.3-cm diameter was made of borosilicate glass with a platinum wire sealed into the base. The generating electrode was a mercury pool magnetically stirred; the auxiliary electrode was platinum foil separated from the cathode by medium-porosity fritted-glass discs. In the case of thioglycollic acid used for gold, copper and mercury, the titration solution was made by mixing a buffer with mercury(II) thioglycollate. With 2-mercaptoethanol the solution of the mercury complex was adjusted to pH 4.6; for higher pH systems ammonia or sodium carbonate was added to a portion of the stock solution. The latter reagent was used successfully for gold, platinum(II), and palladium, copper, mercury and silver. With platinum(IV) the method was not sufficiently accurate. Differentiation of the metals was not possible. In the case of platinum(II) the titration was slow and a more satisfactory method involved generating a slight excess of sulfhydryl and back-titration after about 1 min. In the case of gold, palladium, mercury and silver, successive samples in the same solutions were titrated to a pre-set potentiometric end-point. With the ethanol derivative, titrations showed a 200-mV break at pH 4.6 which is sharper than that for thioglycollate at 7.5. The data for 200 μg–2 mg of gold showed an accuracy of ±0.5%. The authors considered the method for gold comparable in accuracy to the methods described by BARD AND LINGANE[80] and LINGANE[81]. In the case of platinum(II) the back-titration gave an accuracy of ±1%; with platinum(IV) there was a persistent negative error of 2–5%. With palladium, which could be titrated in the presence of rhodium, the first run in a given mercury–MTEG solution was low by several per cent, but subsequent determinations were accurate.

HARRAR AND STEPHENS[82] described a controlled-potential coulometric method for gold in the range of 10–75 mg. Data for 1-mg samples were included and although the authors considered these to be less satisfactory, with a relative standard deviation of 0.22 compared to 0.02 for 10 mg, it is noted that the maximum spread was only 6 μg. The working electrode was a cylindrically-shaped double thickness of 45-mesh platinum connected to the cell by a wire. The 50-ml cell contained a glass stirrer and two glass tubes for salt-bridge connection, one of which contained sulphuric acid and a platinum spiral counter electrode; the second contained 0.5 *M* hydrochloric acid and a silver–silver chloride reference electrode. The gold sample was dissolved in *aqua regia*, boiled to remove nitrogen oxides and treated with sulphamic acid to remove traces of nitrite. The 0.5 *M* hydrochloric acid was electrolyzed at +0.48 V until the current decreased to 15–25 μA. When starting with a cleaned electrode, 5–10 mg of gold was pre-plated at a somewhat lower potential. Following accumulation of 50–75 mg of gold, the latter was stripped with sodium cyanide and hydrogen peroxide. The concentrations of the supporting electrolyte or of sulphamic acid were not critical. Background corrections were negligible and oxygen did not interfere. There were serious interferences from iridium(IV), ruthenium(IV), silver and vanadium(V). Up to 3 mg of iron(III) did not interfere in the presence of 0.5 *M* hydrochloric acid and 1 *M* phosphoric acid. Moderate amounts of platinum(IV) could be tolerated.

For the coulometric titration of gold in copper anode slimes, TSO *et al.*[83] applied the method to 2 μg with an average error of ±0.3%. Platinum was used as the cathode and cadmium as the anode. To detect the end-point, the authors used a potentiometric method with platinum as the indicator. A pretreatment with nitric acid removed interfering ions.

Thin layers of gold alloys on copper plate were analyzed by controlled-potential coulometry. MUTO *et al.*[84] dissolved the thin layer with potassium cyanide. Silver and gold were then deposited on a mercury working electrode at −0.90 and −1.60 V respectively. The analysis required one hour and the precision was of the order of several per cent.

Palladium

Controlled-potential coulometry was used by TAKATA AND MUTO to determine palladium[85] and palladium alloys[86]. When a gold electrode at +0.20 V and a solution containing 1 mg Pd/10 ml were used, the error was large because of adsorption of hydrogen by the gold electrode. This error was reduced to 1% for 1 mg of palladium by substituting a mercury electrode. The electrolyte was *M* hydrochloric acid. In the case of an electrolyte of disodium hydrogen phosphate and ammonia a positive potential of +0.35 V was used. With palladium alloys, the authors[86] determined coulometrically silver, gold+platinum, gold and gold+platinum+palladium. The silver was reduced at −0.15 V in an electrolyte of ammonia and ammonium chloride, with platinum as a working electrode; for gold at the same working electrode, the reduction potential was +0.55 V and the electrolyte was phosphoric acid and disodium hydrogen phosphate; for gold+platinum and the same electrode, the voltage chosen was −0.18 to −0.19 V and the same electrolyte as used for silver. For gold+platinum +palladium, mercury was used as the working electrode, the potential was 0.00 V, and the electrolyte was a phosphate mixture. The data obtained were in adequate agreement with the results from titrimetric methods.

Platinum

An interesting method for the coulometric determination of platinum by titration with tin(II) chloride was described by BARD[87]. This method involved reactions, in principle quite common to the platinum metals, which ought not to take place and do, or perhaps which ought to take place and do not, if one were to predict from recorded potentials. Tin(II) chloride, one of the most useful quantitative reagents for the determination of platinum, may be used to reduce platinum(IV) to the divalent state and in spite of the favourable potentials the metal is not produced. BARD[87] indicated that this "reflects a very slow reaction between platinum(II) and stannous ion". The present author suggests that the problem may be more complex and that the anomaly may involve dissolved constituents yet unknown; our present knowledge of dissolved platinum metals constituents is meagre. As partial support for the hypothesis of a slow reaction, BARD refers to the work of MEYER AND AYRES[88] who postulated a zero valence for the tin(II) chloride–platinum coloured product. This finding has been rejected in subsequent work[89]. For the titration BARD[87] used a supporting electrolyte of 2–4 *M* sodium bromide, 0.2 *M* tin(IV) chloride, and 0.3 *M* hydrochloric acid. A gold generator electrode provided a current efficiency of 99.5–99.9% with current densities of 10–84 mA/cm^2. A 5–10% excess of tin(II) chloride was produced and back-titrated to the equivalence point at 0.24 V with electrogenerated bromine obtained at a 1-cm^2 platinum anode. Nitrogen was used to eliminate dissolved oxygen from both titration and auxiliary chambers. It was noted that the species being reduced by tin(II) differed in colour from the platinum constituent formed on reoxidation. The pale yellow platinum(IV) hexachloride initially present was slowly converted to the more stable bromide complex in the supporting electrolyte and thus the result of the reduction was essentially $[PtCl_4]^{2-}$. Upon reoxidation with bromine the deep yellow colour of the end-point was probably caused by $[PtCl_4Br_2]^{2-}$ with a relatively strong absorption maximum at 380 nm. The average error for the titration of platinum was about ±5%. Although both the appropriate potentials of rhodium or iridium couples suggest co-reduction this did not occur and directions were included to reduce interference by these two metals resulting from secondary reactions. Acceptable results were recorded for 3–10 mg of platinum in the presence of 1–2 mg of palladium, rhodium and iridium. Copper, iron, gold interfered, as well as osmium and ruthenium in their higher oxidation states.

Iridium

The coulometry and polarography of pure iridium solutions was discussed by PAGE[90]. In the case of the latter technique, the data were restricted to indicate that in a 0.2 *M* hydrochloric acid supporting electrolyte, iridium(IV) produced a well-defined diffusion current which could be applied for polarographic determinations. For coulometric determinations a mercury cathode was used in an H-type cell. The two compartments were separated by a coarse fritted-glass disc and an agar–potassium chloride gel. The second compartment contained the silver–silver chloride counter electrode in 1 *M* hydrochloric acid. The reference electrode was a S.C.E. which in the case of perchloric acid solutions of iridium was used with a bridge containing 1 *M* hydrochloric acid. The controlled-potential reduction could be carried out at a platinum cathode at 0 or +0.40 V or at the mercury cathode at 0 V in 0.2 *M* hydrochloric acid. The reduction proceeded to iridium(III) from iridium(IV). To ensure the quadrivalency of iridium, chlorine was added to the solution and then removed by heating. The titrations were made after a pre-electrolysis of the supporting electrolyte, and nitrogen was used to remove dissolved oxygen. After electrolysis for 60 min the background current was negligible. The reduced iridium constituent could be reoxidized to quadrivalency and, after adding and removing excess of chlorine, the titration could be repeated. Attempts to reoxidize the iridium(III) at a platinum anode at +1.0 V failed. Attempts to apply the method to fumed perchloric acid solutions of iridium gave erratic results. In the case of sulphuric acid solutions of iridium, there was no reduction wave before the discharge of the supporting electrolyte at −0.75 V and attempts to reoxidize at +1.0 V failed. A brief study was made of the behaviour of iridium in sodium hydroxide solution with and without ethylenediaminetetraacetic acid with no conclusive results. A few adsorption data were presented to indicate changes in the solution composition of iridium solutions.

VAN LOON[91] was one of the few authors of electrometric methods for the noble metals who proved that their proposed methods were at least equal in efficiency to standard methods when applied to complex industrial products. In principle, milligram amounts of rhodium and iridium were determined in the same solution with no chemical separation of the two metals. Iridium was determined as described above at a potential of +0.25 V with a platinum cathode, being reduced from iridium(IV) to iridium[90,91]. Rhodium was determined subsequently by electrolysis at −0.20 V with an H-cell and a mercury cathode[32,91]. The results of all of the various coulometric determinations indicated good accuracy and precision.

The author used a concentrate, obtained by an electrolytic refining process, which contained about 25% noble metals, except osmium, and about 25 base-metal constituents. VAN LOON first analyzed the concentrate by an adaptation of the method recorded by ZACHARIASEN[92] except that the isolated rhodium and iridium were determined by the coulometric method. Preliminary tests were also made with synthetic rhodium and iridium solutions and with synthetic concentrates simulating the natural material. During these early tests the author examined the effects on the coulometric determination of palladium separated as the dimethylglyoximate and of the usual hydrolytic precipitation of some of the platinum metals. In the case of the mill concentrate, VAN LOON used a slight variation of the fire-assay collection by iron, copper and nickel, together with wet separations. A table describing the interferences from the base metals present in the concentrate was included.

The earlier publication by PAGE[90] of a method for the coulometric determination of iridium(IV) was considered to be "long and rather complicated" by STENINA AND AGASYAN[93], who used electrogenerated copper(I) to determine iridium(IV) coulometrically in the presence of rhodium. Platinum was used for anode and cathode. The auxiliary solution was copper sulphate and hydrochloric acid was added to give a 4 M concentration; the latter acid was also used in the anode compartment. Saturated potassium chloride was used as a bridge. Determinations were carried out with current densities of 2.50 mA/cm^2. The data for 90 μg–4.4 mg indicated acceptable accuracy. Data for the simultaneous presence of rhodium in ratios to iridium of 1:1 up to 50:1 for the range of about 200–400 μg of iridium also indicated acceptable recoveries. In general, the errors were negative. For ratios of rhodium to iridium of 50:1, the error for 180 μg of iridium was -18.2%; for a ratio of 1:1 for 430 μg of iridium, the error was -2.3%. The sensitivity of the method was stated as about 2 μg/ml. End-points were found potentiometrically. Iron(III) interfered although when present without iridium there was no apparent reduction under the experimental conditions. Atmospheric oxygen was without effect.

Because the above method yielded small consistently negative errors and could be applied only over a very limited range of iridium concentrations, STENINA AND AGASYAN[94] continued their investigation of the method and found that reducing impurities in the copper(II) sulphate hydrate produced low results in their earlier experiments[93]. A series of well chosen procedures allowed the production of pure copper sulphate. Data were provided to prove excellent precision and accuracy with a platinum disc or a carbon cylinder as the cathode and a platinum disc as the anode. Slightly better accuracy was obtained with an amperometric end-point, in which case there was no interference from osmium(IV), rhodium(III) and palladium(II) at ratios of about 10:1 with respect to iridium(IV). In the case of ruthenium at ratios of 3:1, the reduction wave was distorted and a potentiometric end-point was used. The latter with less than 0.1 mg of iridium(IV) produced low potential jumps; polarized electrodes did not improve the end-point detection, contrary to the effect on amperometric end-point detection. The authors stated that high accuracy and precision could be obtained for iridium(IV) concentration as low as 0.2 μg/ml. The sensitivity was $1 \cdot 10^{-6}$ M.

Electrogenerated titanium(III) was used by STENINA *et al.*[95] for the coulometric titration of iridium(IV) and ruthenium(IV) with graphite or tungsten electrodes at 1–5 mA/cm^2: 100% generation efficiency was not achieved by platinum electrodes. The electrolyte could be either hydrochloric or sulphuric acid, the optimum concentration varying with the temperature. End-points could be determined amperometrically, potentiometrically at zero current, or photometrically. The first was the most sensitive for iridium at a lower limit of 0.2 μg/ml. For ruthenium the photometric method could be used to 0.4 μg/ml. Platinum(IV) titrated with iridium and ruthenium and thus interfered. There was no interference from osmium, rhodium or ruthenium(II).

Ruthenium

A coulometric method for the determination of ruthenium(IV) by electrically generated titanium was recorded by STENINA AND AGASYAN[96]. The working solution contained known amounts of ruthenium hydroxypentachloride, titanium(IV) chloride and a 1–1.2 or 2 *N* hydrochloric acid solution. The generating current density was 5 mA/cm^2 obtained from a 1-cm^2 tungsten disc. A platinum disc anode was immersed in the supporting electrolyte and connected to the cathode compartment by an electrolytic bridge. The effective titration efficiency reached 99.1%. A stream of nitrogen was passed through a vanadium sulphate solution and the temperature was maintained at 50°. The resulting data for 100–2000 μg of ruthenium in 35 ml, indicated reasonable accuracy with potentiometric end-points. Amperometric or electrophotocolorimetric methods were unsatisfactory. Potentiometric titrations indicated two potential jumps, the first corresponding to the binuclear compound $[Ru^{IV}Cl_5OHCl_5Ru^{III}]^{4-}$ and the second to the complete reduction to ruthenium(III). Satisfactory results were obtained from either the first or the second jump. However, in the case of the former with higher concentrations of ruthenium(IV), the value of the jump decreased and the error increased. The small value of the second jump and the slowness of attaining equilibrium were examined with the hope of increasing sensitivity by the use of polarized platinum electrodes. While no improvement was detected with the second jump, the first equivalence point was improved to the degree that 800 μg could be determined with reasonable accuracy. There was no interference from osmium(IV) at ratios of 5:1.

A potentiostatic coulometric method for determining ruthenium(IV) was described by STENINA *et al.*[97]. The method is somewhat insensitive and not particularly accurate. Weight ratios of 1 mg of ruthenium to 10 mg of osmium could be tolerated. Iridium interfered. There was relatively little interference from platinum(II) or (IV) in ratios of 1:5; of rhodium(III) in ratios of 1:20; copper(II) and iron(III) in ratios of 1:5. The errors ranged from −1.2 to 8.5%. The sensitivity was about 2 mg/ml. The compounds used were $(NH_4)_2[RuOHCl_5]$ and the hexachloro salt. The determination was made in 6 *M* hydrochloric acid as supporting electrolyte with a platinum electrode rotating at 540 r.p.m. and a platinum anode. The half-wave potential was +0.9 V. A potential of +0.5 V was used during the electrolysis, providing a selective reduction in the presence of the above associated metals. Data were obtained by calculation from previously recorded formulas and by a graphic method. Although the proposed method has value in its slight interferences from osmium, more generally useful non-electrometric methods are available.

Lavender-blue solutions of $RuCl_4^{2-}$ were prepared by RECHNITZ[98] who used an applied potential of -0.470 ± 0.001 V and 4 *M* solutions of potassium chloride in hydrochloric acid at pH 1.5. The solvent was deaerated with nitrogen and pre-electrolyzed to remove reducible impurities. Current–time curves for the reduction of K_2RuCl_6 by the above method indicated a 2-electron reaction. Plots of log (current) *vs.* time indicated 100% current efficiency.

AMPEROMETRIC METHODS

Gold

A procedure for the amperometric determination of gold was described by

PASHCHENKO *et al.*[99]. The method was applied to concentrates of copper, lead and zinc, to sulphide ores and to crude copper. The gold contents in g/ton ranged from about 0.7 to 94 and agreed within reasonable ranges with data obtained by assay. The sample was treated with *aqua regia* and various oxidants to remove sulphuric acid and finally evaporated with hydrochloric acid to remove oxides of nitrogen. The solution was titrated with thiourea at +0.7 V with a platinum indicator electrode rotating at 200 r.p.m. The composition of the titrated complex was $[Au(SCN_2H_4)]^+$.

Thiopiperidine was used by TARAYAN AND SARKISYAN[100] for the amperometric titration of gold. Presumably the net result of the reaction was gold(I) sulphide, (Au_2S_2). The titration was carried out at pH 2–6, the optimum gold concentration being 4–840 μg/ml. The method could be used in the presence of copper(II), selenium and tellurium(IV). With copper EDTA was used at pH values below 5 to avoid reduction to gold.

Pyrazolone was used by LUGOVOI *et al.*[101] to determine 20–200 μg/ml of gold amperometrically at pH 2–5. The electrolyte was *M* potassium bromide, the titrant cerium(IV) sulphate in 2 *N* sulphuric acid, and the potential +0.4 V. The average error was ±2.1%. There was no interference from 60-fold platinum or 30-fold palladium. Samples were treated with mercury(I) chloride to produce metallic gold, platinum and palladium, which were then filtered off and the metals dissolved in *aqua regia*. The solution was evaporated as usual with hydrochloric acid and the nitrate-free moist salt was dissolved in *M* potassium bromide. Silver was removed as the bromide or chloride. It was noted that in 0.1 *M* sodium nitrate, the metals are produced by pyrazolone.

A non-compensating electrometric method for the determination of gold in jeweller's alloys containing silver and copper was described by CHIRKOV AND ROMANOVA[102]. The cathode was a gold wire or gold-plated platinum wire, and the anode was a sulphate–copper electrode. The gold was titrated with Mohr's salt without the removal of silver chloride or nitrous acid. The solution was agitated by rotating the beaker at 180 r.p.m. A small loss of gold by deposition on the cathode occurred during the titration; this effect was partially reduced by initial addition of a large proportion of the Mohr's salt required, leaving only an amount equivalent to a small titer. The addition of copper salts to the gold solution improved the shape of the titration curves; silver chloride or nitric acid did not interfere but excess of hydrochloric acid decreased the jump in the titration curve and increased the amount of Mohr's salt consumed. Acidity was therefore controlled by the addition of phosphoric acid. The precipitated gold and the silver chloride were filtered off and the latter was removed by ammonia. The gold was dried, heated and weighed.

Sodium thiosulphate or 2-mercaptobenzothiazole[103] has been used for the amperometric titration of gold, the first for amounts greater than 100 μg and the latter for amounts above 10 μg. The rotating platinum electrode was used and the method applied successfully to slimes and cyanide solutions. EZERSKAYA[103] also described a polarographic titration at −0.9 V in solutions of potassium or sodium hydroxide containing gelatin. The waveheight was proportional to the concentration over a wide concentration range.

The determination of gold in the presence of selenium, tellurium and palladium is not infrequently required. An amperometric titration with hydroquinone was described by REISHAKHRIT AND SUKHOBOKOVA[104]. The method was applied over the range 20 μg–2 mg/ml of gold with an accuracy of 1–10% at 60°. A platinum microelectrode was used rotating at 800–900 r.p.m.; the reference was a saturated calomel electrode. The supporting electrolyte was 2 *N* sulphuric acid. The titration was made at 1.0 V. The limiting current was established quickly after each addition. The method was applied to sludges and ores. In these cases the sample was decomposed by sulphuric acid, the residue calcined and dissolved in *aqua regia*. Nitric acid was removed as usual. The amounts of gold found in 100 g of ore varied from 1.70 to 2.12 mg; in the case of 2.5 g of sludges the recovery was 4.04–4.68 mg. The accuracy compared to standard methods was fair.

Hydroxy and amino compounds of phenols, etc., have been used extensively to determine gold gravimetrically. REISHAKHRIT AND SUKHOBOKOVA[105] used such reagents for the amperometric determination of gold. As one would expect, the selectivity was comparable to that found for the gravimetric method. Titrations were made at 1.0 V with a rotating platinum microelectrode. The range of gold concentration was 2–80 μg/ml of solution.

Palladium

For the determination of 1.3–15 μg/ml of palladium, USATENKO AND TOLUBARA[106] used amperometric titrations with thiourea and the two derivatives, phenylthiourea and 1,1-dimethyl-3-*p*-chlorobenzenesulfonylthiourea (ND). A rotating platinum microelectrode at 0.9–1.0 V was used to indicate the end-point. Nitric acid was removed from the solutions in the usual way. The supporting electrolyte was 0.5–4.0 *N* sulphuric acid. The thiourea method tolerated ten times as much platinum, 20 times as much iridium or rhodium, and very large proportions of copper, nickel, cobalt, bismuth, selenium, tellurium, arsenic, lead, tin, antimony and iron. Gold and silver interfered. Similar results were obtained with the thiourea derivatives. Phenylthiourea could not be used in the presence of platinum and the ND reagent could not be used in the presence of platinum, iridium and copper. The stability and solubility of the palladium complex increased with the derivative–thiourea ratio. The method was applied to enriched sludges from nickel production. These contained platinum, rhodium, ruthenium, iridium, gold and silver, in which case the sludge was treated with *aqua regia*, and the solution treated to remove nitric acid. Gold was removed by extraction with ether. Excess of hydrochloric acid was removed by evaporation with sulphuric acid. Aliquots were analyzed amperometrically. With 0.068–0.78 mg of palladium the relative error was 0–6.6%. The results were compared with data from the following amperometric methods: hexamethylenedithiocarbamate, 8-mercaptoquinoline, 2,4-dithiobiuret and thionalide. In contrast to the thiourea reagent, each of these required one or more masking reagents, amperometric indicators or protective colloids.

The amperometric titration of palladium, silver and copper with benzimidazol-2-ylmethanethiol and its application to brass, aluminium and manganese bronze, copper matte, brazing alloy and Silmanal, was discussed by BERA AND CHAKRABARTTY[107]. Nitric acid solutions of the brazing alloy containing 0.5–4 mg of palladium were treated with chloride and the silver filtered off. An acetate buffer and gelatin were added, and nitrogen was passed through the solution which was then titrated amperometrically at −0.2 V. The equivalence point corresponded to the intersection with the volume axis. The maximum error was less than 1.5% and the coefficient of variation was 1%. Copper, mercury(I) and (II) and platinum(IV) interfered.

2-(*o*-Hydroxyphenyl)benzoxazole was used by WILSON *et al.*[108] for the amperometric determination of palladium. The palladium solution contained gelatin and a sodium acetate–acetic acid buffer. Nitrogen, conditioned by passage through a blank solution, was used and the reagent added. All current measurements were made at −0.5 V and a time schedule for the titration was required. The method was primarily recommended for palladium solution containing only traces of other platinum metals although iridium must be removed.

2-Mercaptobenzoxazole has been used for the amperometric determination of palladium, silver and copper[109]. Dilute alkali solutions of the reagent were used as the titrant and stored in dark bottles in a refrigerator for no more than 48 h. The titration was made at an applied potential of −0.3 V and the titrated solution contained a sodium acetate–acetic acid buffer and gelatin solution through which nitrogen was passed for 10–15 min. The method was applied to solutions containing 1–5 mg of palladium for which the precision was less than 1.5%. Mercury(I) and (II), platinum(IV), and copper interfered. In the presence of silver chloride the titrant was added to the supernatant liquid; 4–5-fold amounts of lead, cobalt, nickel, etc., could be tolerated.

1,2,3-Benzotriazole has been used amperometrically for palladium[110]. The technique used followed closely that recorded by WILSON *et al.*[108] for 2-(*o*-hydroxyphenyl)benzoxazole. Current measurements were made at −0.5 V. The amounts of palladium used were in the low milligram range. There was interference from osmium, ruthenium, iron, gold and nickel.

For the amperometric titration of palladium and silver admixtures SONGINA *et al.*[111] used 0.01–0.00005 *N* potassium iodide, a rotating platinum electrode (200 r.p.m.) at +1.0 V and an electrolyte of sulphuric acid at pH 1–2. The applied concentration range was $2 \cdot 10^{-6}$–10^{-3} *M* and the mean relative error was 1.7%. Platinum and the non-ferrous metals did not interfere. In the presence of silver the total of silver and palladium was titrated and a second aliquot was treated with ammonia to pH 4–5 and silver was titrated alone. The stability constant of $[Pd(NH_3)_4]^{2+}$ was $2.5 \cdot 10^{-30}$ compared to $5.89 \cdot 10^{-8}$ for the silver complex.

Amperometric determinations of palladium by β-furfuraloxime with a rotating platinum electrode were made by BARDIN AND MELEKA[112]. The hydrochloric acid solution of palladium and the sodium nitrate used as the supporting electrolyte, were deaerated with nitrogen. The oxime titrant was added with the microelectrode controlled at a potential of +0.9–1.0 V and the current was measured 40 sec after each addition. The palladium concentration was directly proportional to the volume of the titrant. For concentrations of 10–100 μg/ml of palladium the error was ±2.5–3%.

α-Furildioxime, dimethylglyoxime and its sodium salt, β-furfuraloxime, and 8-hydroxyquinoline were used successfully by BARDIN AND LYALIKOV[113]. With a rotating platinum electrode, an electrolyte of sodium nitrate and a voltage of 0.9–1.0 V, the authors obtained an accuracy of 2–3% over the range of 0.01–1 mg/ml. Although 1-nitroso-2-naphthol was not suitable for use with a rotating electrode, it could be used with a dropping electrode. The equipment used was illustrated and, being hermetically sealed, it could be used without interruption irrespective of the time of titration.

1-Nitroso-2-naphthol was also used by KHADEEV AND GLAZUNOVA[114] for the amperometric determination of palladium and copper. For the former, the accuracy was better than 1%. Over 65 spectrophotometric methods have been recorded for palladium. One may hope that corresponding electrometric methods may not also become the subject of excessive analytical researches.

Iridium

Amperometric titrations of iridium with a platinum electrode rotating at 800–1000 r.p.m. and an S.C.E. as a reference electrode were described by PSHENITSYN AND EZERSKAYA[115]. The titrants were ascorbic acid and hydroquinone. The amounts of iridium determined ranged from about 10 mg to 15 μg in respective volumes of 30 and 10 ml. The supporting electrolyte was sodium chloride and the pH was 1.5. In the case of hydroquinone the anodic oxidation wave had a limiting current starting at about +0.55 V. The half-wave potential for iridium(IV) was +0.73 V. There was no interference from rhodium, platinum, palladium, copper, nickel, selenium and tellurium. Gold interfered and the iron interference could be removed by adding phosphoric acid. Interference from ruthenium could be reduced by varying the technique of dissolution. Interferences in the case of ascorbic acid were similar to those for hydroquinone. At pH 1.5 the half-wave potential for ascorbic acid was 0.7–0.8 V. The curves for the titration at −0.4–0.5 V were similar in shape to those for hydroquinone. Precision for μg amounts of iridium was about 4%, and for milligram amounts 2–9%; the relative errors were respectively 10–15% and 1–5%; 20 μg of iridium in 10 ml was the minimum determinable amount.

An amperometric titration for iridium, free of interference from rhodium and other platinum metals, was developed by LABKOVSKAYA AND ANDREEVA[116]. Hydroquinone was again used as the titrant at the limiting current of +0.4 V in a sodium chloride supporting electrolyte. The applicable iridium range was 10–500 μg/ml; at concentrations greater than 2 mg/ml, the titration curve was distorted. For these larger amounts an iodine titration was made to approach the equivalence point which was then reached with a more dilute iodine solution.

POTENTIOMETRIC METHODS

Gold

For the determination of gold in alloys, OROBINSKAYA[117] titrated with Mohr's salt and claimed increased accuracy. Unfortunately, the original article was not made available.

Palladium

A differential potentiometric determination of palladium in high-grade palladium–platinum alloys was used successfully by BARABAS AND VINARIC[118]. The method required the addition of potassium iodide to a hydrochloric acid solution of the alloy to remove all but a small excess of the palladium which was subsequently titrated with standard potassium iodide using platinum as the indicator electrode with the saturated calomel reference electrode. A standard sample of palladium was treated simultaneously in the same way as the unknown, so that a factor could be deduced from the weight of the pure palladium sponge; this factor was reasonably constant and could be applied to the titration value for each unknown. It was noted that if the palladium alloys with the standard are not analyzed "at the same time the potassium iodide equivalent of palladium is not exactly the same for the two runs". The acidity of the solution was adjusted to 0.2% hydrochloric acid, gold was removed by sulphur dioxide, and silver present as the complex $AgCl_2^-$ was removed by the addition of a small amount of silver nitrate. It would be interesting to know the evidence that "silver chloride acted as a sort of carrier of the soluble silver polychloride". Platinum did not interfere up to twice the concentration of palladium and copper up to 200 times that of palladium. The authors claimed an accuracy which compared favourably with that from gravimetric methods. The procedure is rather ingenious and should be useful in technical analytical work involving many determinations of palladium; however, it cannot be used indiscriminately, depending, as it does, upon the absence of the many constituents which react with potassium iodide. The statement that "there is no limitation as to the size of the sample that can be used" requires reservations.

Osmium

An interesting and potentially useful potentiometric titration for osmium was described by SANTRUECK *et al.*[119]. The method involved the hydrolysis of the hexachloroosmate in a 0.2–1 *N* sodium hydroxide solution. The product was a dehydrated osmium(IV) oxide. In basic solutions of less than 0.2 *N*, negative errors were obtained. If the solutions were greater than 1 *N* in sodium hydroxide, the reactions were slow and high values were obtained. The solution containing the osmium oxide was then treated with tellurous acid to form $Na_2OsO_2(OH)_4$. After the addition of standard permanganate solution to oxidize the tellurate to $Na_2H_4TeO_6$, the titration was continued to produce Na_2OsO_5 from $Na_2OsO_2(OH)_4$. The author discussed the effects of varying the basicity and of the tellurous acid concentration. The data indicate a successful application to 7–37 mg of osmium in 50 ml of solution. The titration curve indicated good breaks, first at the oxidation of tellurous, and then at the oxidation of the osmium complex, corresponding respectively to 230 mV and 420 mV. A detailed procedure was provided. One may hope that this method will receive further attention.

ELECTROGRAVIMETRIC METHODS

Gold

Electrodeposition methods for the determination of gold, and a number of base metals were recorded by DESCHAMPS AND BONNAIRE[120]. The author used a platinum cathode and a silver wire anode. The electrolytes used were hydrochloric acid, nitric acid, or sodium chloride. A potential difference of 500 mV was maintained between the anode and cathode. Data in milligrams were provided for gold solutions and for solutions of a lead alloy containing silver and copper. A method of electro-deposition was used to separate and determine palladium and copper in alloys.

Palladium

A rapid electrogravimetric method for the determination of palladium and for the analysis of pallador was described by VAJGAND AND ZIVKOVIC-COBANOVIC[121]. The report does not seem to have been abstracted and in the present author's opinion, the method will be useful. The solutions of 0.1–0.15 g of palladium were made up to

2 *N* in sulphuric, nitric or hydrochloric acids and to 7–8% in ethanol. Determinations were made at 65°, an operating voltage of 0.8–0.9 V and a current strength of 0.2–0.5 A. A determination could be completed in about 30 min. To separate palladium from copper, the author restricted the operating cathode voltage to 0.39 V *vs.* NHE. For the analysis of pallador, the alloy was dissolved in nitric acid and the gold removed by filtration; silver was separated as the chloride, and sulphuric acid and ethanol were added to the filtrate. Palladium was precipitated on platinum gauze electrodes at 0.39 V *vs.* NHE and at 65°. The electrode was dried for a few minutes at 105° and then weighed. The remaining solution was almost completely neutralized and copper, cadmium and zinc were determined polarographically with 1 *N* ammonia–1 *M* ammonium chloride as the supporting electrolyte with the addition of sodium sulphate and gelatin.

DANH AND VIGUIE[122] dissolved copper–palladium alloys in *aqua regia*, added sulphuric acid and evaporated to fumes, cooled, added sulphuric acid and heated. The volume was adjusted suitably and aliquots containing about 100 mg of palladium were used for the electrolysis. Palladium was deposited at 50° in a *N* sulphuric acid medium at +0.640 V *vs.* NHE. In order to obtain a fine deposit it was necessary that the current density did not exceed 5 mA/cm^2. The electrode was washed with ethanol, dried and weighed. Copper was deposited from the filtrate after adding hydroxylammonium chloride.

An electrolysis method of determining silver and palladium in alloys was described by TSUJI[123]. The solution of the alloy contained ammonia, EDTA and murexide. After the deposition of silver at −0.20 V, palladium was deposited at a cathode potential of −0.70 V. The error for about 100 mg of palladium was −0.2–0.5%. In an earlier paper the author[124] described conditions for the electrolytic deposition of palladium from various acid and basic media.

Platinum

A quantitative electro-deposition of platinum from uranium–platinum alloys was described by GARDNER *et al.*[125]. The method was applied to alloys containing 0.1–5.0% platinum with an average recovery of 99.9% and a relative standard deviation of 0.6%. The sulphuric acid solution of platinum was electrolyzed at room temperature for 30 min, at a current density of 1 A and about 2 V with a rotating cathode. After 30 min the current density was increased to 5 A for 1 min. The cathode was rinsed with water, ethanol and ether, dried and heated for a short time by a Meker burner. This work was well described and executed.

Rhodium

A method for the separation of 6–30 mg of rhodium from not more than 60 mg of iridium as chloride or chloro salts was described by MACNEVIN AND TUTHILL[126]. The separation involved the deposition of rhodium partly as the oxide on a platinum electrode. During the electrolysis the potential was increased at intervals from −0.25 V to −0.4 V. Although iridium did not deposit electrolytically at −1.0 V there was considerable co-deposition at −0.3 V in the presence of rhodium. This was avoided by the use of chlorine to attain quadrivalency, the prior destruction of complex ions, and addition of ammonium chloride. Hydroxylamine hydrochloride was also added to reduce chlorine and to serve as an anodic depolarizer. The authors believed that the co-deposition of iridium was influenced unfavourably because of the presence of precipitated ammonium hexachloroiridate. It was also suggested that the presence of rhodium oxide resulted from hydrolysis in the electrolyte to form a hydrated oxide of rhodium. The oxide was reduced in hydrogen before the cathode was weighed. The results indicate good separations and recoveries of the two metals for 6–30 mg of rhodium with ratios as high as 1:10 of iridium.

An investigation of various characteristics of the electrolytic separation and determination of rhodium in the presence of iridium was recorded by McBRYDE *et al.*[127]. The method was basically that described earlier by MACNEVIN AND TUTHILL[126] but, contrary to the findings of these authors, McBRYDE *et al.* found that the plated rhodium was sometimes contaminated with iridium. The latter authors avoided the use of hydroxylamine by electrolyzing with carbon rods. The solution of rhodium chloride contained ammonium chloride, acetic acid and sodium acetate at pH 4. The cathode was a previously reduced and weighed platinum gauge and the anode spectrographic carbon. The cathode potential was 0.40 V. The electrolysis was continued for 1.5–2 h with a final current of 0 or about 3 or 4 mA. The cathode was dried at 100°, and because the deposit contained rhodium oxide it was reduced in hydrogen before weighing. The data obtained failed to explain the mechanism involved in the deposition of the rhodium. The authors stated that "it is doubtful if the electrolytic method of separation is as reliable as other procedures" and that the experimental data were made available to encourage a more extended investigation. The present author agrees with the conclusions of McBRYDE *et al.* although it is not improbable that continued investigation could result in a reliable electrogravimetric separation of the two metals.

Radioruthenium

Interesting papers dealing with the quantitative electro-deposition of radioruthenium over the range $5\cdot10^{-3}$–$5\cdot10^{-5}$ M and for concentrations below 10^{-5} M were recorded by GRIESS[128] and by LIETZKE AND GRIESS[129]. For the higher concentrations, the authors used natural ruthenium to the solutions of which was added a small amount of tracer; this was evaporated to near dryness and treated with red fuming nitric acid and the solution again taken to dryness. Large excesses of nitric acid were removed with hydrochloric acid. Either of these two acids or sulphuric acid was a suitable electrolyte; good deposits were made in 0.1–0.3 N acid solutions. Copper was the preferred cathode, although nickel, gold and platinum were also used. With a copper cathode at about −0.45 V, a bright adhering deposit was formed, the amount of which could be determined by counting the active tracer. In general, recoveries were about 99%. The author discussed the rate of deposition, optimum composition and techniques. The second paper dealt with depositions from solutions more dilute than 10^{-5} M and here it was also necessary in all cases to convert to the nitroso condition; this was accomplished by bubbling nitrogen dioxide gas through a solution of ruthenium chloride. The data obtained indicated that the ruthenium solution contained at least two different species, one platable on a smooth platinum cathode and a second along with the first on platinum black electrodes. The authors examined the influence of cathode area and material, age of the ruthenium solution, etc. Recorded recovery data obtained at a cathode potential of −0.60 V for concentrations of $5\cdot10^{-4}$ M, $5\cdot10^{-6}$ M and $5\cdot10^{-8}$ M were respectively 99%, 79–83% and

79–83%. The authors assumed that the two dissolved ruthenium nitroso species were not in equilibrium or else the equilibrium was very slowly achieved. One may note here the disadvantages that are a characteristic of a specialized approach to analytical chemistry. The effects of ageing noble metal solutions has been discussed by a number of researchers from points of view restricted by specific analytical techniques and it is the present author's opinion that an integration of this recorded inorganic data would be of very considerable value to the chemist whose work involves, as it generally does, some knowledge of solution composition.

A rapid and non-destructive method of determining gold and silver in alloys was proposed by SHIOBARA[130,131]. A paper, moistened with ammonium chloride for gold, in contact with the alloy was subjected to a pressure of 2 kg/6.25 cm^2 and was stripped at 4 V d.c. and 10 mA, for 10 sec. The paper was then treated with hydroxylamine sulphate in the case of gold. Absorbance measurements were made at 600 nm. This is now a new technique and modifications have proved useful for the identification of alloy and mineral constituents without destroying the alloy. However, any quantitative measurement requires homogeneous alloys.

SUMMARY

This review deals with the published electroanalytical methods of polarography, coulometry, amperometry, potentiometry and electrogravimetry. For polarography, the period covered is subsequent to June 1958. For potentiometry, the reports included are in general those published after a previous review on titrimetric methods. The remaining electroanalytical methods for the noble metals have only recently received significant attention; the review of these methods, as well as the others, covers the chemical abstracts up to January 1968.

During the past decade polarographic methods have taken an important place in industrial laboratories dealing with noble metals; such methods remain largely confined to simple systems although there has occasionally been some integration with other analytical techniques to allow application to complex noble metal systems. Coulometry and amperometry seem to find little application in laboratories concerned with determination of noble metals, possibly because of a lack of analytical emphasis in the reported researches. The review should make clear the paucity of industrial interest in electrogravimetric methods.

RÉSUMÉ

Cette revue a trait aux publications concernant les méthodes d'électroanalyse: polarographie, coulométrie, ampérométrie, potentiométrie et électrogravimétrie. Pour la polarographie, la période couverte par la revue est ultérieure à juin 1968. Pour la potentiométrie, les indications fournies sont en général celles qui furent publiées après une revue antérieure sur les méthodes titrimétriques. Les autres méthodes d'électroanalyse, adaptées aux métaux nobles, n'ont été l'objet d'une attention importante que récemment; la revue de ces méthodes, ainsi que celle des autres, couvre les "Chemical Abstracts" jusqu'en janvier 1968.

Durant la dernière décade, les méthodes polarographiques ont pris une place importante dans les laboratoires industriels ayant affaire aux métaux nobles; de telles méthodes restent principalement confinées dans des systèmes simples, bien qu'il y ait eu occasionnellement quelque intégration avec d'autres méthodes analytiques pour permettre une application, en faisant des complexes de métaux nobles. La coulométrie et l'ampérométrie semblent avoir trouvé peu d'applications dans les laboratoires concernés par la détermination des métaux nobles probablement à cause du manque d'accent analytique que l'on a porté dans les recherches publiées. La revue a pour but de mettre en évidence le manque d'intérêt industriel pour les méthodes électrogravimétriques.

ZUSAMMENFASSUNG

Dieser Überblick behandelt die publizierten elektroanalytischen Methoden der Polarographie, Coulometrie, Amperometrie, Potentiometrie und Elektrogravimetrie. Für die Polarographie wird über den Zeitraum seit Juni 1958 berichtet; für die Potentiometrie schliesst dieser Bericht im allgemeinen an eine früher veröffentlichte Übersicht über titrimetrische Methoden an. Die übrigen elektroanalytischen Methoden haben für die Edelmetalle erst in jüngster Zeit Bedeutung erlangt. Die Übersicht über diese Methoden—ebenso wie die über die anderen—beschäftigt sich mit den Veröffentlichungen, die bis zum Januar 1968 in den Referatenorganen erschienen sind.

Während der letzten 10 Jahre haben polarographische Methoden einen wichtigen Platz in den Industrielaboratorien eingenommen, welche sich mit Edelmetallen beschäftigen. Diese Methoden beschränken sich jedoch vorwiegend auf einfache Systeme, obwohl es ursprünglich einige Zusammenfassungen mit anderen analytischen Techniken gab, um eine Anwendung auf komplexe Edelmetallsysteme zu ermöglichen. Die Coulometrie und Amperometrie scheinen nur wenig Anwendung in Laboratorien, welche sich mit der Bestimmung von Edelmetallen beschäftigen, zu finden, möglicherweise weil in den veröffentlichten Untersuchungen nur mangelhaft auf die analytische Bedeutung hingewiesen wird. Diese Übersicht zeigt das geringe industrielle Interesse an den elektrogravimetrischen Methoden.

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STUDIES IN THE TETRAARYLBORATES

PART IV. THE PREPARATION AND REAGENT PROPERTIES OF SODIUM TETRAKIS(*m*-TRIFLUOROMETHYLPHENYL)BORATE

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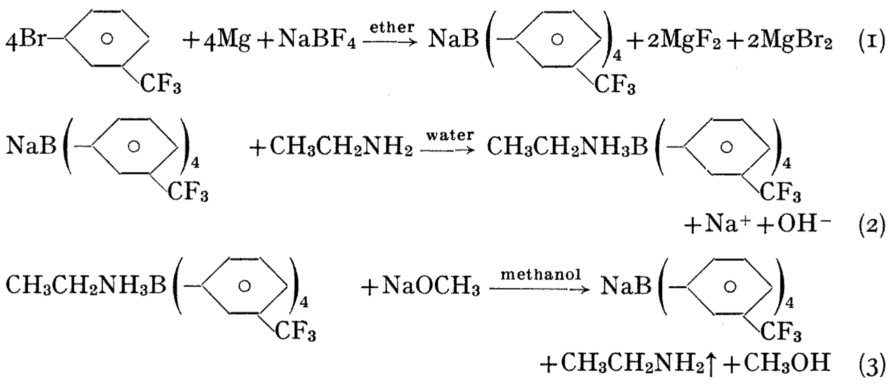
In a continuation of the study of substituent effects on reagent stability and selectivity, sodium tetrakis(*m*-trifluoromethylphenyl)borate has been synthesized. This compound selectively precipitates cesium in the presence of rubidium or potassium, and is comparable in acid stability to the other tetraarylborates which have strongly electronegative substituents in *para* or *meta* positions on the phenyl rings[1-3].

EXPERIMENTAL

*Synthesis of sodium tetrakis(*m*-trifluoromethylphenyl)borate*

The following sequence of reactions was employed in the preparation of sodium tetrakis(*m*-trifluoromethylphenyl)borate:



Distil *ca.* 400 ml of ether dried over sodium into a 3-necked 500-ml flask fitted with a reflux condenser, dropping funnel and magnetic stirrer. Transfer a 100-ml portion of the ether to the dropping funnel, and to this add 45.0 g (0.2 mole) of *m*-bromobenzotrifluoride. Then place 4.9 g (0.2 mole) of dry magnesium turnings in the flask, add a few crystals of iodine to catalyze the Grignard reaction, and start the stirrer. Add *ca.* 10 ml of the solution in the dropping funnel to the flask, and sweep the entire apparatus with dry nitrogen. Raise the temperature to 35° and hold until the reaction begins. Then add 5.5 g (0.05 mole) of finely-ground and dried sodium fluoroborate, cool to 14°, and add the *m*-bromobenzotrifluoride in ether solution dropwise over a 3-h period. Finally, maintain the mixture at 25° for 1 h.

Pour the reaction mixture slowly, with stirring, into 400 ml of ice-cold water containing several g of sodium carbonate which precipitates the inorganic salts from the solution. Separate the ether and aqueous layers in a large separatory funnel, saturate the aqueous phase with sodium chloride and extract three times with 50-ml portions of ether. Combine the ether solutions and pour over 500 ml of water adjusted to pH 8 with dilute sodium hydroxide in a large beaker. Stir this solution vigorously, warm and evaporate all the ether at 35°. Filter the aqueous solution through a "Celite" mat to remove any insoluble material.

Dilute the filtrate to 3 l and stir, while adding an aqueous 7% ethylamine solution dropwise to form the ethylamine tetrakis(*m*-trifluoromethylphenyl)borate salt. Addition of the amine should be discontinued immediately after the white flocculent amine salt ceases to form. If excess amine is added, brown reaction by-products precipitate from the solution and contaminate the desired precipitate. These impurities have solubility characteristics which are similar to those of the amine salt and cannot easily be removed through recrystallization. If the precipitation is carried out carefully, however, powdery white ethylamine tetrakis(*m*-trifluoromethylphenyl)-borate is obtained; m.p. 124–126°, 9.04 g yield.

Dry the ethylamine salt under vacuum and then dissolve in 100 ml of anhydrous methanol. Pour this solution into a 3-necked 250-ml flask equipped with an air condenser, small dropping funnel, stirrer and heating mantle. Bring the mixture to a vigorous methanol reflux and slowly add a solution containing 2.3 g of sodium methoxide in 100 ml of anhydrous methanol from the dropping funnel. Continue heating and stirring until all the ethylamine has been evolved (*ca.* 6 h). Remove methanol under vacuum, yielding a white, powdery residue.

Dissolve the salt in ether, and chromatograph the resulting solution through a column containing 25 g of basic alumina. Collect the chromatographed ether solution (*ca.* 300 ml) and add 75 ml of alkaline (pH 10) water. Evaporate the ether by stirring and heating, and filter the resulting aqueous solution through a fine sintered-glass crucible containing a layer of basic alumina. Saturate the filtrate with sodium chloride and extract 4 times with 50-ml portions of ether. Evaporate the combined ether extracts, with heating and stirring, until they become viscous. Finally, dry the sample under vacuum and over P_2O_5 at 80° for 24 h.

The sodium tetrakis(*m*-trifluoromethylphenyl)borate initially forms a glass which must be powdered to increase the surface area for drying. The total yield was 6.83 g. An NMR spectrum indicated the presence of 0.75 molecule of water per molecule of salt. Elemental analysis gave the following results (in %): C 53.86, H 2.70; calculated: C 53.57, H 2.81. This salt is very hygroscopic and difficult to analyze.

Reagent properties of the tetrakis(m-*trifluoromethylphenyl*)*borate anion*

A 1% solution of the sodium salt was prepared and approximately 1 ml of this reagent was added to 1 ml of a 0.1 *M* solution of the ion to be tested. The following ions gave heavy precipitates: cesium, thallium(I) and silver. Rubidium formed a precipitate only after 2 ml of the reagent were added. No precipitates were obtained with copper, cobalt, nickel, calcium, magnesium, barium, lithium or potassium.

The reagent was tested for sensitivity with 1-ml aliquots of cesium, rubidium and potassium ions in the concentration range from 0.002 to 0.2 mg/ml. An equal volume of 0.03 *M* reagent solution, with pH adjusted to *ca.* 8, was added. Cesium formed precipitates throughout the range of concentrations, but both potassium and rubidium failed to precipitate even in the most concentrated solutions.

The reagent was also tested as a possible precipitant for amines and other compounds containing protonated nitrogen. The compound was dissolved in water, with 0.1 *N* hydrochloric acid added, if necessary, to solubilize it. An equal volume of 1% reagent solution was added. This test was carried out with a series of amines, amino acids and alkaloids. Many compounds formed no precipitates, and those which did form were too colloidal to be useful in qualitative or quantitative analysis.

*The tetrakis(*m*-trifluoromethylphenyl)borate anion as a precipitant for cesium*

A quantity of pure cesium tetrakis(*m*-trifluoromethylphenyl)borate was obtained by adding a 2% reagent solution dropwise to a solution of cesium chloride. The cesium salt was recrystallized twice from a methanol–water mixture and dried under vacuum and over P_2O_5 at 80°. An elemental analysis gave the following results (in %): C 46.32, H 2.41; calculated: C 46.44, H 2.23.

The rubidium salt was obtained by adding a large excess of the reagent to a solution of rubidium chloride. It was recrystallized from methanol–chlorobenzene and dried under vacuum and over P_2O_5 at 80°. No potassium salt could be precipitated.

Solubilities of the cesium and rubidium salts were obtained. The values were calculated from flame photometric data on the cations in solution after equilibration for 48 h. These figures are listed in Table I and show that both the cesium and the rubidium salts are more soluble in basic than in acidic solutions. The rubidium salt is approximately 100 times more soluble than the cesium salt. Furthermore, the cesium salt is significantly more soluble at 25° than at 0°.

TABLE I

SOLUBILITIES OF CESIUM TETRAKIS (*m*-TRIFLUOROMETHYLPHENYL)BORATE AND RUBIDIUM TETRAKIS (*m*-TRIFLUOROMETHYLPHENYL)BORATE

(Equilibration time, 48 h)

Salt	*pH*	*Temp. (°)*	*Solubility (g/l)*
$CsB(C_6H_4m\text{-}CF_3)_4$	2.6	25	0.123
	6.5	25	0.131
	10.5	25	0.228
	2.6	0	0.078
	6.5	0	0.141
	10.5	0	0.144
$RbB(C_6H_4m\text{-}CF_3)_4$	2.7	25	8.442
	10.6	25	10.778

The precipitation of cesium from pure cesium ion solutions was carried out in the following manner. A sample of cesium solution was adjusted to 50 ml. This solution was heated to 90° and 25 ml of a 2% reagent solution, pH 8, which had previously been filtered through alumina, were added dropwise. The sample was allowed to stand at room temperature for 1 h, transferred to an ice-bath for 1 h, and collected on a previously tared fine sintered-glass filtering crucible. It was washed with three 5-ml portions of cold water and dried at 110° for 1 h. Finally, it was cooled in a desiccator and weighed. The quantity of cesium recovered was calculated by multiplying the weight of the precipitate times the gravimetric factor 0.1835. These results are given in Table II.

Precipitations of cesium in the presence of rubidium or potassium ions were carried out under somewhat different conditions. In the case of cesium in the presence of rubidium, a solution containing both ions was adjusted to 50 ml. This mixture was heated to 70° with constant stirring, and the 2% reagent solution was added dropwise. Addition was discontinued when no further precipitation was visible. The sample was cooled for 1 h at room temperature and for 1 h in an ice-bath. The precipitate was transferred to a tared fine sintered-glass filtering crucible, washed with three 5-ml portions of cold water, dried at 110° for 1 h, cooled in a desiccator and weighed. The presence of rubidium was checked by dissolving the weighed sample in 95% ethanol and carrying out a standard additions determination on the flame photometer. No

TABLE II

RECOVERY OF CESIUM FROM PURE CESIUM SOLUTIONS

Cs taken (mg)	*Cs found (mg)*	*% Recovery*
24.78	24.39	98.4
24.78	24.34	98.2
24.78	24.32	98.1
24.78	24.37	98.3
24.78	24.59	99.2
24.78	24.56	99.1
	S.D. = ±0.12	
9.91	9.38	94.6
9.91	9.14	92.2
9.91	9.34	94.3
9.91	9.16	92.4
9.91	9.25	93.3
9.91	9.30	93.8
	S.D. = ±0.10	

TABLE III

RECOVERY OF CESIUM IN THE PRESENCE OF RUBIDIUM

Cs taken (mg)	*Rb taken (mg)*	*Rb found (mg)*	*Cs found (mg)*	*% Cs recovery*
24.95	24.99	0.00	24.20	97.0
24.95	24.99	0.00	24.48	98.1
24.95	24.99	0.00	24.65	98.8
24.95	24.99	0.00	24.90	99.8
24.95	24.99	0.00	24.45	98.0
24.95	24.99	0.00	24.25	97.2
			S.D. = ±0.26	

TABLE IV

RECOVERY OF CESIUM IN THE PRESENCE OF POTASSIUM

Cs taken (mg)	*K taken (mg)*	*K found (mg)*	*Cs found (mg)*	*% Cs recovery*
24.95	30.00	0.00	24.61	98.6
24.95	30.00	0.00	24.52	98.3

rubidium was detected in these samples, with the flame photometer's detection limit of *ca.* 2 p.p.m. The results are given in Table III.

Several cesium precipitations in the presence of potassium ion were carried out in an analogous manner. No potassium was detected in these precipitates (Table IV).

DISCUSSION

Sodium tetrakis(*m*-trifluoromethylphenyl)borate has been synthesized. Tables III and IV show that this compound is a highly selective reagent for the cesium ion, even in the presence of equivalent quantities of rubidium or potassium ions.

The compound does not appear suitable for precipitating amines or other basic nitrogen-containing compounds.

This reagent, when in solution at pH 8, has remained clear and coloress and is still effective in precipitating cesium after standing for 4 months. An equivalent solution of sodium tetraphenylborate shows visible signs of decomposition after the same length of time.

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SUMMARY

Sodium tetrakis(*m*-trifluoromethylphenyl)borate has been synthesized and shown to be a highly selective reagent for cesium ion even in the presence of other alkali metal ions. Equivalent amounts of rubidium or potassium do not interfere.

RÉSUMÉ

Le tétrakis (*m*-trifluorométhylphényl) borate de sodium a été synthétisé; c'est un réactif très sélectif pour l'ion césium même en présence d'autres ions de métaux alcalins. Des quantitées équivalentes de rubidium ou de potassium n'interfèrent pas.

ZUSAMMENFASSUNG

Natrium-Tetrakis(*m*-trifluoromethylphenyl)-borat wurde synthetisiert und erwies sich als ein hoch selektives Reagenz für Cäsiumionen, auch in Gegenwart anderer Alkalimetallionen. Äquivalente Gehalte von Rubidium oder Kalium stören nicht.

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THE DETERMINATION OF SODIUM AND POTASSIUM AFTER SEPARATION FROM EACH OTHER AND OTHER IONS BY MEANS OF AMMONIUM PHOSPHOMOLYBDATE AND OTHER ION EXCHANGERS

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The use of synthetic ion exchangers has been demonstrated as a quick and satisfactory method for the separation of alkali metal ions. Insoluble (usually ammonium) salts of heteropoly acids have been successfully applied as cation exchangers for the separation of micro as well as macro quantities of cation[1-9]. K_d values for the exchange of trace concentrations of alkali cation on ammonium 12-molybdophosphate (AMP) in 0.1 M ammonium nitrate solutions found in the present work are shown in Table I. The value of $\alpha_{Li}{}^{Na}$ is small (1.37); moreover, the K_d value for sodium is so small that it probably will be eluted with lithium. A quantitative separation of the above-mentioned ions will not be easily obtained. The ratio $\alpha_{Na}{}^{K}$ (6.03) suggests the possibility of a quantitative separation. A very weak eluant must be used for sodium because of the smallness of the K_d value for potassium; a very dilute nitric acid solution might be possible, as the K_d value for hydronium ion is just larger than that for sodium. The α values for the ion pairs Rb/K and Cs/Rb are fairly large (56.6 and 15.1 respectively) and separations should be easy. Owing to the large K_d value for cesium, it would be difficult to find a suitable eluant for it; it would therefore be possible in a Cs/Rb separation to choose an eluant for rubidium that would give a sharp elution peak.

TABLE I

K_d VALUES FOR THE EXCHANGE OF TRACE CONCENTRATIONS OF ALKALI CATION ON AMP IN 0.1 M AMMONIUM NITRATE SOLUTIONS

Cation	K_d
Li^+	0.57
Na^+	0.78
K^+	4.7
Rb^+	266
Cs^+	4024
H_3O^+	0.84

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The possibility thus exists for the separation of lithium from potassium, rubidium and cesium as well as the separation of sodium, potassium, rubidium and cesium in any combination from each other. In this work the main interest was in a fast quantitative separation of large quantities of sodium and potassium from each other before an alkalimetric titration with a conventional ion exchanger in the hydroxide form.

EXPERIMENTAL

Chemicals and exchange columns

All chemicals used were of A. R. grade. The ammonium 12-molybdophosphate (AMP) was prepared by precipitating a known quantity of potassium dihydrogen phosphate with a citric acid–molybdate solution.

AMP–asbestos columns were prepared by mixing equal weights of each, and transferring it with a 0.1 *M* ammonium nitrate solution into a glass tube of 1-cm diameter, with an asbestos mat supported by glass wool and fitted with a stopcock for regulating the flow speed (1 ml/min). Before the column was used for sodium/potassium separations, it was treated with about 3 column-volumes of 0.01 *M* nitric acid solution to remove any excess of ammonium ions. The columns could be used up to 10 times. When used several times, the AMP–asbestos mass tends to pack down to such an extent that the flow speed becomes inconveniently small. The entire content of the column was then emptied into a beaker and, after being mixed with an additional 0.5 g of asbestos to ensure a greater flow speed, returned to the column.

The ion-exchange columns in the EDTA and hydroxide forms were prepared as described by SAMUELSON *et al.*[5,6].

The sodium and potassium in the eluates were determined flame photometrically.

Separations of sodium and potassium

In Fig. 1 the separation of 0.038 meq each of sodium and potassium on a small AMP–asbestos column (5.2 ml) containing 0.55 g of each is shown.

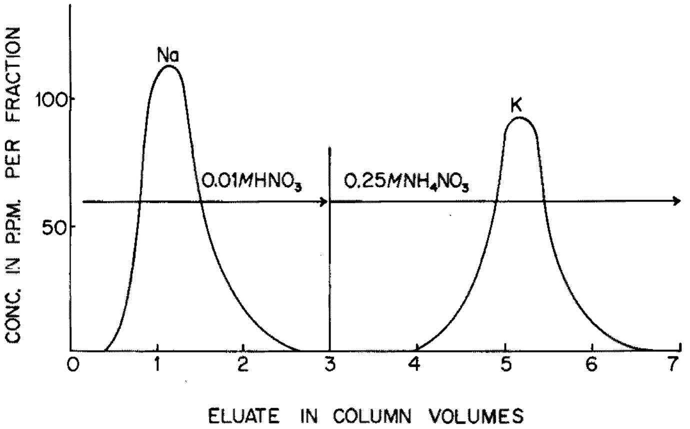

Fig. 1. Elution curves for the separation of 0.038 meq of sodium and potassium each on a 5-ml AMP–asbestos column containing 0.55 g of each.

In all following experiments, the columns used were prepared from 4 g of AMP, and 4 g of asbestos; a 0.01 *M* nitric acid solution was used in each case as eluant for sodium. When the column load was increased to 0.25 meq each of sodium and potassium, no clean separation was found; all the sodium was eluted with three column-volumes of eluate but after the first column-volume had passed through, a little potassium was found together with the sodium in each fraction of eluate. Larger columns tended to pack down rapidly, resulting in low flow rates.

As the quantities of alkali cation used in these experiments were of suitable magnitude for alkalimetric titration the possibility of separating sodium and potassium at the ratio in which they appeared in the first 3–4 column-volumes on a second column, after concentration to a small volume, was investigated.

Figures 2 and 3 show the separation of 0.25 meq each of sodium and potassium on two columns (i) and (ii) each containing 4 g of AMP mixed with an equal weight of asbestos. All sodium together with part of the potassium was eluted with three column-volumes of 0.01 *M* nitric acid solution from column (i). The solution was then concentrated and separated on column (ii), as shown in Fig. 3. Figure 2 shows the elution of the potassium remaining on column (i) with 0.25 *M* ammonium nitrate solution.

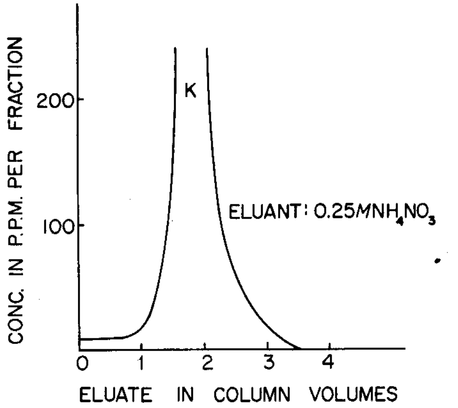

Fig. 2. Elution of potassium from column (i) (17 ml, 4 g AMP, 4 g asbestos) with 0.25 *M* ammonium nitrate solution.

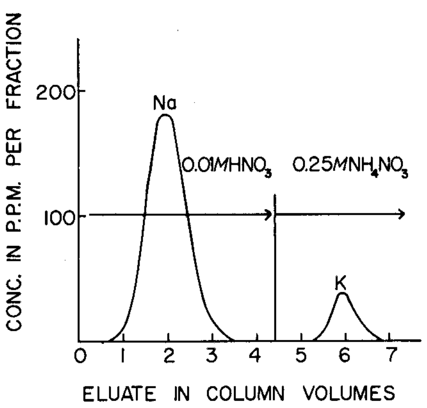

Fig. 3. Elution curves for the separation on column (ii) (23 ml, 4 g AMP, 4 g asbestos) of 0.25 meq sodium from the small amount of potassium eluted together with the sodium from column (i).

The separation of double the quantities of sodium and potassium by the above-mentioned method was unsuccessful, as was the separation of 0.25 meq of potassium from 0.5 meq of sodium. The column load with potassium seemed to be too high as it was eluted together with the sodium on the second column in both cases. To see if separations depended on the amount of sodium, a lower amount of potassium (0.10 meq) was chosen and the amount of sodium was progressively raised in successive experiments. Clean separations were found in all cases with a single AMP–asbestos column containing 4 g of each. All sodium was eluted with three column-volumes of 0.01 *M* nitric acid solution and potassium was eluted with the same volume of a 0.25 *M* ammonium nitrate solution. The results are shown in Table II.

In the separation of sodium and potassium on AMP–asbestos columns, the column load with potassium seems to be the determining factor. Amounts of 0.25 meq of each ion could not be separated on a single 4-g AMP column, though 0.15 meq of potassium could be separated from 0.25 meq of sodium. By lowering the quantity of potassium still further (0.10 meq), the Na/K ratio could be enlarged without any influence on the effectiveness of the separation.

TABLE II

THE SEPARATION OF SODIUM AND POTASSIUM ON SINGLE AMP–ASBESTOS CATION-EXCHANGE COLUMNS CONTAINING 4 G OF EACH

(Sodium and potassium determined flame-photometrically)

	meq Na	*meq K*	*Na/K*
Taken	0.5000	0.1000	5
Found after sepn.	0.4999	0.09995	
Taken	5.000	0.1000	50
Found after sepn.	5.002	0.09998	
Taken	50.00	0.1000	500
Found after sepn.	50.01	0.09995	

The alkalimetric titration of sodium and potassium

By the method of SAMUELSON *et al.*[5], alkali salts can be determined accurately by passing the salt solution through a strongly basic anion-exchange column in the hydroxide form, with a 60% ethanol solution as eluant. The method was tested with standard sodium and potassium chloride solutions, which were also determined by flame photometry (Table III). The ion-exchange method compares favorably with the flame-photometric method in the particular concentration range.

TABLE III

COMPARISON OF THE ALKALIMETRIC AND FLAME-PHOTOMETRIC METHODS FOR THE DETERMINATION OF SODIUM AND POTASSIUM

(The values given are the mean of at least five determinations in each case)

	Flame photometric	*Alkalimetric*	*Theoretical*
Na (meq)	0.2499 ± 0.0001	0.2500 ± 0.0001	0.2500
K (meq)	0.2501 ± 0.0001	0.2501 ± 0.0001	0.2500
Na+K (meq)	—	0.5000 ± 0.0001	0.5000

The separation of a sodium–potassium mixture followed by alkalimetric titration

Equivalent amounts of sodium and potassium (0.25 meq) of each were separated as described above. The eluates containing the potassium and sodium fractions were treated as follows. The sodium-containing eluate was evaporated to dryness once with 5 ml each of concentrated nitric and hydrochloric acid and then three times with 5-ml portions of distilled water. The combined potassium-containing eluate was evaporated to dryness four times with a solution containing 5 ml each of concentrated nitric and hydrochloric acid to remove ammonium ions, followed by three evaporations to dryness with 5-ml portions distilled water.

During the separations a very small amount of AMP dissolved, which resulted in a light yellow precipitate of molybdic acid when the solutions were evaporated to dryness. Because of its insolubility, it did not interfere in the subsequent titration.

The (concentrated) eluate was transferred to the anion-exchange column (in the OH^- form) with a 60% ethanol solution and was washed through with 150 ml of 60% ethanol solution. The eluate was collected and titrated with a standard 0.01 *M* hydrochloric acid solution and methyl red as indicator. Table IV shows results for sodium and potassium determinations after separation on AMP–asbestos columns.

The separation of sodium and potassium mixture from other cations followed by their determination

SAMUELSON *et al.*[6] showed that sodium and potassium salts could be separated quantitatively from multivalent cations by passing the mixture through anion-exchange columns in the EDTA and acetate forms. The alkalimetric titration of sodium

TABLE IV

TITRATION OF SODIUM AND POTASSIUM AFTER SEPARATION ON AMP–ASBESTOS ION-EXCHANGE COLUMNS

(0.2500 meq of each ion was taken)

meq Na	*meq K*	*meq Na+K*
0.2494	0.2507	0.5001
0.2493	0.2502	0.4995
0.2498	0.2499	0.4997
0.2499	0.2501	0.5000
0.2502	0.2500	0.5002
0.2500	0.2501	0.5001

TABLE V

THE DETERMINATION OF SODIUM AND POTASSIUM AFTER SEPARATION FROM MAGNESIUM, CALCIUM AND COPPER

Taken (mmol)					*Found (mmol)*		
Mg	*Ca*	*Cu*	*Na*	*K*	*Na*	*K*	*Na+K*
0.25	0.25	—	0.250	0.250			0.4998
0.25	0.25	—	0.250	0.250			0.5002
0.10	0.10	0.10	0.250	0.250			0.4999
0.10	0.10	0.20	0.250	0.250			0.4999
0.20	0.20	0.20	0.250	0.250	0.2496	0.2503	
0.25	0.25	—	0.250	0.250	0.2499	0.2501	
0.25	0.25	0.25	0.250	0.250	0.2500	0.2498	
0.10	0.10	0.10	0.250	0.250	0.2501	0.2500	
0.40	0.40	0.25	0.250	0.250	0.2500	0.2500	
0.25	0.25	—	0.500	0.100	0.4998	0.1000	
0.25	0.25	—	0.500	0.100	0.4997	0.1000	

and potassium after such a separation followed by a separation on AMP columns should be possible and was tested as follows.

Samples containing sodium, potassium, magnesium and calcium (a few also contained copper) were concentrated to a volume of 5 ml and placed on anion-exchange columns containing a mixture of the resin in the hydroxide and acetate forms. The alkali metal ions were eluted with 150 ml of 60% ethanol. After concentration of the eluate to a suitable volume by evaporation, the sodium and potassium were determined alkalimetrically either together or separately after separation on an AMP column as described above (Table V).

The results show that the separate titration of sodium and potassium after an ion-exchange separation from divalent cations and from each other is possible. With modifications in the preliminary ion-exchange separation like those of SAMUELSON *et al.*[6] it should be possible to determine sodium and potassium accurately in presence of a large number of cations.

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SUMMARY

The separation of sodium and potassium by means of ammonium molybdophosphate (AMP) cation-exchange columns is described. Up to 0.1 meq of potassium can be separated quantitatively from amounts up to 50 meq of sodium on a small (4 g AMP) column. With as much as 0.25 meq of potassium, quantitative separation can be effected by the successive use of two small columns. By a combination of this separation with conventional ion-exchange methods, sodium and potassium can be determined individually in the presence of various other cations.

RÉSUMÉ

On décrit la séparation du sodium et du potassium dans des colonnes échangeuses de cations au phosphomolybdate d'ammonium (AMP). Dans une petite colonne (4 g d'AMP), on peut séparer jusqu'à 0.1 meq de potassium de quantités allant jusqu'à 50 meq de sodium. Pour des quantités égales à 0.25 meq de potassium, une séparation quantitative peut être effectuée par emploi successif de deux petites colonnes. En combinant cette séparation avec les méthodes conventionnelles d'échange d'ions, on peut déterminer le sodium et le potassium individuellement en présence d'autres cations divers.

ZUSAMMENFASSUNG

Die Trennung von Natrium und Kalium mit Ammoniummolybdophosphat-Kationenaustauscherkolonnen wird beschrieben. Bis hinauf zu 0.1 mäq Kalium können quantitativ von 50 mäq Natrium mit 4 g Austauscherharz abgetrennt werden. 0.25 mäq Kalium lassen sich durch 2 kleine aufeinanderfolgende Kolonnen abtrennen. Durch Kombination dieser Trennung mit konventionellen Ionenaustauschermethoden können Kalium und Natrium einzeln in Gegenwart zahlreicher anderer Ionen bestimmt werden.

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CONCENTRATION AND DETERMINATION OF TRACES OF METAL IONS

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Atomic absorption spectrophotometry has been widely accepted as an excellent technique for the determination of metals. The technique is very selective and quite sensitive. But, except for a few metal ions such as cadmium and zinc, atomic absorption methods cannot be successfully employed for the direct determination of metal ions below 1 p.p.m. levels. Studies to improve the sensitivity of atomic absorption methods and to concentrate the metal ions from dilute solution are necessary for the determination of trace constituents. The improvements in burner design and other means of atomization will enhance the sensitivity of atomic absorption methods, but preconcentration will always be an added advantage.

Solvent extraction procedures offer great advantages over other commonly used concentration techniques such as ion exchange and coprecipitation. Ion-exchange methods are effective but time-consuming[1]. In coprecipitation procedures a very large amount of precipitating materials is added and such compounds are not free from impurities[2]. Solvent extraction procedures in conjunction with atomic absorption spectrophotometry have proved to be useful for the determination of a variety of elements[3,4]. The sensitivity of atomic absorption methods is enhanced by the use of chelates and organic solvents[5–7]. In addition, interferences from large amounts of commonly found compounds and ions such as sodium, calcium(II) and magnesium(II), etc., are avoided. Numerous solvent extraction systems have been reported in which the conditions are so adjusted that selective extractions are possible. For atomic absorption methods, highly selective extraction systems are not necessary. On the contrary, nonselective solvent extraction procedures are desirable for rapid determinations. This paper describes the conditions for extraction of seven different metal ions in one step and their subsequent determination by atomic absorption.

The chelate and the solvent

Ammonium pyrrolidine dithiocarbamate has been used for the extraction of a variety of metal ions[3]. Sodium diethyldithiocarbamate and cupferron[4] have also been reported for certain extractions. Diphenylthiocarbazone (dithizone) is one of the strong complexing compounds. It forms complexes with 17 metal ions and procedures for colorimetric determinations have been reported[8]. Most of the dithizone extraction systems reported use chloroform or carbon tetrachloride as solvent for extraction. Chlorinated solvents are undesirable for atomic absorption methods because flame is used for the atomization. Recently WEST *et al.*[6] reported the use of ethyl propionate for the extraction of silver. Various solvents other than chloroform and carbon tetrachloride were tried for the extraction of lead dithizonate. Most ketones and alcohols oxidize dithizone; hydrocarbons such as cyclohexane do not extract the dithizonate. Esters such as *n*-amyl acetate, *n*-butyl acetate, iso-butyl acetate and ethyl propionate have been found to be satisfactory for the extraction of dithizonates. Of all the esters mentioned above, ethyl propionate has been found to be more useful for two reasons: first, it burns very smoothly in air–acetylene flame; and secondly, the dithizonates are stable in this solvent.

Stability of dithizonates

Dithizonates of all the seven metals were extracted into ethyl propionate. The absorption for each of the metals was noted at its absorption wavelength as shown in Table IV. All the metal dithizonates studied have been found to be stable in ethyl propionate for as long as 8 days. Slight oxidation of dithizone was observed after 8 days and further study was discontinued.

Effect of pH on the extraction

The effect of pH on the extraction of cadmium, cobalt, copper, lead, nickel, silver and zinc by dithizone was studied in the following manner. Each of the above-mentioned metal ions was extracted from tartrate medium at various pH values between 1 and 10. The results are shown in Fig. 1.

The percentage absorption plotted against the pH for extraction was obtained by using appropriate hollow-cathode lamp, wavelength and flame conditions as shown in Table IV. The results indicate that at pH 7.5, all seven metals can be simultaneously extracted. Because the sensitivity for the determination of each of the metal ions is different, an appropriate concentration for each ion was chosen in

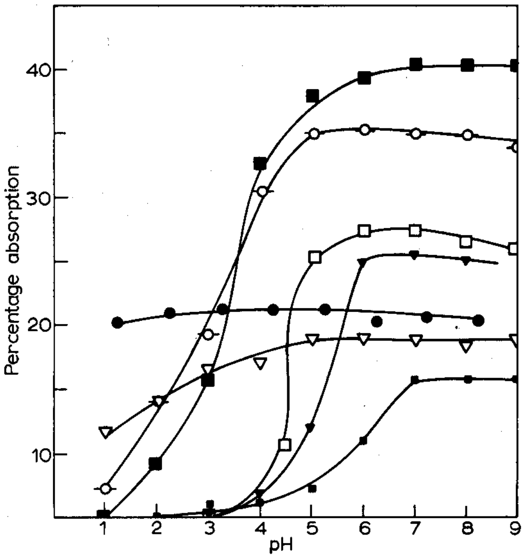

Fig. 1. Effect of pH on the extraction. Concentration of metal ions in ethyl propionate (µg/ml). ■ Lead 5.0; ○ Cadmium 0.5; □ Zinc 0.5; ▼ Cobalt 2.0; ● Silver 1.0; ▽ Copper 2.0; ▪ Nickel 0.5.

order to study the pH effect. Therefore, the heights of the curves in Fig. 1 do not show the comparative sensitivity for these metals.

Simultaneous extraction of all seven metal ions

Each of the metal ions solution was extracted with dithizone, individually as well as in the presence of the other six kinds. The concentration of the respective metal ions was the same in both solutions. Absorption was measured using the appropriate hollow-cathode lamp. The results shown in Table I indicate that these metal ions can be extracted just as efficiently in the presence of others as alone.

TABLE I

SIMULTANEOUS EXTRACTIONS

Metal ion	*Absorption wavelength (Å)*	*Concentration (µg/ml)*	*Percentage absorption in*		
			Aqueous solution	*Ethyl propionate*	*Ethyl propionate in the presence of other six metals*
Ag^+	3281	0.5	3.0	11.0	11.0
Cd^{2+}	2288	0.5	6.7	29.3	29.5
Co^{2+}	2407	1.0	2.0	8.0	7.7
Cu^{2+}	3247.5	0.5	2.5	12.0	11.5
Ni^{2+}	2320	1.0	2.7	14.5	14.5
Pb^{2+}	2170	3.0	2.2	10.6	10.6
Zn^{2+}	2138	0.5	7.6	15.2	15.0

A dithizone solution of 0.1% (w/v) has been found to be quite sufficient for the simultaneous extraction of small quantities of all seven kinds of metal ions. The data in Table I also show 3–5 fold enhancement by the use of the organic medium. The procedure cannot be used for the determination of trace impurities in metals such as lead, zinc or mercury, etc., which form strong complexes with dithizone.

Effect of rate of aspiration

By the use of organic solvents the rate of aspiration of sample to the flame is generally increased. Because the organic solvent used for the extraction also works as a secondary fuel, it completely alters the nature of the flame. Therefore, the rate of aspiration of the solution affects the method in two ways: first, it transports the metal chelates into the flame; and secondly, it makes the flame more reducing in nature. For the determination of metals in question, an oxidizing flame provides better conditions than a reducing flame. The oxidizing nature of the flame can be maintained by reducing the aspiration rate which can be easily achieved by attaching a polyethylene capillary tubing of suitable inner diameter and length to the capillary of the burner. The lower rate of aspiration reduces the amount of sample reaching the flame and this lowers the sensitivity for the determination. In order to obtain optimum sensitivity a compromise between the two factors must be made. With the flame conditions useful for this work an aspiration rate of 3 ml/min is the best and can be achieved very easily by attaching a polyethylene capillary tube of 0.015 in inner diameter and 2.5 in length to the capillary of the burner. If a different kind of burner assembly is used, the flow of air and acetylene should be so regulated that the solution aspirates at a flow rate of 3 ml/min and the flame thus obtained should not be luminous. The flame conditions and the sensitivities for the seven metals are described in Table IV.

Positioning of the burner

In general, the light beam passes through the length of the flame near its base. But, in these experiments it was observed that best sensitivities can be obtained when the light beam passes through the flame about a centimeter above its base.

INTERFERENCE STUDY

Interference effects of about 38 diverse ions and compounds were studied. These ions and compounds are listed in Table II.

TABLE II

INTERFERENCE STUDY

Group	
I	Li^+, Na^+ and K^+
II	Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Hg^{2+}
III	BO_2^-, $B_4O_7^{2-}$, Al^{3+} and Ce^{3+}
IV	CO_3^{2-}, Sn^{4+}, and SiO_3^{2-}
V	NH_4^+, NO_3^-, HPO_4^{2-}, Sb^{5+}, $HAsO_4^{2-}$, VO_3^- and Bi^{3+}
VI	SeO_3^{2-}, $Cr_2O_7^{2-}$, Cr^{3+} and TeO_3^{2-}
VII	F^-, Cl^-, Br^-, I^- and Mn^{2+}
VIII	Fe^{3+}
	Miscellaneous: oxalic acid, citric acid, chlorine, water and detergents (Tide and Dreft).

Method for testing interference

A stock solution containing cadmium 0.1 µg/ml, cobalt 0.2 µg/ml, copper 0.2 µg/ml, lead 0.3 µg/ml, nickel 0.2 µg/ml and zinc 0.2 µg/ml was prepared. A 100-ml portion of this solution was extracted with 10 ml of 0.1% (w/v) dithizone solution in ethyl propionate. A similar solution containing all six ions and 500 µg/ml of the interfering ions except Hg^{2+}, Sb^{5+}, Bi^{3+} and Mn^{2+} which form strong complexes with dithizone, was extracted with 10 ml of the dithizone solution. The ions which form complexes with dithizone were added at 10 µg/ml concentration. Detergents were added at 100 µg/ml concentration and 1 ml of a saturated solution of chlorine in water was added to 100 ml of the solution containing metal ions. The absorption for each of the metals except silver was measured with appropriate hollow-cathode lamps and other conditions as described in Table IV. An interference study of silver has already been reported by West *et al.*[6].

Interference effects

Among the ions and compounds listed, only silicate, tellurite, tin(IV) and antimony(III) were found to be incompatible with the extraction system. These ions hydrolyze under the experimental conditions and prevent the extraction from being quantitative. At low concentrations, *e.g.* with silicate at 50 µg/ml and tellurite, tin(IV) or antimony(III) at 5 µg/ml, the interference effects are negligible. Similarly, for the determination of lead, ions such as sulfate and molybdate which form insoluble precipitates, should be absent.

EXPERIMENTAL

Equipment

Atomic absorption spectrophotometer (Perkin-Elmer Model 303), HETCO burner with air–acetylene head (Jarrell Ash Co., Waltham, Mass.), gas flow meter (Hoke's Model 993), hollow-cathode lamps for cadmium, cobalt, copper, lead, nickel, silver and zinc, and a pH meter (Leeds and Northrup).

Calibration curves

Calibration curves were obtained by extracting 100-ml portions of standard aqueous solutions containing varying amounts of metal ions with 10 ml of 0.1% solution of dithizone in ethyl propionate following the extraction procedure described below. The ranges in which the calibration curves have been found to be linear are shown in Table III. If any of the metal ions are present in larger concentrations, an absorption wavelength of lower sensitivity should be used[9]. If most of them are present in relatively larger concentrations (0.5–1.0 μg/ml), a smaller volume of sample will reduce the sensitivity of the procedure.

TABLE III

RANGE FOR LINEAR CALIBRATION CURVE

Metal ion	*Wavelength (Å)*	*Range for linear calibration curve (μg/ml)*
Ag^+	3281	0.0–0.3
Cd^{2+}	2288	0.0–0.1
Co^{2+}	2407	0.0–0.4
Cu^{2+}	3247.5	0.0–0.2
Ni^{2+}	2320	0.0–0.4
Pb^{2+}	2170	0.0–0.6
Zn^{2+}	2138	0.0–0.1

Determination

Take 100 ml of aqueous solution into a 250-ml beaker. Add 10 ml of 1 *M* ammonium tartrate, and adjust the pH to 7.5 by adding 0.5 *M* ammonium hydroxide or aqueous 10% tartaric acid, whichever is necessary. Transfer the solution to a 150-ml separatory funnel, and add 10 ml of 0.1% (w/v) dithizone in ethyl propionate. Shake the solution briskly for 1 min, allow to stand (about 3–5 min) until the two layers are separated. Reject the aqueous layer and pour the organic phase into a glass-stoppered bottle. Measure the absorption for each of the seven metals under the optimum conditions shown in Table IV. Convert the absorption readings to absorbance and by the use of calibration curves find out the concentration of the respective metal in the original aqueous solution.

TABLE IV

OPTIMUM CONDITIONS

Metal ion	*Wavelength (Å)*	*Spectral slit-width (Å)*	*Lamp current (mA)*	*Flame*		*Sensitivity*[b] *(µg/ml)*
				Air flow[a]	*Acetylene flow*[a]	
Ag^+	3281	2.0	8	10	2.2	0.002
Cd^{2+}	2288	6.5	8	10	2.5	0.001
Co^{2+}	2407	2.0	12	10	2.0	0.004
Cu^{2+}	3247.5	2.0	5	10	2.0	0.002
Ni^{2+}	2320	2.0	12	10	2.5	0.004
Pb^{2+}	2170	2.0	30	10	2.2	0.004
Zn^{2+}	2138	2.0	14	10	2.0	0.001

[a] Flow units are arbitrary scale units on Hoke's flow meter model 993.
[b] Sensitivity is given for aqueous solution using 10 × concentration.

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SUMMARY

A procedure for the preconcentration and determination of Ag^+, Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} is presented. The conditions for the simultaneous extraction of all these metal ions with dithizone in ethyl propionate are described. The metal dithizonates are very stable in ethyl propionate and the chelate–solvent system enhances the sensitivity for the atomic absorption method used for the determination. With 10:1 aqueous–organic solvent ratios, the sensitivities for 1% absorption of the signal range from 0.001 µg/ml for Cd^{2+} and Zn^{2+}, to 0.004 µg/ml for Pb^{2+}. Interference effects of 38 diverse ions and compounds were studied and their tolerance levels are given. The resulting procedure is very sensitive and selective.

RÉSUMÉ

On présente un procédé pour la préconcentration et la détermination de l'Ag^+, du Cd^{2+}, du Co^{2+}, du Cu^{2+}, du Ni^{2+}, du Pb^{2+} et du Zn^{2+}. Les conditions pour l'extraction simultanée de tous ces ions métalliques avec de la dithizone dans le propionate d'éthyle sont décrites. Les dithizonates de métaux sont très stables dans le propionate d'éthyle et le système "chelate-solvant" accroît la sensibilité de la méthode de l'absorption atomique utilisée pour la détermination. Avec des rapports de solvants aqueux/organiques (10:1), les sensibilités pour 1% d'absorption du signal vont de 0.001 µg/ml pour le Cd^{2+} et le Zn^{2+} à 0.004 µg/ml pour le Pb^{2+}. Les effets d'interférence de 38 ions divers et composés ont été étudiés et leurs degrés de tolérance sont donnés. Le procédé, qui résulte de cette méthode, est très sensible et sélectif.

ZUSAMMENFASSUNG

Es wird ein Verfahren zur Voranreicherung und Bestimmung von Ag, Cd, Co, Cu, Ni, Pb und Zn vorgeschlagen. Die Bedingungen für die gleichzeitige Extraktion aller dieser Metallionen mit Dithizon in Ethylpropionat werden beschrieben. Die Metalldithizonate sind sehr stabil und können empfindlich mit der Flammenabsorptionsspektrometrie bestimmt werden. Bei einem Verhältnis von 10:1 für Wasser: organischem Lösungsmittel betragen die Empfindlichkeiten für 1% Absorption 0.001 μg/ml für Cd und Zn und 0.004 μg/ml für Pb. Störungen von 38 anderen Ionen und Verbindungen wurden untersucht; die zulässigen Mengen werden angegeben. Das Verfahren ist sehr empfindlich und selektiv.

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COMPLEX FORMATION IN THE COPPER(II)-TARTARIC ACID SYSTEM

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Although tartaric acid is widely used as a complexing agent in analytical chemistry, knowledge about the stoicheiometry, structure and stability of its complexes is rather scarce. As far as copper(II) tartrates are concerned, preparative and physico-chemical investigations indicate that in acidic media simple complexes (probably mononuclear chelates) are formed and—with decreasing acidity—polynuclear and/or hydrolyzed complex species appear to become predominant[1-6]. FRONAEUS[7] has observed stepwise formation of mononuclear copper tartrates, their composition being CuT, CuT_2, CuT_3, and CuT_4 (where T denotes the anion of tartaric acid). Furthermore, he has found a difference in the solution stabilities of copper(II) complexes with (+)- and (±)-tartaric acids. These controversial findings prompted a more detailed study of the solution chemistry of copper(II) tartrates. In this paper the polarographic investigations are discussed.

EXPERIMENTAL

Reagents

All the materials used were of analytical-reagent grade. Twice-distilled water was used throughout. Copper nitrate stock solutions (0.01 *M*) were standardized by compleximetric titration[8].

Determination of acid dissociation constants

Acid dissociation constants were determined by a potentiometric titration method. The titration curves were recorded by means of an automatic titrimeter (Titrigraph SBR 2c and Titrator TTT 1c, Radiometer, Copenhagen) equipped with a glass electrode G 202 B and a saturated calomel electrode (K 4312) which was separated from the solution by a porous ceramic pin. Before and after each experiment, the equipment was standardized against perchloric acid solution of exactly known concentration (total ionic strength 1 *M*, adjusted with sodium nitrate). Therefore all the pH values refer to hydrogen ion concentrations rather than activities. Approximately 0.4 *M* sodium hydroxide solution (which was 1 *M* in sodium nitrate), prepared by a procedure similar to that described by PREGL[9], served as the titrant. The solutions to be titrated were *ca.* 1 m*M* in (+)-tartaric acid and also 1 *M* in sodium nitrate. An inert atmosphere was maintained inside the titration cell by bubbling purified nitrogen gas through it. The titration cell and its contents were kept at 20.0 ± 0.05°. The stirring was accomplished by means of a magnetic stirrer.

Polarographic measurements

In order to determine successive complex formation constants, the polarographic half-wave potential was determined in a series of solutions containing a constant amount (0.1 M) of (+)-, (−)-, or (±)-tartaric acid and copper(II) nitrate (0.5 mM). The ionic strength was kept constant at 1.00 M by adding sufficient sodium nitrate. Triton X-100 ($8 \cdot 10^{-4}\%$) was added as a maximum suppressor. The concentration of free tartrate ion was varied by varying the pH in this series of solutions in the range $2 \leqslant \text{pH} \leqslant 5$ (measured by a glass electrode and the Titrator TTT 1c in connection with Scale Expander PHA 630 T).

The polarograms were recorded by means of a pen recording polarograph (Polariter PO 4, Radiometer, Copenhagen) as well as with a manual apparatus. The latter consisted of a 100-ohm potentiometer fed from a 2-V storage battery, a "Pye" Scalamp galvanometer and the Titrator TTT 1c together with the Scale Expander PHA 630 T. A saturated calomel electrode (KCl-type) served as the reference electrode. The capillary characteristics were as follows: $m = 1.90$ mg. sec^{-1}, drop-time 3.20 sec (measured in 0.1 M tartaric acid made up with sodium nitrate to an ionic strength of 1.00; $E = 1.000$ V *vs.* S.C.E.). The solutions to be polarographed were deaerated by bubbling purified hydrogen gas through them for about 30 min. The temperature was 20.0 ± 0.1°.

Calculations

The pK values were calculated by the so-called "Projection-Strip" method[10] from the protonation curve which was computed according to the expression

$$\bar{n}_H = (2 - a) - (h - K_w/h)C_0^{-1}.$$

$\bar{n}_H$ denotes the average number of protons bound to one tartrate ion, a is the degree of neutralization (equivalents of added alkali per mole of tartaric acid), h is the hydrogen ion concentration, C_0 is the analytical concentration of tartaric acid, and K_w has its usual meaning.

The obtained half-wave potentials ($E_{\frac{1}{2}}$), after being corrected for the iR drop, were used to calculate the fraction of free copper(II) (α_0):

$$(E_{\frac{1}{2}})_s - (E_{\frac{1}{2}})_c = 29.1 \log (I_s/I_c) - 29.1 \log \alpha_0.$$

Subscripts s and c refer to the hydrated copper(II) ion and to the complex ion, respectively. I denotes the diffusion current constant.

From α_0, if the free ligand concentration (a) is known, stability constants of complex species can be calculated:

$$\alpha_0 = \left(\sum_{n=0}^{n=N} \beta_n \; \mathrm{a}^n \right)^{-1} \cdot$$

n is the degree of complexity and β_n denotes the cumulative stability constant of the n-th complex. The computation can be performed either by the conventional DeFord–Hume–Leden method of successive extrapolations or by a least-squares method, *e.g.* that suggested by IRVING[11].

Because tartaric acid was in a large excess with respect to the copper(II) ions, it was assumed that the presence of the latter did not affect appreciably the free ligand concentration (except possibly in the most acid part of the pH range studied).

The half-wave potentials were evaluated graphically as described by MONNIER AND RUSCONI[12]. This method was compared to WEBER's least-squares method[13], and it was found that the former simple method is quite satisfactory for the accuracy aimed at.

RESULTS AND DISCUSSION

It was found that, under the experimental conditions employed, copper(II) gave a well developed reduction wave. Because the limiting current was directly proportional to the square root of the mercury reservoir height and the Heyrovský–Ilkovič equation was strictly obeyed, the wave was considered to be diffusion-controlled. The reduction was found to be a two-electron process. With solutions whose pH was higher than 5, the polarographic waves became irreversible.

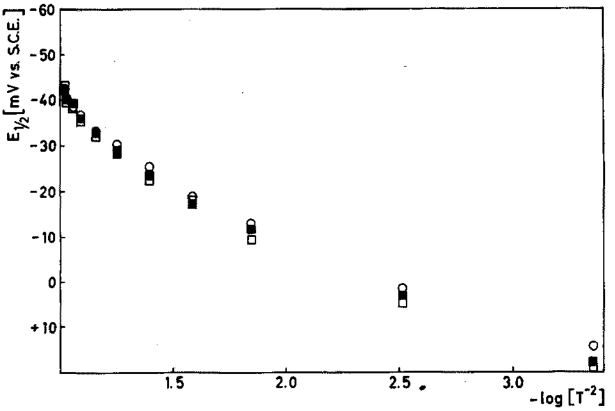

Fig. 1. The dependence of the half-wave potential of the copper(II) wave on the concentration of free tartrate. ○ (+)-, □ (−)-, ■ (±)-isomer.

TABLE I

STABILITY CONSTANTS OF COPPER(II) COMPLEXES WITH VARIOUS STEREOISOMERIC FORMS OF TARTARIC ACID

	Stereoisomeric form		
	(+)	*(−)*	*(±)*
log K_1	3.21	3.20	3.14
Standard deviation	0.11	0.13	0.12
Standard error of the mean	0.03	0.04	0.04
99% confidence limits	0.10	0.13	0.13

The dependence of the half-wave potential on the logarithm of the free ligand concentration is shown in Fig. 1. Within the limits of experimental error, no difference in the behaviour of stereoisomeric tartrates could be observed.

Both the least-squares analysis[11] and the successive extrapolations revealed the existence of only one complex species under the conditions employed. This species should have the composition CuT. Its stability constant, K_1 (for all the three stereoisomeric forms of the ligand) and the appropriate statistical parameters are given in Table I.

To calculate the free ligand concentration the following pK values were used: p$K_1 = 2.66$ and p$K_2 = 3.61$. These values were determined as described above, and were reproducible within ± 0.01 log units. The third and fourth stages of dissociation of tartaric acid were neglected because of the extremely low values of the respective ionization constants[14]. It should be pointed out again that all the equilibrium constants quoted in the present paper are stoicheiometric (concentration) constants.

The results obtained are in satisfactory agreement with most of the values which can be found in the literature (see *e.g.* ref. 15 and references therein). The value of K_1 is in excellent agreement with the value of $10^{3.20}$ found by FRONAEUS[7] for (+)-tartaric acid. His result ($10^{3.00}$) for the racemic form of the ligand differs slightly from our value. This difference is, however, statistically significant at the 99% level. From the results quoted in Table I it can be seen that no difference in the complexing ability can be observed between different isomeric tartaric acids. This finding is in agreement with results obtained with simple amino-acids and a number of bivalent metal cations[16].

We are indebted to Professor I. FILIPOVIĆ for permission to use the PO 4 polarograph in the Laboratory of Inorganic Chemistry of the Technological Faculty. Thanks are due to Miss B. ŠVIGIR for her skilful technical assistance.

SUMMARY

Copper(II) complexes with (+)-, (−)-, and (±)-isomeric forms of tartaric acid have been investigated by a polarographic method. At pH 2–5 only one complex species was found: monotartrato–copper(II), with a stability constant of $10^{3.2}$. No difference between the isomeric tartaric acids was found as far as their complexing abilities are concerned.

RÉSUMÉ

Les complexes cuivriques de l'acide tartrique (formes (+)-, (−)- et (±)-) ont été étudiés par une méthode polarographique. Dans une zone de pH comprise entre 2 et 5, une seule espèce complexe a été observée: le monotartrato-cuivre(II), dont la constante de stabilité est $10^{3.2}$. En ce qui concerne les propriétés de complexation des diverses formes isomériques de l'acide tartrique, aucune différence n'a été observée.

ZUSAMMENFASSUNG

Kupferkomplexe mit (+)-, (−)- und (±)-isomerer Weinsäure wurden mit einer polarographischen Methode untersucht. Beim pH-Wert 2–5 wurde nur Monotartratokupfer(II) mit einer Stabilitätskonstante von $10^{3.2}$ gefunden. Zwischen den isomeren Weinsäuren wurden keine Unterschiede festgestellt soweit ihre Komplexmöglichkeiten betrachtet wurden.

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STUDIES OF URANIUM(VI) COMPLEXES OF OXINE IN CHLOROFORM

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Uranium(VI) forms three complexes with oxine: the dark red complex[1], $UO_2(Ox)_2 \cdot HOx$, the dark green complex[2], $UO_2(Ox)_2$, and the orange complex[3], $(UO_2Ox_2)_2 \cdot HOx$, where HOx refers to 8-hydroxyquinoline. From spectral studies of the complexes dissolved in chloroform, it has been supposed that the 1:3 and 1:2 complexes possess different identities only in the solid state[4]. Extraction data[5] also support the view that uranium(VI) is extracted by chloroform or hexone as the 1:2 complex.

Recently, it was reported that the 1:3 complex was present in organic solvents and the extra molecule of oxine in this complex was coordinated to uranyl ion[6,7]. It was also suggested that the 1:2 complex was not stable in solution, but decomposed completely to the 1:3 complex and a solvated uranyl ion. The presence of the 1:3 complex in chloroform was also confirmed by the extraction data[8] of uranium(VI) with oxine.

It is the object of this investigation to show new aspects of these uranium(VI)–oxine complexes by measurements of the absorption spectra and solubility into chloroform.

EXPERIMENTAL

Materials and apparatus

Oxine (G.R. grade) was used without further purification.

Chloroform (G.R. grade) containing 0.5% (v/v) of ethanol was dehydrated by passing through a column filled with silica gel calcined at about 400°. Chloroform free from ethanol was prepared by washing with distilled water twice and shaking with anhydrous sodium sulfate twice before dehydration by the silica gel column.

The 1:3 uranium(VI)–oxine complex, $UO_2Ox_2 \cdot HOx$, was prepared as follows. To 200 ml of a solution containing 1 g of uranyl nitrate hexahydrate, was added 1 g of oxine in 100 ml of 1 *N* hydrochloric acid. The solution was heated to about 70° and 2 *N* ammonia was added dropwise while stirring with a magnetic stirrer until no further precipitate appeared on addition of ammonia. After digestion for 1 h the precipitate was filtered on a glass filter and washed with hot distilled water until the yellow color of oxine in the filtrate disappeared. The product was then dried in a desiccator over phosphorus pentoxide.

The 1:2 complex, UO_2Ox_2, was prepared by heating the 1:3 complex at 260° for 1 h. The temperature was chosen from WENDLANDT's data[9].

The compositions of these complexes were verified from the yield of the complexes on preparation, the weight loss on ignition of the complexes at 950°, and the usual bromometric titration of oxine in the complexes.

A Shimadzu-Bausch-Lomb Spectronic 20 Colorimeter was used for measurements of absorbances of solution, with the accessory 0.5-in diameter test tubes. A Hitachi Recording Spectrophotometer EPS-2U was used for measurements of absorption spectra with 1.0-cm cells.

Determination of uranium and oxine

Uranium in a chloroform solution was determined as described by ONISHI AND HIGUCHI[10]. An aliquot of a sample solution was heated at 150° to remove chloroform and excess of oxine. The residue was dissolved in 6 *N* hydrochloric acid and fine zinc powder was added. After about 30 min, when the zinc had dissolved completely, a 0.1% solution of arsenazo III was added in the ratio of 1 ml of the reagent solution to 10 ml of the hydrochloric acid solution. The absorbance at 670 nm was then measured against a reagent blank. Oxine in chloroform was determined by the usual bromometric titration.

Solubility determination of the 1:3 complex in the presence of oxine

About 70 mg of the 1:3 complex was added to 60 ml of chloroform, which was allowed to stand for a week with occasional shaking, a dark red solution and crystalline residues being obtained. Then 5 ml of the chloroform solution saturated with the 1:3 complex was added to a glass-stoppered tube containing a suitable known amount of oxine, and the contents were allowed to stand with occasional shaking. After a month, the supernatant solution was removed for the uranium determination.

RESULTS AND DISCUSSION

Dissolution of the 1:2 complex

The dark green 1:2 uranium(VI)–oxine complex dissolved gradually in

TABLE I

ANALYSIS OF THE SUPERNATE OF THE 1:2 COMPLEX DISSOLVED IN CHLOROFORM

mg UO_2Ox_2 taken/ ml $CHCl_3$	*U calcd. (M)*	*U found (M)*	*HOx found (M)*	*HOx/U*
Pure $CHCl_3$				
7.0/25	$5.03 \cdot 10^{-4}$	$3.98 \cdot 10^{-4}$	$8.12 \cdot 10^{-4}$	2.04
25.0/50	$8.95 \cdot 10^{-4}$	$4.08 \cdot 10^{-4}$	$8.87 \cdot 10^{-4}$	2.17
$CHCl_3$ containing C_2H_5OH				
15.0/25	$1.08 \cdot 10^{-3}$	$6.70 \cdot 10^{-4}$		
80.0/500	$2.87 \cdot 10^{-4}$	$1.97 \cdot 10^{-4}$	$5.00 \cdot 10^{-4}$	2.54
58.4/365	$2.87 \cdot 10^{-4}$	$2.14 \cdot 10^{-4}$	$5.14 \cdot 10^{-4}$	2.40
8.0/25	$5.74 \cdot 10^{-4}$	$3.56 \cdot 10^{-4}$	$9.00 \cdot 10^{-4}$	2.53
4.0/25	$2.87 \cdot 10^{-4}$	$1.86 \cdot 10^{-4}$		
8.0/100	$1.43 \cdot 10^{-4}$	$1.05 \cdot 10^{-4}$	$2.47 \cdot 10^{-4}$	2.41
1.5/50	$5.38 \cdot 10^{-5}$	$2.39 \cdot 10^{-5}$		
1.0/100	$1.79 \cdot 10^{-5}$	$7.64 \cdot 10^{-6}$		
			Mean	2.47

chloroform; solubility equilibrium was attained in 1–2 days. The concentrations of uranium and oxine in a supernate are shown in Table I.

The 1:2 complex dissolved in chloroform in its original composition and the solubility of the complex was found to be $3.99 \cdot 10^{-4}$ *M*.

In chloroform containing ethanol, the 1:2 complex dissolved in a different manner. The complex always gave a dark red solution with a brown residue. The concentration of uranium in the supernate increased with increasing amount of the complex added in chloroform; the concentration was about 2/3 of that expected in the case of complete dissolution, and the concentration ratio of oxine to uranium remained constant at 2.5. The molar ratio of uranium to oxine of the dark brown residue obtained was determined to be 1:1 and the content of uranium was evaluated to be 51.6%. From these data, it was concluded that the 1:2 complex decomposed in chloroform containing ethanol:

$$3UO_2Ox_2 + C_2H_5OH \rightarrow (UO_2Ox_2)_2HOx + UO_2Ox \cdot OH_5C_2 \downarrow \quad (1)$$

This is a modified expression of the hypothesis given by BULLWINKEL AND NOBLE[6] who suggested two molecules of the 1:3 complex and the solvated uranyl ion as the decomposition products of three molecules of the 1:2 complex.

The 2:5 complex was prepared and reported to decompose to the 1:3 and 1:2 complexes when it was dissolved in chloroform[11]. However, as the conclusion was drawn from the observation of the color of the solution alone, it was not always clear whether the 2:5 complex was present in chloroform or not.

The 1:2 complex dissolved in chloroform saturated with water gave a reddish brown solution with a very small amount of brown residue. The results are summarized in Table II. The concentration of uranium found in the supernate (the 3rd column) was about a half of that expected in the case of complete dissolution (the 2nd column) in the first two experiments and was lower in the remaining ones. The ratio of the concentration of oxine to uranium in solutions varied from 3.5 to 7.

The decomposition of the 1:2 complex in chloroform saturated with water is supposed to be principally in accordance with eqn. (2):

$$2UO_2Ox_2 + H_2O \rightarrow UO_2Ox_2 \cdot HOx + UO_2OxOH\downarrow \quad (2)$$

where the partially hydrolysed complex is present as precipitate in chloroform. The 2:5 complex may be unstable in chloroform containing water. As shown in Table II, the concentration of uranium and the ratio of concentration of uranium to oxine

TABLE II

ANALYSIS OF THE SUPERNATE OF THE 1:2 COMPLEX DISSOLVED IN CHLOROFORM SATURATED WITH WATER

mg UO_2Ox_2 taken/ ml $CHCl_3$	*U calcd. (M)*	*U found (M)*	*HOx found (M)*	*HOx/U*
15.0/25	$1.07 \cdot 10^{-3}$	$5.24 \cdot 10^{-4}$	$1.85 \cdot 10^{-3}$	3.53
8.0/25	$5.73 \cdot 10^{-4}$	$2.90 \cdot 10^{-4}$	$1.02 \cdot 10^{-3}$	3.52
4.0/25	$2.87 \cdot 10^{-4}$	$1.11 \cdot 10^{-4}$	$5.00 \cdot 10^{-4}$	4.59
8.0/100	$1.43 \cdot 10^{-4}$	$5.35 \cdot 10^{-5}$	$2.68 \cdot 10^{-4}$	5.01
3.0/100	$5.38 \cdot 10^{-5}$	$1.52 \cdot 10^{-5}$	$1.07 \cdot 10^{-4}$	7.01
1.0/100	$1.79 \cdot 10^{-5}$	$1.52 \cdot 10^{-6}$		

were near the value expected from eqn. (2) in the first two experiments, but deviations were observed with decreasing amounts of the 1:2 complex added in chloroform. This may be due to hydrolysis of the 1:3 complex and UO_2OxOH, to UO_2OxOH and/or uranyl hydroxide, which diminishes the concentration of uranium, liberates oxine from the complexes and gives higher ratios of oxine to uranium than 3.

Solubility of the 1:3 complex in chloroform

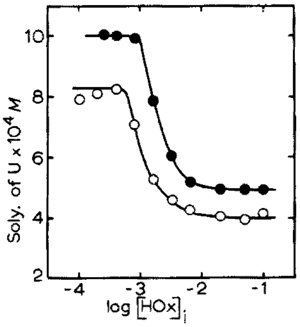
The solubility of the 1:3 complex in chloroform is given in Table III. The solubility of the complex in pure chloroform was a little smaller than that in chloroform containing ethanol, and both values were changed by addition of oxine to the solution. The solubility of uranium as complexes in chloroform is shown in Fig. 1 as a function of the initial concentration of oxine.

In either case, the solubility of uranium did not change when the concentration of oxine was lower than $5 \cdot 10^{-4}$ *M*, while it decreased with increasing concentration of oxine and became constant when the concentration of oxine was higher than

TABLE III

SOLUBILITY OF THE 1:3 COMPLEX IN CHLOROFORM

mg $UO_2Ox_2 \cdot HOx$/ml $CHCl_3$	*Solub. of U (M)*	*mg $UO_2Ox_2 \cdot HOx$/ml $CHCl_3$*	*Solub. of U (M)*
Pure $CHCl_3$		*$CHCl_3$ containing C_2H_5OH*	
5.0/5.0	$8.74 \cdot 10^{-4}$	5.0/5.0	$9.48 \cdot 10^{-4}$
10.0/5.0	$8.74 \cdot 10^{-4}$	8.0/5.0	$10.12 \cdot 10^{-4}$
20.0/5.0	$8.16 \cdot 10^{-4}$	15.3/5.0	$9.66 \cdot 10^{-4}$
40.0/5.0	$8.21 \cdot 10^{-4}$	24.9/5.0	$9.48 \cdot 10^{-4}$
40.0/5.0	$7.89 \cdot 10^{-4}$	40.4/5.0	$10.58 \cdot 10^{-4}$
	Mean $8.35 \cdot 10^{-4}$		Mean $9.86 \cdot 10^{-4}$



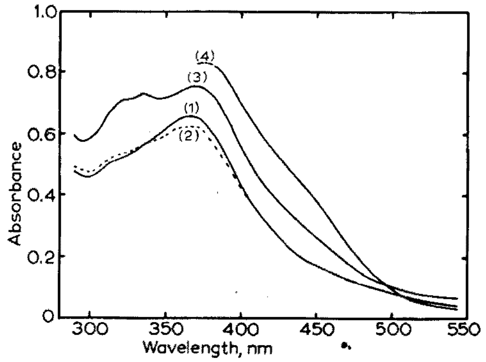


Fig. 1. Effect of the concentration of oxine on the solubility of uranium(VI)–oxine complex. ○ Pure $CHCl_3$; ● $CHCl_3$ containing C_2H_5OH (0.5% (v/v)).

Fig. 2. Absorption spectra of uranium–oxine complexes. (1) UO_2Ox_2 dissolved in pure $CHCl_3$ (1:2 complex), (2) UO_2Ox_2 dissolved in $CHCl_3$ containing C_2H_5OH (0.5% (v/v)) (2:5 complex), (3) $UO_2Ox_2 \cdot HOx$ dissolved in pure $CHCl_3$ (1:3 complex), (4) $UO_2Ox_2 \cdot HOx$ dissolved in pure $CHCl_3$ containing oxine (0.01 *M*) (1:4 complex). Identical spectra with those of (3) and (4) are obtained with $CHCl_3$ containing C_2H_5OH. Reference: pure $CHCl_3$ for (1), (2), and (3), pure $CHCl_3$ containing oxine (0.01 *M*) for (4). $[U] = 1.00 \cdot 10^{-4}$ *M*.

$5 \cdot 10^{-3}$ *M*. As shown in Fig. 1, when the excess of oxine was added to a chloroform solution saturated with the 1:3 complex, precipitate containing uranium was obtained The composition of the precipitate was found to be $UO_2Ox_2 \cdot HOx \cdot CHCl_3$, which was the same crystalline product prepared by HALL *et al.*[7] on recrystallization of the 1:3 complex from chloroform.

The decrease in solubility with increasing concentration of oxine may be due to formation of the 1:4 complex from the 1:3 complex. It is assumed that the solubility of the 1:4 complex is lower than that of the 1:3 complex, but as the 1:4 complex is unstable in the solid state, the 1:3 complex precipitates instead. It may be difficult for uranyl ion to combine with the increased number of large molecules of oxine, so that a weakly bound molecule of oxine is liberated on crystallization. The reaction would be in accordance with eqn. (3):

$$UO_2Ox_2 \cdot HOx + HOx \rightleftarrows UO_2Ox_2 \cdot 2HOx \tag{3}$$

$$K_{1,4} = \frac{[UO_2Ox_2 \cdot 2HOx]}{[UO_2Ox_2 \cdot HOx][HOx]} \tag{4}$$

The equilibrium constant, $K_{1,4}$ can be rewritten as:

$$K_{1,4} = \frac{[UO_2Ox_2 \cdot 2HOx]}{(S-[UO_2Ox_2 \cdot 2HOx])([HOx]_i-[UO_2Ox_2 \cdot 2HOx])} \tag{5}$$

where S is the apparent solubility of the uranium at a given concentration of oxine and the subscript i refers to the initial concentration. The concentration of the 1:4 complex is regarded as the minimum solubility in Fig. 1. The $K_{1,4}$ values determined by eqn. (5) are given in Table IV.

TABLE IV

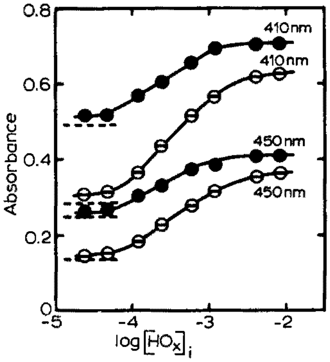
DETERMINATION OF $K_{1,4}$ FROM SOLUBILITY DATA

Init. concn. of HOx (M)	*Pure CHCl₃*		*CHCl₃ containing C₂H₅OH*	
	Solub. of U (M)	$K_{1,4}$	*Solub. of U (M)*	$K_{1,4}$
$1.00 \cdot 10^{-1}$	$4.15 \cdot 10^{-4}$		$4.90 \cdot 10^{-4}$	
$5.00 \cdot 10^{-2}$	$3.96 \cdot 10^{-4}$		$4.90 \cdot 10^{-4}$	
$2.00 \cdot 10^{-2}$	$4.06 \cdot 10^{-4}$		$4.91 \cdot 10^{-4}$	
$6.67 \cdot 10^{-3}$	$4.25 \cdot 10^{-4}$	$10^{3.53}$	$5.17 \cdot 10^{-4}$	$10^{3.47}$
$3.33 \cdot 10^{-3}$	$4.60 \cdot 10^{-4}$	$10^{3.40}$	$6.02 \cdot 10^{-4}$	$10^{3.19}$
$1.67 \cdot 10^{-4}$	$5.24 \cdot 10^{-4}$	$10^{3.42}$	$7.87 \cdot 10^{-4}$	$10^{3.15}$
$8.33 \cdot 10^{-4}$	$7.06 \cdot 10^{-4}$	$10^{3.49}$	$9.90 \cdot 10^{-4}$	
$4.16 \cdot 10^{-4}$	$8.23 \cdot 10^{-4}$		$10.07 \cdot 10^{-3}$	
$2.08 \cdot 10^{-4}$	$8.05 \cdot 10^{-4}$		$10.26 \cdot 10^{-3}$	
$1.04 \cdot 10^{-4}$	$7.91 \cdot 10^{-4}$			
		Mean $10^{3.46}$		Mean $10^{3.27}$

Absorption spectra of uranium–oxine complexes

The absorption spectra of uranium–oxine complexes dissolved in chloroform are given in Fig. 2. These are essentially the same as those given by MOELLER AND RAMANIAH[4], but differ in absorption intensity. The disagreement may be due to difficulty of dehydration of chloroform by simple distillation.

It is natural that the absorption spectra of the 1:2 complex dissolved in pure chloroform and that containing ethanol are somewhat different, for the molar ratios of oxine to uranium of these solutions were different, as shown in Tables I and II. The difference in the absorption spectra of the 1:2 and 1:3 complexes dissolved in pure chloroform proved that they were different identities. The presence of ethanol in chloroform had no significant effect on the absorption spectra of the solutions of the 1:3 complex in the absence and presence of oxine.



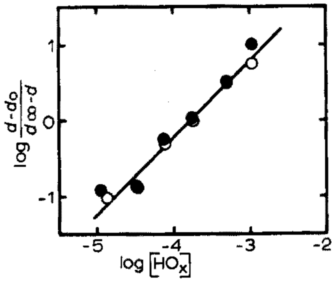


Fig. 3. Effect of oxine on the absorbance of the solution of the 1 : 3 complex. ● $CHCl_3$ (containing C_2H_5OH); ⊖ $CHCl_3$ saturated with water. $[U]=1.18\cdot10^{-4}$ *M*.

Fig. 4. Determination of $K_{1,4}$. ● 410 nm; ○ 450 nm.

The presence of the 1:4 complex was also suggested from the result that the absorbance of the solution of the 1:3 complex increased with increasing concentration of oxine as shown in Fig. 3 (the absorbance by oxine was negligible above 400 nm); in this case, chloroform containing ethanol was used for convenience. Since the absorption spectrum in Fig. 3 shows that the 1:3 complex was present in chloroform, the increase in the absorption intensity can be explained by eqn. (3). The concentrations of the 1:3 and 1:4 complexes and oxine at equilibrium are given by eqns. (6), (7), and (8):

$$[UO_2Ox_2\cdot HOx] = \frac{d_\infty - d}{d_\infty - d_0}C \tag{6}$$

$$[UO_2Ox_2\cdot 2HOx] = \frac{d - d_0}{d_\infty - d_0}C \tag{7}$$

$$[HOx] = [HOx]_i - \frac{d - d_0}{d_\infty - d_0}C \tag{8}$$

where C represents the initial concentration of the 1:3 complex, d is the absorbance of the mixture of the uranium–oxine complexes, and d_0 and d_∞ are the absorbances of the solutions of the 1:3 and 1:4 complexes, respectively. The subscript i refers to the initial concentration. In this case d_0 corresponds to the absorbance of a solution of the 1:3 complex in the absence of oxine (a dotted line in Fig.3) and d_∞ corresponds to that in the presence of a large excess of oxine. Consequently, eqn. (4) can be rewritten as follows:

$$K_{1,4} = \frac{d - d_0}{(d_\infty - d)[HOx]} \tag{9}$$

A log–log plot of $(d-d_0)/(d_\infty-d)$ against [HOx] is shown in Fig. 4, a straight line of unit slope being obtained as expected by eqn. (9). The $K_{1,4}$ value was determined graphically to be $10^{3.75}$, which is somewhat larger than the values obtained by solubility measurements (Table IV). This may be due to difference in the activity of the complexes in chloroform.

When chloroform saturated with water was used as solvent, increase in absorbance similar to that shown in Fig. 3 was observed. Though a log–log plot of eqn. (9) gave a straight line of unit slope, it was considerably altered by the wavelength selected, possibly because of the presence of other chemical species than those given in eqn. (4), *e.g.* hydrated complexes, in the solution.

The author is grateful to Dr. JUN'ICHI KOBAYASHI for his helpful discussions, and to Miss HIDEKO KOIKE for her experimental help. Thanks are also due to Dr. TAICHI SATO for revising this paper.

SUMMARY

The solubilities and absorption spectra of uranium(VI)–oxine complexes in chloroform were studied. The solubility of the 1:2 complex in chloroform was found to be $3.99 \cdot 10^{-4}$ *M*. In chloroform containing ethanol, the 1:2 complex decomposed: $3UO_2Ox_2 + C_2H_5OH \rightarrow (UO_2Ox_2)_2HOx + UO_2Ox \cdot OH_5C_2$. The solubilities of the 1:3 complex in chloroform and chloroform containing ethanol were $8.35 \cdot 10^{-4}$ *M* and $9.86 \cdot 10^{-4}$ *M*, respectively. The presence of a 1:4 complex, $UO_2Ox_2 \cdot 2HOx$, was suggested by the decrease in the solubility of the 1:3 complex with increasing amount of oxine in chloroform. The presence of the 1:4 complex was also supported by the spectral change of a solution containing the 1:3 complex when oxine was added to the solution. The absorption spectra of the 1:2, 2:5, and 1:4 complexes are given.

RÉSUMÉ

Les solubilités et les spectres d'absorption des complexes uranium(VI)–oxine dans le chloroforme ont été étudiés. On a trouvé que la solubilité du complexe (1:2) dans le chloroforme était de $3.99 \cdot 10^{-4}$ *M*. Dans le chloroforme contenant de l'éthanol, le complexe (1:2) se décomposait:

$$3UO_2Ox_2 + C_2H_5OH \rightarrow (UO_2Ox_2)_2\,HOx + UO_2Ox \cdot OH_5C_2$$

Les solubilités du complexe (1:3) dans le chloroforme et dans le chloroforme contenant de l'éthanol sont de $8.35 \cdot 10^{-4}$ *M* et de $9.86 \cdot 10^{-4}$ *M*, respectivement. La présence d'un complexe (1:4) $UO_2Ox_2 \cdot 2HOx$ a été suggérée par la diminution de la solubilité du complexe (1:3) quand on augmente la quantité de l'oxine dans le chloroforme. La présence du complexe (1:4) était aussi en accord avec la modification du spectre d'une solution contenant le complexe (1:3) quand l'oxine était ajoutée à la solution On donne les spectres d'absorption des complexes (1:2), (2:5) et (1:4).

ZUSAMMENFASSUNG

Die Löslichkeit und Absorptionsspektren des Uran(VI)–Oxin-Komplexes

in Chloroform wurden untersucht. Die Löslichkeit des 1:2-Komplexes beträgt 3.99·10⁻⁴ *M*. Enthält das Chloroform Äthanol, so wird der Komplex zersetzt: $3UO_2Ox_2 + C_2H_5OH = (UO_2Ox_2)_2HOx + UO_2Ox \cdot OH_5C_2$. Die Löslichkeiten des 1:2-Komplexes in Chloroform und in Chloroform, das Äthanol enthält, betrugen $8.35 \cdot 10^{-4}$ *M* bzw. $9.86 \cdot 10^{-4}$ *M*. Die Gegenwart eines 1:4-Komplexes wurde vermutet auf Grund der Abnahme der Löslichkeit des 1:3-Komplexes mit steigendem Anteil von Oxin im Chloroform. Der spektrale Wechsel einer Lösung mit dem 1:3-Komplex bei Zugabe von Oxin wies ebenfalls darauf hin. Die Absorptionsspektren werden angegeben.

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SOURCES OF ERROR IN THE USE OF ARSONIUM REAGENTS

PART I. COMPOSITIONS AND THERMAL STABILITIES OF SOME TETRAPHENYL- AND TRIPHENYLMETHYL-ARSONIUM SALTS

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Arsonium salts have often been used as analytical reagents but sources of error in their use have not been systematically investigated. A simple source of error may be easily overlooked if not explicitly defined. For instance, reference has been made to the fact that arsonium salts form hydrates[1-6] but it has not been made clear that their existence can lead to error. A commercial sample labelled "Tetraphenylarsonium chloride, $(C_6H_5)_4AsCl$, MW 418.80" proved to be $(C_6H_5)_4AsCl \cdot 1.7\ H_2O$ (MW 449. 42) *i.e.* −6.8% error. The sample was dried to convert it to the anhydrous salt. This was hygroscopic and changed to the monohydrate during the handling of the sample before weighing; what was weighed as the anhydrous salt was really the monohydrate and the molarity of the standard solution prepared from this sample was correspondingly in error (−4.3%).

After this and other like errors were discovered, a systematic examination was made of the compositions and thermal stabilities of a number of tetraphenylarsonium and triphenylmethylarsonium salts in order to define their properties, to check published data on these compounds and to discover how the properties of these reagents could contribute to errors in their use.

EXPERIMENTAL

Melting points were measured on a flame-heated aluminum block. Standard samples had melting points within ± 2° of published values in the range 50°–260°.

Arsenic was determined by a modification of the method of SCHULEK AND VILLECZ[7]; 50-mg samples were weighed into # 0 gelatin capsules and digested in 100-ml Kjeldahl flasks with 5 ml of acid mixture ($H_2SO_4/HNO_3/H_2O$; 10:3:4 v/v) and 1 ml of 30% hydrogen peroxide. Hydrogen peroxide was added at intervals in 1–2 ml portions until the digest was colorless. The residue was reduced with 100 mg of hydrazine sulfate and the arsenite was titrated with 0.01 *N* iodine to a starch end-point in bicarbonate buffer. Assays of standard samples showed arsenic recoveries of 100.0 (± 0.2)% for 3–15 mg of arsenic (20 samples).

Water assays were done with a Cenco Karl Fischer Moisture Determinator; 0.5-g samples were titrated with SO-K-3 Karl Fischer Reagent (Fisher Scientific Co.) to a dead-stop end-point. The reagent was standardized with a standard solution of water in methanol.

Thermogravimetric analyses (TGA) were done with an ADAMEL recording thermobalance (Chevenard system). The furnace liner was a 39-mm (i.d.) silica tube. Temperatures were measured with a platinum/10% rhodium-in-platinum thermocouple; the hot junction of the thermocouple was about 5 mm above the sample. Thermocouple readings were checked by measuring the boiling points (80°–250°) of some standard liquids; the results agreed with published values within 3°. The sample was held in a Coors 00000/D31 porcelain crucible supported by a silica rod with a ring-top. Samples were heated in air and the products were removed by natural convection. Samples weighing 40–50 mg were heated at a temperature increase of 220°/h and samples weighing 350–450 mg were heated at 80°/h. Both conditions gave essentially the same form of TGA curve in the 25°–200° range for all samples examined. The balance was calibrated with a 50.00 ($\pm$0.05) mg weight before each run. The sensitivity was about 1 mg per chart division, readable to 0.1 division, and the chart span was 100 divisions.

Vapor pressures were measured in a U-tube manometer system which could be evacuated to 5 μ Hg and immersed in a water bath with the temperature controlled to $\pm$0.1°. The manometer fluid was Welch Duo-Seal vacuum pump oil. The density of the oil was measured by pycnometer at 2° intervals between 20° and 28° and densities at other temperatures were found by interpolation. These densities were used to convert all measured pressures to units of mm Hg. The oil was degassed by exposure to vacuum for at least 24 h before each run.

Aqueous solutions of arsonium salts wet clean glass surfaces unevenly, as if greasy. Therefore stock solutions were not dispensed by volume but instead were made to known weight compositions and dispensed by weight, with hypodermic syringes as weight burettes.

All reagents were standard analyzed-reagent grade unless otherwise stated.

Results were analyzed, when possible, by standard statistical methods[8]. All bracketed errors are estimated standard deviations ($\pm \hat{S}$).

SYNTHESES AND ASSAY RESULTS

Unless otherwise stated, all products were crystallized from water as white or colorless needles; they were sucked dry after crystallization and air-dried for at least 24 h or until the product could be ground to a free-flowing powder.

The following were prepared by published procedures: *triphenylarsine*[9], plates from methanol, dried under water-pump vacuum, m.p. 59°–60°, lit. m.p. 59°–60° [10]; *triphenylarsine oxide*[11], plates from toluene or benzene, dried under water-pump vacuum, m.p. 188°–189°, lit. m.p. 189° [11]; *triphenylarsine oxide monohydrate*[6], leaflets, m.p. 85° by rapid heating in capillary or m.p. 188°–189° by slow heating on block, lit. m.p. 117°–118° and 191°–192° [6], 108° [12], 112°–114° [13] (H_2O: found 5.62%, calc. 5.30%); *tetraphenylarsonium hydrogen dichloride dihydrate*[11], from 10 *M* hydrochloric acid, m.p. 254°–256°, lit. m.p. 204°–208° [11] (As: found 15.18%, calc. 15.25%; H_2O: found 6.95%, calc. 7.33%); *tetraphenylarsonium chloride dihydrate*[14], m.p. 256°–257°, lit. m.p. 256°–257° [14], 258°–260° [5] (As: found 16.37%, calc. 16.47%; H_2O: found 7.63%, calc. 7.92%); *triphenylmethylarsonium iodide*[15], very pale yellow, m.p. 175°–176°, lit. m.p. 174°–175° [15] (As: found 16.63%, calc. 16.72%; H_2O: found 0.02%, calc. 0.00%).

Other TPA and TPMA salts were prepared from the chloride and iodide respectively. TPA fluoride was prepared by percolating the chloride through a column of Dowex 1-X8 (fluoride form) ion-exchange resin. The other soluble and moderately soluble salts were prepared by stirring the halide with an aqueous suspension of well-washed silver oxide and neutralizing the filtrate with the appropriate acid. The resulting solutions were clarified with activated carbon and filtered. The easily soluble salts were isolated from solution by evaporation at room temperature and the moderately soluble salts by evaporation and cooling of the solution until crystallization occurred at or near room temperature. The insoluble salts were precipitated from solution by addition of the appropriate sodium or potassium salt and were recrystallized by extraction with aqueous 20% ethanol in an all-glass Soxhlet-type extractor (the ethanol controlled frothing of the boiling solution).

The following tetraphenylarsonium salts were synthesized: *tetraphenylarsonium fluoride trihydrate,* m.p. 166°–168° (As: found 16.90%, calc. 16.42%; H_2O: found 10.98%, calc. 11.84%); *tetraphenylarsonium bromide dihydrate,* m.p. 279°–281°, lit. m.p. 273°–275° [14] (As: found 15.14%, calc. 15.01%; H_2O: found 7.22%, calc. 7.22%); *tetraphenylarsonium iodide,* m.p. 314°, lit. m.p. 312°–313° [14] (As: found 14.69%, calc. 14.68%; H_2O: found 0.03%, calc. 0.00%); *tetraphenylarsonium nitrate,* m.p. 257°–258°, lit. m.p. 260°–262° [16] (As: found 16.84%, calc. 16.82%; H_2O: found 0.11%, calc. 0.00%); *tetraphenylarsonium sulfate hexahydrate,* m.p. 260°–262°, lit. m.p. 257°–258° [16] (As: found 15.37%, calc. 15.43%; H_2O: found 11.23%, calc. 11.13%); *tetraphenylarsonium perchlorate,* m.p. 356°–357° (As: found 15.47%, calc. 15.52%; H_2O: found 0.02%, calc. 0.00%).

The following triphenylmethylarsonium salts were synthesized: *triphenylmethylarsonium chloride monohydrate,* m.p. 184°–186°, lit. m.p. 121° [17] (As: found 20.51%, calc. 19.99%; H_2O: found 4.87%, calc. 4.81%); *triphenylmethylarsonium bromide monohydrate,* m.p. 200°–202°, lit. m.p. 194°–195° [15] (As: found 17.76%, calc. 17.87%; H_2O: found 4.38%, calc. 4.30%); *triphenylmethylarsonium nitrate,* m.p. 127°–128°, lit. m.p. 131°–133° [18] (As: found 19.51%, calc. 19.55%, H_2O: found 0.23%, calc. 0.00%); *triphenylmethylarsonium sulfate dihydrate,* sticky prisms, m.p. 137°–138° (As: found 19.20%, calc. 19.34%; H_2O: found 5.20%, calc. 4.65%); *triphenylmethylarsonium perchlorate,* m.p. 155°–156° (As: found 17.77%, calc. 17.81%; H_2O: found 0.01%, calc. 0.00%).

Some of these salts have been described in earlier work but the reported data are sometimes either incomplete or incorrect.

When the results of the arsenic and water assays are examined, allowance must be made for the occluded water which is normally present in salts which have been crystallized from water and air-dried. Even the anhydrous salts can be expected to contain a little water.

TPA fluoride has been reported[19] to be "fairly insoluble"; it is in fact so soluble that it is difficult to crystallize it from aqueous solution.

TPA hydrogen dichloride dihydrate is named in a standard reference source[11] as the "chloride hydrochloride", presumably by mistaken analogy with amine hydrochlorides. The HCl_2^- anion is a now well-recognized member[20–22] of the class of hydrogen-bonded complex anions of general formula HX_2^-. BLICKE AND MONROE's assay[14] of the supposed anhydrous hydrochloride was misinterpreted by them; their experimental results actually support the dihydrate formula.

TPMA iodide, when recrystallized from water, has been reported[6] to form a monohydrate which is stable even when dried over phosphorus pentoxide. The present results do not agree with that report; the arsenic and water assays of recrystallized and air-dried TPMA iodide fit only the anhydrous salt. This is supported by the TGA results given later in this paper. No weight loss occurs below 160° although ARMSTRONG *et al.*[6] stated that their "monohydrate" lost water when oven-dried at 85°.

Triphenylarsine oxide monohydrate is sometimes described as triphenylarsine dihydroxide[13,17] because of its formation from triphenylarsine dichloride[12]. Its infrared absorption spectra support only the hydrate formula[6]. The melting points reported for the oxide and its hydrate are inconsistent because allowance was not made for the existence of the hydrate which melts at 85° and loses water readily to form the anhydrous oxide which melts at 189°. The first melting point (or perhaps dissolution point) can be measured only by rapidly heating the sample in a capillary; the second can be measured only if the water is allowed to evaporate completely before 180°.

THERMOGRAVIMETRIC RESULTS

The TGA curves are shown in Figs. 1–5. Samples were occasionally heated to particular stages of a TGA curve and then assayed; the results of such assays are included below.

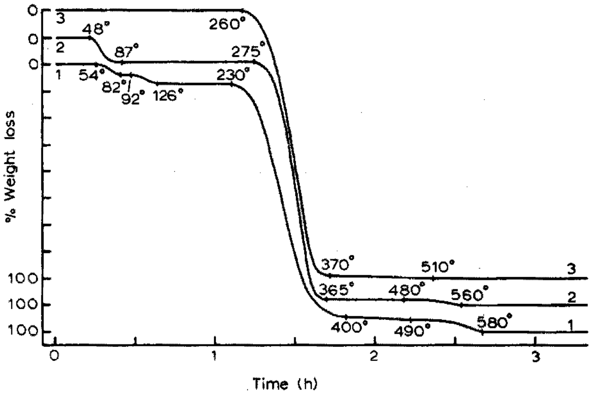

Fig. 1. TGA curves of (1) tetraphenylarsonium chloride dihydrate, (2) tetraphenylarsonium bromide dihydrate, (3) tetraphenylarsonium iodide.

TPA fluoride trihydrate shows only overlapping loss regions, representing various unresolved decomposition reactions. The first loss at 40°–110° probably represents dehydration (loss: found 15.6%, calc. 11.84%). The 110°–162° loss may represent the loss of fluorobenzene (loss: found 12.2%, calc. 21.1%) and the 162°–370° loss would then represent the evaporation of triphenylarsine. This last part of the TGA curve matches that of triphenylarsine fairly well.

TPA chloride dihydrate loses water at 54°–82° and 92°–126° to form the monohydrate and anhydrous salt respectively (losses: found, 3.84%, 4.04%, calc., 3.96%, 3.96%). The anhydrous salt decomposes almost completely at 230°–400°, leaving a small tarry residue which disappears at 490°–580°.

TPA bromide dihydrate is similar to the chloride. It loses water in one step at 48°–87° (loss: found, 6.92%, calc., 7.22%) to form the anhydrous salt. This decomposes almost completely at 275°–365°, leaving a tarry residue which disappears at 560°.

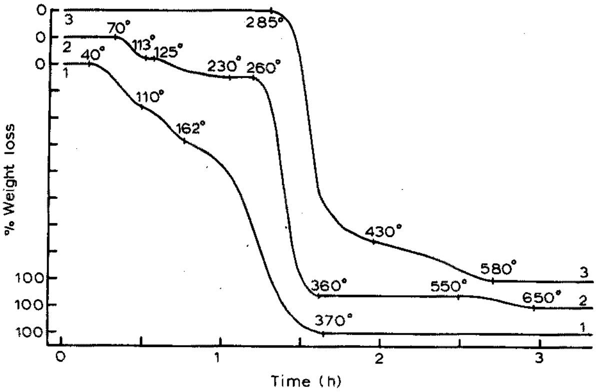

Fig. 2. TGA curves of (1) tetraphenylarsonium fluoride trihydrate, (2) tetraphenylarsonium hydrogen dichloride dihydrate, (3) tetraphenylarsonium nitrate.

TPA iodide is anhydrous. The major loss is at 260°–370°; a tarry residue is left which disappears at 510°.

The major decomposition of each of the halides, in the region of 150°–250°, is probably to triphenylarsine and the corresponding phenyl halide. The bromide is known to decompose this way[16].

$$(C_6H_5)_4AsBr \rightarrow (C_6H_5)_3As + C_6H_5Br$$

TPA hydrogen dichloride dihydrate loses water at 70°–113° to form the anhydrous salt (loss: found 7.32%, calc. 7.33%; HCl: found 7.8%, calc. 7.4%) and this loses hydrogen chloride at 125°–230° to form the anhydrous chloride (loss: found 6.88%, calc. 7.42%; HCl: found 0.15%, calc. 0.00%). The chloride decomposes almost immediately at 260°–360°.

TPA sulfate hexahydrate loses water at 35°–125° to form the anhydrous salt (loss: found 11.7%, calc. 11.1%). The anhydrous salt decomposes completely in overlapping reactions at 246°–330°, 330°–495° and 495°–555°.

TPA nitrate is anhydrous. It decomposes almost completely at 285°–430° and the residue disappears at 580°.

TPA perchlorate is anhydrous. It decomposes rapidly and completely at 320°. The sample sometimes explodes instead of decomposing smoothly; the temperature and mode of decomposition depend on the sample size and rate of heating. Small samples (1–5 mg) can be melted on a metal block at 356°–357° with considerable browning. COLE AND PFLAUM[23] observed some decomposition beginning at 230° and a violent decomposition at 300° during TGA of a TPA perchlorate sample.

TPMA chloride monohydrate loses water at 70°–118° (loss: found, 3.04%,

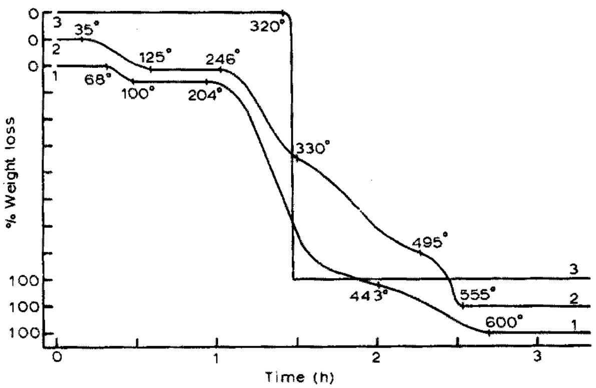

Fig. 3. TGA curves of (1) triphenylarsine oxide monohydrate, (2) tetraphenylarsonium sulfate hexahydrate, (3) tetraphenylarsonium perchlorate.

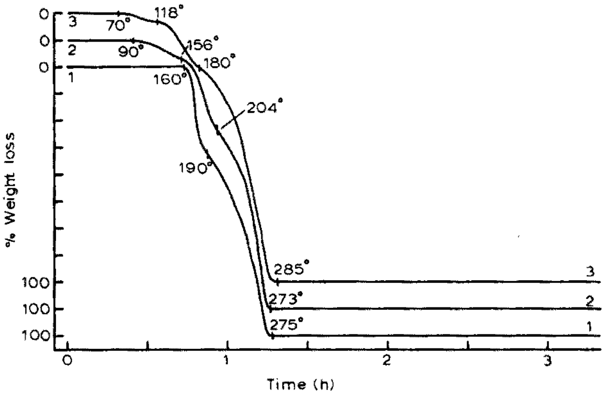

Fig. 4. TGA curves of (1) triphenylmethylarsonium iodide, (2) triphenylmethylarsonium bromide monohydrate, (3) triphenylmethylarsonium chloride monohydrate.

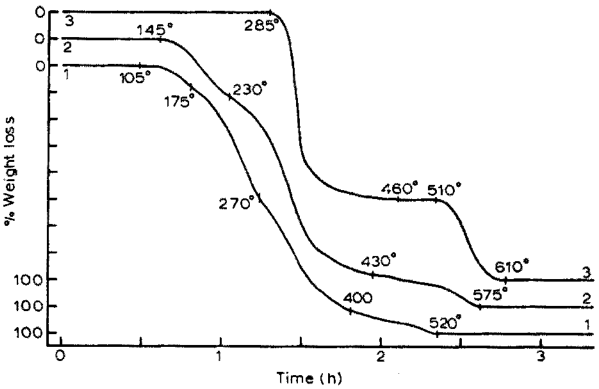

Fig. 5. TGA curves of (1) triphenylmethylarsonium sulfate dihydrate, (2) triphenylmethylarsonium nitrate, (3) triphenylmethylarsonium perchlorate.

calc., 4.81%) and the anhydrous chloride immediately decomposes by two overlapping reactions at 118°–180° and 180°–285°.

TPMA bromide monohydrate loses water at 90°–156° (loss: found 7.19%, calc. 4.30%) and the anhydrous bromide immediately decomposes by two overlapping reactions at 156°–204° and 204°–273°.

TPMA iodide is anhydrous. It decomposes completely by two overlapping reactions at 160°–190° and 190°–275°.

The major decompositions of each of the three halides, beginning near 120°–160°, is probably to triphenylarsine and the corresponding methyl halide; this is known to occur with the iodide[16].

$$(C_6H_5)_3CH_3AsI \rightarrow (C_6H_5)_3As + CH_3I$$

TPMA nitrate is anhydrous. It decomposes by two overlapping reactions at 145°–230° and 230°–430° to a tarry residue which disappears at 575°.

TPMA sulfate dihydrate decomposes by a sequence of poorly resolved reactions, which begin at 105° and involve inflections at 175°, 270° and 400°, and disappears at 520°.

TPMA perchlorate decomposes or explodes at 285°. If the sample does not explode, then there is a very rapid decomposition to a tarry residue at 460° which disappears at 510°–610°.

Triphenylarsine oxide monohydrate loses water at 68°–100° (loss: found 5.85%, calc. 5.30%). It decomposes at 204°–443° to a tarry residue which disappears at 600°.

Triphenylarsine shows a steady loss at 136°–300°; this is probably by evaporation. The vapor pressure[24] is 0.2 mm Hg at 136°, 4 mm at 200° and 110 mm at 300°. (No TGA curve is shown for triphenylarsine.)

In general, these TGA results are consistent with the compound formulae found from arsenic and water assays.

It is clear from the TGA results that considerable decomposition occurs at or before the melting point for most of the arsonium salts. (The only exception appears to be TPMA perchlorate which melts at 155°–156° but shows no signs of decomposition until 285°. This is surprising because TPMA salts and organic perchlorates are not typically stable in the molten state.) The experimental melting points are not true melting points and can be expected to be dependent on sample size, rate of heating and other conditions of measurement. (MANN AND WATSON[3] found that consistent melting points of some arsonium salts could be obtained only in evacuated capillaries.) However, the melting points are still useful for empirical characterization.

The TGA curves suggest the possibility of a simple synthesis of TPA chloride by heating the hydrogen dichloride dihydrate to remove hydrogen chloride and water, instead of the indirect synthesis cited earlier[14]. When a sample of the hydrogen dichloride dihydrate was heated at 105° under water-pump vacuum, it lost all the water within 2 h and then showed no weight loss for 24 h. However, when it was heated at 105° in air for 14 days, it was wholly converted to the anhydrous chloride, so there was a very slow loss of hydrogen chloride at 105°. When heated at 160° for two days it was converted to the chloride but some degradation occurred; the product was discolored and contained some water-insoluble material.

It is obvious from the TGA results that some of the salts cannot be dried at 105° without decomposition (in addition to loss of water). Samples of the various salts were dried in an oven at 105° for several days and weighed occasionally and inspected for signs of decomposition. After a few days, the following salts had neither lost weight nor discolored: TPA chloride, bromide, iodide, sulfate and perchlorate, TPMA perchlorate and triphenylarsine oxide. The following salts showed loss of weight or discoloration: TPA hydrogen dichloride, fluoride and nitrate, and TPMA chloride, bromide, iodide, nitrate and sulfate. These results are in harmony with the TGA results. Discoloration of samples of the stable salts during drying was found to be a good indication of the presence of impurities. This was particularly true of triphenylarsine oxide.

VAPOR PRESSURES OF HYDRATES

Anhydrous TPA chloride and bromide are hygroscopic. TPA chloride (0.25 g) changed to the monohydrate in 50% yield in 20 min when exposed in an open weighing bottle. The monohydrate was completely formed within 24 h and did not increase in weight thereafter. The bromide behaved in like manner. On the other hand, the dihydrates could be exposed for up to 3 weeks without loss.

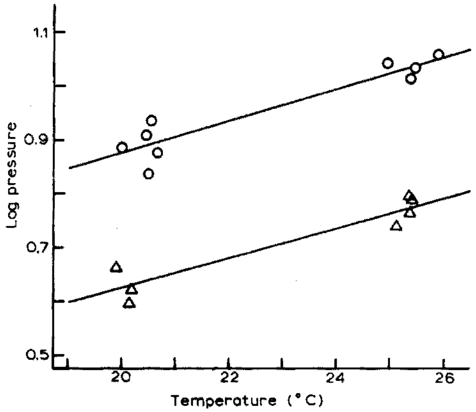

Fig. 6. Vapor pressures of arsonium salt hydrates. –○—○– Tetraphenylarsonium chloride dihydrate; –△—△– tetraphenylarsonium bromide dihydrate.

Measurements of the vapor pressures of the dihydrates were made to discover which phase was stable at normal humidities. TPA chloride dihydrate was pumped down to 7 μ Hg pressure and the vapor pressure was measured at 20.0°. After 7 days the pressure was still rising slowly. The sample was again pumped down and then held at 25.0° until the pressure was relatively steady and then the temperature was dropped to 20.0°. This time the pressure fell and steadied within 8 h and thereafter remained steady for 10 days. This showed that the "solid to vapor" transition was slow and the "vapor to solid" transition was relatively fast. From then on, all measurements were made by approaching equilibrium from temperatures and pressures greater than those of interest. The results are shown in Fig. 6; the regression equations for these data and the corresponding standard errors of Y on X $(\hat{S}_{y,x})$

and correlation coefficients (r) are shown below, in terms of the pressure (p) in mm Hg and the temperature ($t°$):

$$\log_{10} P_{\mathrm{Cl}} = 0.0294 \cdot t° + 0.287 \quad (\hat{S}_{y,x} = 0.0288, \quad r = 0.930)$$

$$\log_{10} P_{\mathrm{Br}} = 0.0277 \cdot t° + 0.0706 \quad (\hat{S}_{y,x} = 0.0278, \; r = 0.931)$$

The vapor pressures of the salts and their equivalent equilibrium relative humidities (RH) were calculated at 25°:

chloride: pressure = 10.5 mm Hg; RH = 43%

bromide: pressure = 5.80 mm Hg; RH = 24%

At relative humidities greater than these, the dihydrates are stable and at relative humidities lower than these the monohydrates are stable. Samples stored in screw-top jars were found to change their water contents over periods of several months, hence the hydrated salts cannot be used as standard materials without a check of their water contents immediately before use.

Attempts to measure the vapor pressures of the monohydrates of TPMA chloride and bromide were unsuccessful. The pressures were very low and equilibrium was approached very slowly even at 40°. A few results suggested that the vapor pressure at 25° was about 1 mm or less (equivalent $\mathrm{RH} \leqslant 5\%$). TPMA chloride or bromide monohydrates should be quite stable at the usual humidities.

TPMA sulfate dihydrate was deliquescent at high humidities. A sample was exposed and observed in conjunction with RH measurements. The salt was only deliquescent at 38% RH or above.

Triphenylarsine oxide is hygroscopic. An 0.5-g sample exposed at 30–50% RH was changed to the monohydrate in 50% yield after 36 h and completely changed after one month. This finding contradicts an earlier report[16] that triphenylarsine oxide is not hygroscopic. The earlier workers were probably misled by the fact that the rate of absorption of water is slow.

SUMMARY

A search has been made for sources of error in the use of arsonium salts as reagents. Compositions, thermogravimetric curves and hydrate vapor pressures have been measured for a variety of tetraphenylarsonium and triphenylmethylarsonium salts and triphenylarsine oxide. Some of the salts are hygroscopic and form hydrates. Tetraphenylarsonium salts are more stable to heat than triphenylmethylarsonium salts. Some published data on these compounds are incorrect.

RÉSUMÉ

Une recherche a été effectuée pour déterminer les sources d'erreur quand on emploie les sels d'arsonium comme réactifs. Les compositions, les courbes thermogravimétriques et les pressions de vapeur des hydrates ont été mesurées pour une variété de sels de tétraphénylarsonium et de triphénylméthylarsonium et pour l'oxyde de triphénylarsine. Quelques-uns des sels sont hygroscopiques et forment des hydrates. Les sels de tétraphénylarsonium sont plus stables à la chaleur que les sels de triphénylméthylarsonium. Quelques valeurs publiées sur ces composés ne sont pas correctes.

ZUSAMMENFASSUNG

Es wurden in einer Untersuchung die Fehlerquellen bei der Verwendung von Arsoniumsalzen als Reagens zusammengestellt. Die Zusammensetzung, das thermogravimetrische Verhalten, der Wasserdampfdruck wurden von Tetraphenylarsonium- und Triphenylmethylarsonium-Salzen und Triphenylarsinoxid untersucht. Einige dieser Salze sind hygroskopisch und bilden Hydrate. Tetraphenylarsonium-Salze sind gegenüber Wärme stabiler als Triphenylmethylarsonium-Salze. Einige der veröffentlichten Daten dieser Verbindungen sind ungenau.

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SPECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM WITH CHROME AZUROL S

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Chrome azurol S (3''-sulpho-2'',6''-dichloro-3,3'-dimethyl-4'-hydroxyfuchson-5,5'-dicarboxylic acid) has been used for the detection of beryllium[1,2], and has been applied widely for the spectrophotometric determination of beryllium[3-14, 21,22]; it has also been suggested as indicator in titrations of beryllium solutions[23]. The composition and properties of the beryllium complexes with chrome azurol S formed in solution were uncertain for a long time[6,10,11,14] and widely different conditions have been prescribed for the spectrophotometric determination of beryllium with chrome azurol S.

In the present paper, several procedures for this determination are described; these are based on a detailed study of the reaction of beryllium(II) with chome azurol S[15], which showed that three different complexes of beryllium with chrome azurol S are possible.

It is shown that polyvinyl alcohol has a favorable effect on the optical properties of the reaction system in slightly acidic medium and that the use of calcium polyaminopolycarboxylic acid chelates as masking agents allows the establishment of sensitive and selective procedures.

EXPERIMENTAL

Chemicals

Beryllium standard. Solutions containing 0.4506 mg Be/ml were prepared from beryllium nitrate (Specpure; Johnson-Matthey, London) and standardized gravimetrically as beryllium ammonium phosphate.

Chrome azurol S. Technical products (J. R. Geigy, Basel) contained traces of Ca, Mg, Si, Fe and 15.3% sodium (theor. for pure trisodium salt: 11.4%). Coloured spots with R_F values of 0.86 and 0.68 were detected by descending paper chromatography from acetic acid : ethanol : water mixture as (60:30:10). The Geigy product was purified by the method of Langmyhr and Klausen[16]. The less soluble tetrabasic acid dihydrate of chrome azurol S was twice precipitated from hydrochloric acid (1 : 1), dried at 30–50° and stored over phosphorus pentoxide.

The contents of the active product ($C_{23}H_{16}O_9SCl_2 \cdot 2H_2O$) in two purified samples were 94.87% and 95.4%, evaluated by elemental analysis and by differential potentiometric titration with 0.1 *M* sodium hydroxide; 3 protons of the reagent are titratable.

Aqueous solutions of the reagent were stable for at least two days at pH 1–13.

All the chemicals used were of analytical-reagent grade. Various buffer solutions were prepared by mixing 1 *M* solutions of the required salt and corresponding acid: formate (pH 4.85), acetate (pH 4.8 or 5.0), phthalate (pH 4.75) and citrate (pH 4.75). Pyridine–nitric acid buffer (pH 5.0) was prepared from 81.3 ml of twice-distilled pyridine and 42 ml of concentrated nitric acid (d = 1.39) diluted to 1 l with water.

Pyridine, hexamethylenetetramine, triethanolamine or tris(hydroxymethyl)-aminomethane (sufficient to give 1 M solutions on dilution) were dissolved in a little water and the pH was adjusted to 6.7 ± 0.3 with 1 M perchloric or nitric acid before dilution with water to 1 l.

Polyvinyl alcohol (Mowiol, Germany) with *ca.* 12% unhydrolysed acetate groups was used as a 4% (w/v) solution in water.

Instruments

A Radiometer PHM 4d pH meter with a precision of ±0.02 pH units was used with Radiometer glass electrodes.

Unicam SP 500 and 700 (England) and SFD-2 (USSR) spectrophotometers were used with 5–40-mm cells. The absorbance was measured against water but the absorbance differences $\Delta A = A - A_{OR}$ were always plotted where A_{OR} is the absorbance of the total reagent concentration in blank solutions under exactly the same conditions.

COMPLEX EQUILIBRIA OF BERYLLIUM(II) WITH CHROME AZUROL S

As was shown previously[15], three different complexes, $BeRH^-$, $Be_2R_2^{4-}$ and $BeR(OH)_x^{y-}$, are formed stepwise in solutions containing a limited excess of reagent, as a function of pH; the three complexes are formed between the pH intervals 4.8–5.0, 6.4–7.0, 9.7–10.3, respectively.

Detergents such as polyvinyl alcohol, cetylpyridinium bromide or cetyltrimethylammonium bromide considerably increase the apparent molar absorptivity at pH 5.5–8.0 as well as bathochromically shift the absorption maxima of the beryllium–chrome azurol S complexes (Fig. 1). Similar observations have been made in other systems containing metal chelates with highly negatively charged dye anions[17–19] and in the system uranyl–chrome azurol S[20].

The particular colour changes are indicated in Table I, which shows the differences in absorption maxima between the particular ligand forms and the beryllium complexes.

However, the transition of the red H_2R^{2-}-form to the yellow HR^{3-}-form of the reagent can greatly affect measurements below pH 5, if excess of reagent is present, unless the pH is strictly controlled in both the standard and sample solutions.

TABLE I

SOME DATA ON BERYLLIUM(II) CHELATES WITH CHROME AZUROL S

pH	*Complex*	λ_{max} *(nm)*	*Reagent form*	λ_{max} *(nm)*	$\Delta\lambda_{max}$ *(nm)*
4.8	$BeRH^-$	568	H_2R^{2-}	499	69
6.7	$Be_2R_2^{4-}$	540	HR^{3-}	429	111
		615[a]			186[a]
10.0	$BeR(OH)_x^{y-}$	490	HR^{3-}	429	61

[a] In the presence of ≧0.5% polyvinylalcohol.

The pH interval 6.5–10.0 is more suitable for the determination of beryllium, since the yellow HR^{3-}-form of the ligand which alone exists under these conditions, absorbs only slightly (*cf.* the dissociation constants of particular ligand forms[15]).

DETERMINATION OF BERYLLIUM AT pH 4.9±0.1

Effect of the reagent concentration and ionic strength

Almost constant absorbance is obtained when a 3–5-fold excess of the reagent is present ($c_M = 2.0 \cdot 10^{-5} M$; $c_R = 7 \cdot 10^{-5} M$), but a 10-fold excess is recommended for practical purposes. The concentration of the reagent in solution is limited by its solubility and by its absorbance at the wavelength of maximum absorbance of the $BeRH^-$ complex (568 nm).

The theoretical molar absorptivity for the $BeRH^-$ complex of $\varepsilon_{11} = 51,300$ at 568 nm, earlier calculated for solutions with a large excess of metal ion, could not be achieved when excess of ligand was present. Molar absorptivities between 19,500 ± 300 and 21,400 ± 250 were obtained for reagent concentrations of $1.0 - 2.4 \cdot 10^{-4}$ *M* and metal concentrations of $2.0 \cdot 10^{-5}$ *M* in 0.1 *M* sodium perchlorate and nitrate media, respectively, the sensitivity limits being 4.6–4.2 ng Be/ml, respectively. The influence of ionic strength on the absorbance was negligible for $\mu = 1.1$ (sodium perchlorate) at pH = 4.9 ± 0.1. However, the absorbance considerably increased above an ionic strength of 2, where partial precipitation of the red-violet beryllium(II) species and of the excess of dye occurs.

The validity of Beer's law and the influence of buffers

Beer's law was strictly obeyed for solutions containing 10–280 ng Be/ml at 568 nm when the reagent concentration was more than 10^{-4} *M*. For solutions without buffers, the absorbance was always interpolated from absorbance–pH plots for the pH requested; all the beryllium(II) concentrations were taken in account. Between the above limits, the absorbance–beryllium concentration plots were always linear even in

TABLE II

EFFECT OF BUFFERS IN 0.1 *M* CONCENTRATION AND OF EDTA ON THE APPARENT MOLAR ABSORPTIVITY

Buffer	*pH*	$\bar{\varepsilon}_1$ *(568 nm)*	*Sensitivity limit in ng Be/cm^2 for $A = 0.01$*
Pyridine–nitrate[a,b]	5.0	22,335 ± 200	4.05
Acetate[a]	5.0	19,795 ± 200	4.6
	4.80	19,600 ± 200	4.6
Formate[c]	4.85	20,750 ± 200	4.2_5
Phthalate[c]	4.75	4,950 ± 50	18.4
Citrate[c]	4.75	2,150 ± 50	42.0
Pyridine + EDTA[a,d]	5.01	18,745 ± 270	4.8
Acetate + EDTA [a,d]	4.99	17,200 ± 300	5.2_5

[a] $c_R = 2.4 \cdot 10^{-4} M$; $c_M = 3.0 \cdot 10^{-5} M$.
[b] 0.02–0.20 *M* buffer.
[c] $c_R = 10^{-4} M$, $c_M = 2 \cdot 10^{-5} M$.
[d] Containing $2.5 \cdot 10^{-3}$ *M* EDTA.

the presence of a constant 0.02–0.11 M concentration of various buffers such as pyridine, acetate, formate, phthalate or citrate in the pH interval 4.8–5.0. However, the apparent molar absorptivity may decrease; the interfering effect of buffers increased in the order: pyridine < acetate ~ formate < phthalate < citrate (Table II). Pyridine and acetate buffers were used in 0.1 M concentration to minimize interference in the presence of $2.5 \cdot 10^{-4}$ M reagent.

The effect of various ions and masking agents

The limiting concentrations causing a relative deviation in absorbance of ± 2% are given in Tables III and IV. The interference of various cations was considerably reduced at pH 4.9 in the presence of $2.5 \cdot 10^{-3}$ M EDTA. EDTA is the only suitable masking agent, but a special calibration plot must be used for the concentration of EDTA used, since the absorbance of the $BeRH^-$ complex is slightly affected by EDTA.

TABLE III

LIMITING RATIOS OF ANIONS AND MASKING AGENTS AGAINST BERYLLIUM
($c_R = 2.5 \cdot 10^{-4}$ M; $c_{Be} = 10^{-5}$ M)

Agent	c_x/c_{Be}[a]	c_x/c_{Be}[b]	*Agent*	c_x/c_{Be}[a]	c_x/c_{Be}[b]
Nitrate	480	1500	Tartrate	120	25
Chloride	600	1200	Oxalate	9	15
Sulphate	270	150	NTA	35	10
Carbonate	60	15	EDTA	70	7
Phosphate	50	0.5	CDTA	25	6
Perchlorate	2500	1500			

[a] pH = 4.85; 0.1 M acetate buffer.
[b] pH = 6.60; 0.1 M TRIS buffer.

TABLE IV

LIMITING RATIOS OF CATIONS AGAINST BERYLLIUM
($c_R = 2.5 \cdot 10^{-4}$ M; $c_{Be} = 10^{-5}$ M)

Cation	c_x/c_{Be}[a]	c_x/c_{Be}[a,b]	c_x/c_{Be}[c]	c_x/c_{Be}[c,d]
Fe^{3+}	1.0	50	0.05	60
Al^{3+}	0.1	40	0.1	80
Cu^{2+}	2	25	0.1	160
Zr^{IV}	0.5	10	0.1	10
UO_2^{2+}	1	2;120[e]	0.1	20
Ni^{2+}	5	100	5	125
Bi^{3+}	1	125	5	500
Pd^{2+}	1	50	0.1	450
Ga^{3+}	2	200	0.2	500
In^{3+}	1.5	400	0.1	500
Y^{3+}	3	100	0.5	550
Cr^{3+}	1	20	0.2	100
Pb^{2+}	20	500	—	—
Zn^{2+}	35	650	300	5000
Mg^{2+}	300	500	120	2000
Ca^{2+}, Ba^{2+}	500	—	150	—

[a] pH = 6.60; 0.1 M TRIS buffer.
[b] With $2.5 \cdot 10^{-3}$ M EDTA and $3 \cdot 10^{-3}$ M Ca.
[c] pH = 4.90; 0.1 M acetate buffer.
[d] With $2.5 \cdot 10^{-3}$ M EDTA.
[e] In the presence of 0.05% hydroxylamine hydrochloride.

Recommended procedure

Pipette 5 ml of $2.5 \cdot 10^{-3}$ *M* (*ca.* 0.15% w/v) of chrome azurol S tetrabasic acid solution into a 50-ml volumetric flask containing 25 ml of slightly acidic sample solution (10–280 ng Be). Add 5 ml of 1 *M* pyridine–nitric acid or acetate buffer of pH 5.0 and dilute to the mark with water. Check the pH of this solution (4.9 ± 0.1) and measure the absorbance at 568 nm after 20 min against a reagent blank prepared under the same conditions.

The coefficient of variation was ±0.8% at the 95% confidence level for 10 determinations on solutions without interfering ions or masking agents in the concentration interval 50/200 ng Be/ml.

DETERMINATION OF BERYLLIUM AT pH 6.7 ± 0.2

Effect of reagent concentration and ionic strength

Only the $Be_2R_2^{4-}$-form of the chelate is formed at pH 6.7 ± 0.2. Maximal absorbance is obtained with a more than two-fold excess of reagent in pure solution, but a 10-fold excess is recommended. In solutions with an ionic strength exceeding 1.1, the beryllium chelate flocculates and the dye coprecipitates; this can also be observed if insufficient reagent is present.

Validity of Beer's law and influence of buffers

Beer's law was obeyed over the same range at pH 6.7 and 4.9 (10–280 ng Be/ml) when measurements were made at 540 and 568 nm, respectively, for solutions with $c_R = 2.5 \cdot 10^{-4}$. However, at pH 6.7 less strict pH control was needed. The value of the apparent molar absorptivity $\bar{\varepsilon}_{22}$ found at pH 6.7 ± 0.2 ($\bar{\varepsilon}_{22} = 14{,}350$) was considerably lower than the theoretical molar absorptivity for the dinuclear complex $\varepsilon_{22} = 70{,}350$ for 540 nm estimated earlier ($\varepsilon_{22} - 2\varepsilon_{22} = 28{,}700$)[15]. The sensitivity was 6.3 ng/cm² for $A = 0.01$

The buffers examined were pyridine, hexamethylenetetramine, triethanolamine, tris(hydroxymethyl)aminomethane (TRIS) and acetate. Acetate decreased the absorbance of the $Be_2R_2^{4-}$-chelate solution as its concentration increased from 0.005 *M* to 0.2 *M*, whereas the other buffers tested increased the absorbance slightly as their concentration increased. Triethanolamine gave brown-red colloidal precipitates of colloid solutions in more than 0.06 *M* concentrations. The sensitivity for $A = 0.01$ was 6.8 ng Be/cm² when TRIS buffer was used, compared to sensitivities of 7.3–7.5 with other buffers at 0.1 *M* concentrations. Apparent molar absorptivities ($\bar{\varepsilon}_{22}$) are between 1.14 and $1.33 \cdot 10^4$.

Effect of various ions and masking agents

The limiting concentrations of various ions and masking agents causing a relative absorbance deviation of ±2% are listed in Tables III and IV. Masking agents such as NTA, EDTA, CyDTA, oxalate and 2,3-dimercaptopropanol decreased the absorbance of the $Be_2R_2^{4-}$ complex solutions above pH 6.5 even when a 10-fold excess of reagent was present. Such reagents had less effect above pH 10, but at these pH values the yellow RH^{3-}-form of the reagent begins to dissociate to the violet R^{4-}-form ($\lambda_{max} = 598$ nm, $pK_{a4} = 11.79$) which strongly affects the sensitivity of the method.

However, the calcium(II)–EDTA chelate in the presence of a slight excess of calcium(II) proved to be a suitable masking agent for various ions at pH 6.5–6.9. Any beryllium bound by EDTA is replaced by calcium(II) or barium(II), but the latter ions did not affect the absorbance of the $Be_2R_2^{4-}$-chelate even at Be:Ca(Ba) ratios of 1:500. The recommended proportion for masking is Ca:EDTA = 1.25:1 for $2.5 \cdot 10^{-3}$ *M* EDTA solutions. The limiting concentrations of various ions with and without calcium-(II)–EDTA are shown in Tables III and IV.

The recommended procedure is similar to that given for pH 4.9, except that 1 *M* TRIS buffer is added instead of 1 *M* acetate buffer, and the absorbance is measured at 540 nm. Under these conditions, the coefficient of variation was found to be ±1%.

DETERMINATION OF BERYLLIUM AT pH 6.5±0.4 IN PRESENCE OF POLYVINYL ALCOHOL

A different absorption maximum for the $Be_2R_2^{4-}$ chelate at 615 nm, and a considerable increase in molar absorptivity were observed at pH 5.5–8.0 in the presence of detergents such as polyvinyl alcohol, cetyltrimethylammonium bromide and cetylpyridinium bromide (Fig. 1). The bromides were unsuitable because the beryllium chelate tended to form colloidal solutions. In the presence of polyvinyl alcohol the violet solutions turned blue if excess of metal was present; with excess of reagent present, the yellowish-orange colour became brown-green with considerable dichroic effects.

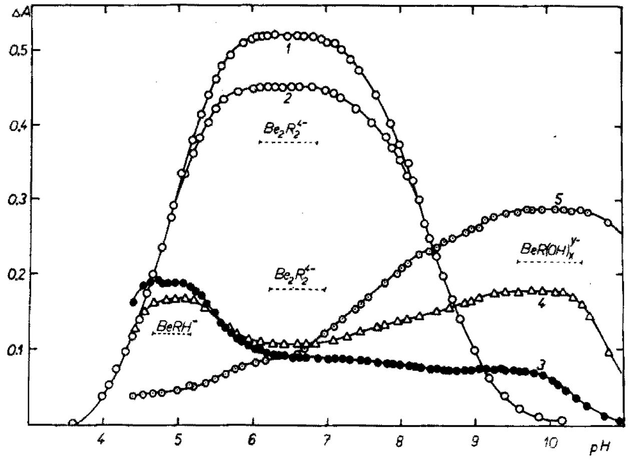

Fig. 1. pH–absorbance curves in the system beryllium–chrome azurol S for solutions with or without polyvinyl alcohol (PVA) (reagent blank subtracted).
$\mu = 0.1$, $c_R = 1.0 \cdot 10^{-4}$ *M*, $c_M = 1.0 \cdot 10^{-5}$ *M*. Measured after 30 min. Curve 1. 615 nm, 0.5% PVA, $\mu \to 0$; curve 2. 615 nm, 0.5% PVA, $\mu \to 0$, measured after 2 min only; curve 3. 568 nm, without PVA; curve 4. 540 nm, without PVA; curve 5. 500 nm, without PVA.

The absorbance maximum of the beryllium chelate solutions depended on the concentration of polyvinyl alcohol but reached a constant value of 615 nm above 0.5% (w/v) polyvinyl alcohol; this is a shift of 75 nm compared to the wavelength of maximum absorbance in the absence of polyvinyl alcohol. The alcohol had little effect on the absorption spectrum of the RH^{3-}-form of the reagent.

The pH–absorbance plot had plateaux which depended on the wavelength for solutions with a 10-fold excess of reagent, *i.e.* at pH 6.1–6.9 for 615 nm, pH 4.9–5.0 at 568 nm, or pH 9.8–10.4 for 490–568 nm. The largest increase in molar absorptivity was observed at pH ~6.6.

Effect of variables

The absorbance at 615 nm and at pH 6.6 reached its maximum after 20–30 min and then remained constant for 5 h. Above a 0.5% (w/v) concentration of polyvinyl alcohol, the alcohol concentration did not affect the absorbance; a 0.8% concentration was used. Maximum absorbance was achieved with a 10-fold excess of reagent ($c_R = 10^{-4}$ *M*) under these conditions.

Validity of Beer's law and effect of buffers

Beer's law was obeyed over the range 5–130 ng Be/ml at pH 6.6–6.9 and at 615 nm in solutions containing $1 \cdot 10^{-4}$ *M* reagent and 0.8% (w/v) polyvinyl alcohol. The absorbance was always measured against a reagent blank at the same pH value.

The apparent molar absorptivity values under these conditions was 52,000, giving a sensitivity of 1.75 ng Be/cm² for $A = 0.01$.

Nitrate and chloride in concentrations corresponding to $\mu = 0.2$–1.0 had a negligible effect on the absorbance. Sulphate precipitated the beryllium chelate from $5 \cdot 10^{-3}$ *M* concentrations, and perchlorate decreased the absorbance even at $\mu \geqq 0.02$.

Various buffers such as triethanolamine (TEA), tris(hydroxymethyl)aminomethane (TRIS), pyridine and hexamethylenetetramine (HMT) were tested; hexamine had the least effect on the absorbance at pH 6.6–6.9. Apparent molar absorptivities are compared for various concentrations of buffers in Table V. Hexamine buffer of pH 6.60 in 0.1 *M* concentration was selected for practical use. TEA in low concentrations increased the absorbance but decreased it at higher concentration; moreover, the calibration plot showed a change in slope at *ca.* 40 ng Be/ml (Fig. 2).

TABLE V

APPARENT MOLAR ABSORPTIVITIES FOR VARIOUS CONCENTRATIONS OF BUFFERS

($c_{Be} = 5 \cdot 10^{-6}$ *M*; $c_{PVA} = 0.8\%$ (w/v); $c_R = 10^{-4}$ *M*)

Buffer	*pH*	$\bar{\varepsilon}_{22} \cdot 10^4$ *(615 nm)*			
		0.02 M	*0.1 M*	*0.15 M*	*0.20 M*
TEA	6.50	6.01	5.85	5.46	4.87
HMT	6.60	4.95	4.93	4.94	4.88
TRIS	6.60	4.90	4.60	4.41	4.11
Pyridine	6.60	4.87	4.48	4.36	4.25

Effect of interfering ions

Current masking agents considerably interfered with the chelate formation at pH 6.5–7.0 (Table VI), but the calcium–EDTA chelate could again be used for masking when the ratio of EDTA to calcium was 1:1.2–1.3; the excess of calcium was not critical.

The limiting ratios of diverse ions for a ±2% deviation from the theoretical absorbance are shown in Table VII.

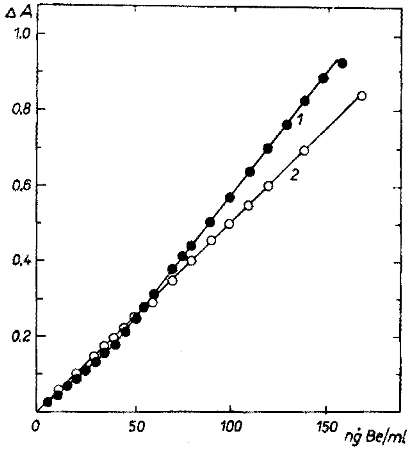

Fig. 2. Beer plot in solutions containing 0.8% PVA. $c_R = 10^{-4}$ M, 615 nm, measured after 30 min. Curve 1. pH 6.65 and 0.1 M TEA buffer; curve 2. pH 6.60 and 0.1 M HMT buffer.

TABLE VI

LIMITING RATIOS OF ANIONS AND SOME MASKING AGENTS AT pH 6.65 AND 9.85

Agent	c_x/c_{Be}[a]	c_x/c_{Be}[b]	*Agent*	c_x/c_{Be}[a]	c_x/c_{Be}[b]
Sulphate	100	1000	5-Sulphosalicylate	0.2	20
Perchlorate	4000	1000	Citrate	2.5	40
Chloride	2550	4000	Acetate	105	80
Nitrate	4000	4000	NTA	200	7
Phosphate	15	50	EDTA	20	10
Carbonate	30	12.5	CDTA	15	10
Tartrate	3.5		Fluoride	0.1	
Oxalate	20	200			

[a] pH 6.65 in presence of 0.8% polyvinyl alcohol (0.1 M TRIS); $c_R = 10^{-4}$ M; $c_M = 10^{-5}$ M.
[b] pH 9.85; $c_R = 2.5 \cdot 10^{-4}$ M; $c_M = 10^{-5}$ M.

TABLE VII

LIMITING RATIOS FOR CATIONS AGAINST BERYLLIUM(II) AT pH 6.65 IN THE PRESENCE OF 0.8% (w/v) POLYVINYL ALCOHOL

(10^{-5} M Be, 10^{-4} M reagent, 0.1 M TRIS, 615 nm)

Cation	c_x/c_{Be}[a]	c_x/c_{Be}[b]	*Cation*	c_x/c_{Be}[a]	c_x/c_{Be}[b]
Cu^{2+}	0.1	85	V^{IV}	50	160
Zn^{2+}	25	135	Cr^{3+}	0.5	42
Ag^{+}	30	270	UO_2^{2+}	2	4
Hg^{2+}	30	365	Mn^{2+}	10	140
Sc^{3+}	6	55	Fe^{3+}	0.15	32
Y^{3+}	4	22	Co^{2+}	12	160
La^{3+}	3	20	Ni^{2+}	15	170
Al^{3+}	0.2	50	Pd^{2+}	2	310
Ga^{3+}	2	30	Cd^{2+}	30	305
In^{3+}	4	50	Ti^{IV}	2	10
Zr^{IV}	3	3	Bi^{3+}	1	20
Th^{IV}	8	25	Ca^{2+}, Ba^{2+}	3000	—
Pb^{2+}	25	60	Mg^{2+}	1500	—

[a] Without Ca–EDTA mixture.
[b] With Ca–EDTA mixture.

Recommended procedure

Add 5 ml of 10^{-3} *M* chrome azurol S tetrabasic acid (pH 5–6), 10 ml of aqueous 4% (w/v) polyvinyl alcohol solution and the slightly acidic sample solution containing 5–130 ng Be to a 50-ml volumetric flask. Dilute with water and add 2.5 ml of 0.1 *M* disodium-EDTA solution and 3 ml of 0.1 *M* calcium nitrate solution. Shake carefully, add 5 ml of 1 *M* hexamethylenetetramine buffer (pH ~6.6) and dilute to the mark with water. Check that the pH is between 6.4 and 6.7 and measure the absorbance at 615 nm after 20–30 min against a reagent blank. If water is used as reference, subtract the absorbance of the reagent blank from the total absorbance.

The coefficient of variation was found to be ±1.5% at the 95% confidence level, calculated from 10 pure solutions containing 10–100 ng Be/ml.

DETERMINATION OF BERYLLIUM AT pH 10.0±0.2

Only the $BeR(OH)_x^{y-}$ chelate is formed at pH 9.7–10.4 in solutions with a small excess of reagent. The differential curve showed maximum absorbance at 490–500 nm. Beer's law was obeyed over the range 10–180 ng Be/ml at pH 10.0±0.2 with a $2.5\cdot10^{-4}$ *M* reagent solution. The apparent molar absorptivity was 25,300±200 (500 nm, extrapolated value), giving a sensitivity of 3.6 ng Be/cm² for $A = 0.01$.

Effect of ionic strength, buffers and diverse ions

The ammonia–ammonium chloride buffer used to adjust the pH had very little effect on the absorbance; the apparent molar absorptivity increased from 25,900 for 0.02 *M* buffer to 27,100 for 0.2 *M* buffer.

Inert salts such as nitrate or perchlorate had no effect up to $\mu = 2$, but further increase in concentration caused the formation of colloidal solutions or precipitates. Masking agents again interfered seriously (Table VI), but the calcium(II) and barium(II) chelates or NTA, EDTA or CDTA did not interfere even at ratios c_{Ca}/c_{Be} or

TABLE VIII

LIMITING RATIOS OF CATIONS AGAINST BERYLLIUM AT pH 9.85

(10^{-5} *M* Be, $2.5\cdot10^{-4}$ *M* reagent, 0.1 *M* buffer; 500 nm)

Cation	c_x/c_{Be}	c_x/c_{Be}[a]	*Cation*	c_x/c_{Be}	c_x/c_{Be}[a]
Cu^{2+}	0.03	90	In^{3+}	2	340
Mg^{2+}	30	400	Zr^{IV}	0.1	4
Ca^{2+}	50	650	Th^{IV}	4	15
Ba^{2+}	100	800	Pb^{2+}	0.1	75
Zn^{2+}	1	260	V^{IV}	10	185
Cd^{2+}	2.5	310	Bi^{3+}	2	50
Hg^{2+}	1	25	Cr^{3+}	0.25	3;25[b]
Sc^{3+}	2	35	UO_2^{2+}	2	10;80[c]
Y^{3+}	2	16	Mn^{2+}	2.5	162
La^{3+}	0.2	17	Fe^{3+}	0.4	160
Al^{3+}	0.15	25	Co^{2+}	7.5	450
Ga^{3+}	2	85	Ni^{2+}	7.5	900
Pd^{2+}	7.5	550			

[a] In the presence of $c_{Ca} = 3\cdot10^{-3}$ *M*; $c_{CDTA} = 2.5\cdot10^{-3}$ *M*.
[b] In the presence of 0.01% BAL.
[c] In the presence of 0.005% hydroxylamine hydrochloride.

c_{Ba}/c_{Be} of 50 or 100, respectively. CDTA and calcium nitrate in the ratio 1:1.2 were used to mask various interfering ions at this pH (Table VIII). Hydroxylamine decreased the interference of uranyl ion, and 2,3-dimercaptopropanol decreased that of chromium(III).

Recommended procedure

To 5 ml of $2.5 \cdot 10^{-3}$ *M* chrome azurol S tetrabasic acid reagent in a 50-ml volumetric flask, add 20 ml water, the slightly acidic or neutral solution of sample containing 10–180 ng Be, 5 ml of $2.5 \cdot 10^{-2}$ *M* CDTA, 5 ml of $3 \cdot 10^{-2}$ *M* calcium nitrate and 5 ml of 1 *M* ammonia–ammonium chloride buffer. Dilute to the mark with water. Check that the pH is 9.8–10.1 and measure the absorbance at 500 nm after 20 min against a reagent blank.

The coefficient of variation was ±1.5% for 10 pure solutions containing 50–150 ng Be/ml.

DISCUSSION

In their work on the determination of beryllium with chrome azurol S, SILVERMAN AND SHIDELER[3,4] suggested that pH 6.0 (pyridine buffer) was optimal. A similar pH was recommended by SINHA AND DEY[5], but changes in the pH interval 4.0–6.8 were said not to be critical.

WOOD[12] earlier recommended pH 7.0 (ammonium acetate), KATSUBE *et al.*[11] pH 5.8 (acetate buffer) while UMEMOTO[21] suggested alkaline medium. Interfering ions were separated by oxinate precipitation or by anion exchangers. On the other hand, MUSTAFIN *et al.*[9,10] preferred pH 4.4–4.6 in the presence of acetate buffer and EDTA as masking agent, ADAMOVIČ *et al.*[14] pH 4.5, and PAKALNS[7,8] pH 4.6 in the presence of acetate, EDTA and ascorbic acid.

As is shown above, chrome azurol S is one of the most promising reagents for the spectrophotometric determination of beryllium but the conditions of the method must be carefully controlled. At pH 4.9±0.1 in the presence of limited concentrations of EDTA, the determination of beryllium is reasonably selective, but the absorbance is considerably affected by various buffers or slight pH changes and the absorbance of the H_2R^{2-}-form in excess of the reagent considerably increases the total absorbance of the beryllium complex solution. Pyridine–nitric acid or acetate buffers (0.1 *M*) of pH 4.9±0.1 are suitable. Beryllium in the range 10–280 ng may be determined at 568 nm under these conditions with a relative error of less than ±1.0%. The spectrophotometric sensitivity is 4.8–5.3 ng Be/cm² for $A = 0.01$.

The determination of beryllium at pH 9.8–10.1 in the presence of ammonia–ammonium chloride buffer or in unbuffered solutions is also possible when interfering ions are screened by the calcium(II)–CDTA chelate. Beryllium in the range 10–180 ng may be determined with a ±1.5% error at 490–505 nm. The spectrophotometric sensitivity is 3.8 ng Be/cm² for $A = 0.01$ .The strongly absorbing R^{4-}-form of the reagent may seriously interfere if the prescribed pH is overstepped.

The most promising procedure is at pH 6.5–6.9 in the presence of *ca.* 0.8% (w/v) polyvinyl alcohol and 0.1 *M* hexamethylenetetramine buffer. Beryllium in the range 5–130 ng may be determined at 615 nm with a ±1.5% error with the best sensitivity (1.75 ng Be/cm² for $A = 0.01$). Triethanolamine may also be used as buffer but a slope change is then observed on the calibration plot at 40 ng Be/ml. A similar observation has been made for the determination of beryllium with eriochromcyanine R (C.I. Mordant Blue 3)[24]. The interference of various ions can be removed by the calcium–EDTA chelate. Without polyvinyl alcohol at pH 6.5–6.9, measurements can be made at 540 nm in the presence of 0.1 *M* tris(hydroxymethyl)aminomethane buffer, but the sensitivity is lower (6.8 ng Be/cm^2 for $A = 0.01$).

SUMMARY

The well-known determination of beryllium with chrome azurol S may be carried out at pH 4.9 ± 0.1 (pyridine or acetate), at pH 6.7 ± 0.2 (TRIS buffer), at pH 10.0 ± 0.2 in aqueous medium, or at pH 6.5 ± 0.4 (hexamethylenetetramine) in the presence of polyvinyl alcohol. These conditions correspond to the sole presence of three particular complexes of beryllium with chrome azurol S. In presence of polyvinyl alcohol, the sensitivity reaches 1.75 ng Be/ml for an absorbance of 0.01 at 615 nm. EDTA, Ca–EDTA and Ca–CDTA are effective masking agents in the different procedures.

RÉSUMÉ

La détermination bien connue du béryllium avec le chrome-azurol S peut être faite dans différentes conditions: à un pH de 4.9 ± 0.1 (pyridine ou acétate), à un pH de 6.7 ± 0.2 (solution de tampon TRIS), à un pH de 10 ± 0.2 en solution aqueuse, à un pH de 6.5 ± 0.4 (héxaméthylène tétramine), en présence d'alcool polyvinylique. Ces conditions correspondent à la présence unique de trois complexes particuliers du béryllium avec le chrome-azurol S. En présence d'alcool polyvinylique, la sensibilité atteint 1.75 ng Be/ml pour une absorption de 0.01 à 615 nm. L'EDTA, le Ca–EDTA et le Ca–CDTA sont des agents effectifs de masquage dans les différents procédés.

ZUSAMMENFASSUNG

Die wohlbekannte Bestimmung von Beryllium mit Chromazurol S kann bei den drei pH-Werten 4.9, 6.7 und 10.0 entsprechend den drei besonderen Komplexen des Berylliums mit dem Reagenz durchgeführt werden. Bei einem pH-Wert von 6.5 ± 0.7 (Hexamethylentetraamin) in wässrigem Medium und in Gegenwart von Polyvinylalkohol reicht die Empfindlichkeit bis zu 1.7 ng Be/ml bei 615 nm. ÄDTE, Ca-ÄDTE und Ca-CDTE sind wirksame Maskierungsmittel in den verschiedenen Verfahren.

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SPECTROPHOTOMETRIC DETERMINATION OF MAGNESIUM WITH CHROMOTROPE 2R

APPLICATION TO ZINC AND ALUMINUM ALLOYS

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Although the formation of the magnesium–xylidyl blue II (magon)[1] complex provides one of the most sensitive methods for determining magnesium, the method suffers from nonselectivity. The titan yellow method[2] is somewhat less sensitive and carefully controlled conditions are essential. Numerous other methods have been based on the use of molecules containing suitably disposed hydroxyl groups[3], especially *o,o'*-dihydroxyazo compounds including eriochrome black T[4–6], lumomagneson IREA[7], magneson IREA[8] and calmagite[9], but none of these procedures is very selective. Pontacyl violet 4BSN[10], an *o*-hydroxyazo compound, is a good reagent for magnesium. The solvent extraction of the magnesium–eriochrome black T complex[11] provides a very sensitive method, but it is inselective and the precision is not satisfactory. Chlorophosphonazo III[12] is a good reagent, but this material is not readily available and its synthesis is rather difficult. There is undoubtedly room for alternative reagents of good sensitivity and selectivity for the determination of small amounts of magnesium.

Recently, the colour reaction between magnesium and 2-(benzeneazo)-1,8-dihydroxynaphthyl-3,6-disulfonic acid (disodium salt; chromotrope 2R, CI, 29:16570, acid red 29) was reported briefly[13]. The properties of this complex have now been studied in greater detail and a simple, precise and sensitive method for determining magnesium has been developed. The method has been successfully applied to the direct spectrophotometric determination of magnesium (0.01–4%) in zinc and aluminum alloy die casting.

Although chromotrope 2R has a very simple structure, the sensitivity of the method is excellent. The reagent is not specific for magnesium, but with suitable masking agents, magnesium can be determined in the presence of excesses of many other ions. The preparation and purification of the reagent are very easily accomplished. The sensitivities of various methods for magnesium are compared in Table I.

EXPERIMENTAL

Reagents

Stock solution of magnesium. Dissolve 1.000 g of magnesium metal (99.99%) in 30 ml of hydrochloric acid (1 + 1) and dilute to 1 l.

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TABLE I

SENSITIVITY OF SOME METHODS FOR MAGNESIUM

Reagents	*Sensitivity* $\mu g\ Mg/cm^2$ *for* $\log I_0/I = 0.001$
Brilliant yellow[2]	0.02
Quinalizarin[2]	0.017
Titan yellow[2]	
in absence of Ca	0.017
in presence of 500 p.p.m. Ca	0.013
8-Hydroxyquinoline[2]	0.007
Arsenazo I[14]	(~1 p.p.m.)
Methythymol blue[15]	(~1 p.p.m.)
Eriochrome black T[2]	0.0011
Sodium 1-azo-2-hydroxy-3-(2,4-dimethylcarboxyanilido)-naphthalene-1′-(2-hydroxybenzene-5-sulfonate)[a,16]	
in absence of Ca	0.0008
in presence of Ca	0.0005
Pontacyl violet 4BSN[10]	0.0008 ($\varepsilon = 3.1 \cdot 10^4$)
1-Azo-2-hydroxy-3-(2,4-dimethylcarboxyanilido)-naphthalene-1′-(2-hydroxybenzene)[b,1]	(0.5 p.p.m.~)
Solochrome black PV[17]	(0.05–3 p.p.m.)
Phenazo-3,3-dinitro-4,4-bis-(4-hydroxyphenylazo)-biphenyl[18]	(0.02 p.p.m.~)
Chromotrope 2R	0.00012 ($\varepsilon = 3.7 \cdot 10^4$)
Chlorophosphonazo III[12]	(0.004–0.4 p.p.m.) $\varepsilon = 4.8 \cdot 10^4$
Eriochrome black T[11]	
n-amyl alcohol extraction	(0–0.08 p.p.m.)

[a] Xylidyl blue I, Magon sulfonic acid.
[b] Xylidyl blue II, Magon.

Chromotrope 2R (0.1% solution). Dissolve 0.50 g of chromotrope 2R (disodium salt, $C_{16}H_{10}N_2O_8S_2Na_2$) in 200 ml of water and dilute to 500 ml. This solution is stable for several months.

Buffer solution (pH 10.8). Dissolve 10.6 g of ammonium chloride in water and add sufficient ammonia to give a pH of 10.8 in 1 l of solution.

All other reagents used in this work were made from analytical grade chemicals or from purified materials and all solutions were prepared with redistilled water.

Apparatus

All measurements were made with a Model EPS-2 Hitachi recording spectro photometer and GPO-2A Hitachi spectrophotometer with 1-cm cells. A Yanagimoto 42-A type pH meter was used.

Procedure

Transfer an aliquot of the slightly acidic solution containing 0–10 μg of magnesium to a 25-ml volumetric flask. Add 2.0 ml of chromotrope 2R solution, 2 ml of ammonia–ammonium chloride buffer and 10 ml of acetone, and dilute to the mark. Measure the absorbance at 570 nm in 1-cm cells against a reagent blank taken through the procedure.

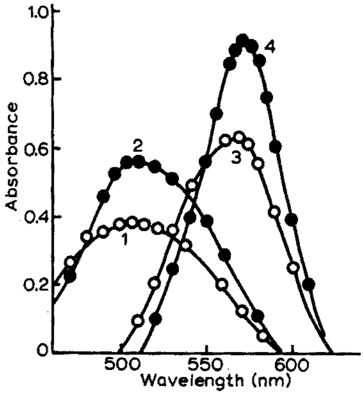
RESULTS AND DISCUSSION

Spectral characteristics and effect of acetone

The absorbance curves of reagent and its magnesium complex are shown in Fig. 1.

It can be seen that the absorbance of the reagent alone ($\lambda_{max} = 507$ nm) is very small at the wavelength of maximum absorption (570 nm) of its magnesium complex.

The development of coloured complexes in partially organic media to improve both stability and sensitivity has frequently been exploited; aqueous acetone is often used. When the magnesium–chromotrope 2R complex was prepared in aqueous acetone solution a stable and more sensitive coloured complex resulted. The sensitivity varied with the amount of acetone present, 40% (v/v) of acetone being the optimum composition (Fig. 2).



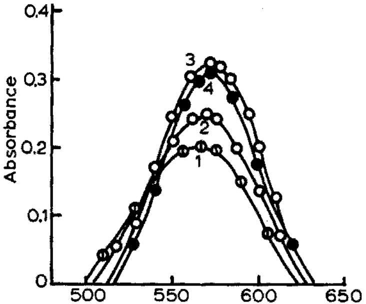


Fig. 1. Absorbance curves of chromotrope 2R and its magnesium complex (at pH 10.8). (1) Chromotrope 2R, $8.0 \cdot 10^{-5} M$, in aqueous solution; (2) Chromotrope 2R, $8.0 \cdot 10^{-5} M$, in aqueous 40% acetone solution; (3) Chromotrope 2R, $1.8 \cdot 10^{-4} M$ plus Mg, $2.2 \cdot 10^{-4} M$ in aqueous solution against a reagent blank; (4) Chromotrope 2R, $1.8 \cdot 10^{-4} M$ plus Mg, $2.2 \cdot 10^{-4} M$, in aqueous 40% acetone solution against a reagent blank.

Fig. 2. Effect of acetone. (1) aqueous solution; (2) aqueous 20% (v/v) acetone; (3) aqueous 40% (v/v) acetone, (4) aqueous 60% (v/v) acetone.

The spectra of the reagent and of the magnesium–chromotrope 2R complex in aqueous acetone solution are shown in Figs. 1 and 2. The introduction of acetone does not cause spectral shift, but increases the optical density of the reagent, while simultaneously greatly increasing that of the complex. Other solvents, notably dioxan and ethanol, had less effect on the sensitivity and stability of the complex.

Optimum pH and amount of reagent

Standard amounts of magnesium and chromotrope 2R solution were buffered at varying pH values. The final pH of each solution was measured with a pH meter and the absorbance measured at 570 nm. A plot of absorbance against pH showed that maximum absorbance was obtained at 10.5–11.0. Subsequent determinations were therefore carried out at pH 10.8. The absorbance increased gradually as the pH increased from 9.5 to 10.5, but decreased rapidly above pH 11.

The absorbance of a series of solutions containing known amounts of magnesium and 0.5–3 ml of 0.1% chromotrope 2R solution buffered at pH 10.8 were measured. It was found that 1.5 ml of 0.1% reagent solution sufficed to complex 10 µg of magnesium; with higher concentrations the absorbance was essentially constant.

Colour development, stability and effect of temperature

The maximum colour of the magnesium–chromotrope 2R complex was found to develop instantaneously and to be stable for at least 90 min.

Absorbance measurements at 15°, 25° and 35°, respectively, showed the complex to be independent of normal variations in laboratory temperature.

Beer's law and sensitivity

The absorbances of the magnesium complex in aqueous and aqueous acetone solution were found to be linearly related to the concentration of metal. In aqueous 40% acetone solution, Beer's law was obeyed up to at least 10 µg of magnesium per 25 ml, the molar absorptivity being $3.7 \cdot 10^4$ at 570 nm. The sensitivity of the colour reaction is 0.00012 µg magnesium per cm^2 for $\log I_0/I = 0.001$.

Interferences

Numerous cations and anions were examined by applying the method to fixed amounts of magnesium in the presence of increasing quantities of the ion being studied. The results are shown in Tables II and III.

It is evident that most anions have no effect at the levels studied. Among the

TABLE II

DETERMINATION OF 5.0 µg OF MAGNESIUM IN THE PRESENCE OF FOREIGN IONS

Foreign ions added (µg)		*Weight ratio of Mg : Me*	*Error caused (µg Mg)*	*Foreign ions added (µg)*		*Weight ratio of Mg : Me*	*Error caused (µg Mg)*
Al^{3+}	20	1 : 4	±0.0	Mn^{2+}	20	1 : 4	±0.0
	50	1 : 10	−0.5		50	1 : 10	−0.6
Ba^{2+}	1000	1 : 200	±0.0	Ni^{2+}	20	1 : 4	±0.0
	1500	1 : 300	+1.5		50	1 : 10	+4.0
Be^{2+}	5	1 : 1	±0.0	Pb^{2+}	500	1 : 100	±0.0
	20	1 : 4	+1.5		600	1 : 120	−0.4
Ca^{2+}	40	1 : 8	±0.0	Sn^{4+}	200	1 : 40	±0.0
	50	1 : 10	+2.0		500	1 : 100	−0.4
Co^{2+}	20	1 : 4	±0.0	Sr^{2+}	500	1 : 100	±0.0
	50	1 : 10	+2.0		1000	1 : 200	+1.0
Cr^{3+}	20	1 : 4	±0.0	Ti^{4+}	500	1 : 100	±0.0
	40	1 : 8	−1.0		1000	1 : 200	−0.5
Cr^{6+}	20	1 : 4	±0.0	V^{5+}	40	1 : 8	±0.0
	40	1 : 8	−1.0		50	1 : 10	−1.0
Cu^{2+}	1000	1 : 200	±0.0	Zn^{2+}	200000	1 : 40000	±0.0
	1500	1 : 300	+1.5		500000	1 : 100000	−0.5
Fe^{3+}	20	1 : 4	±0.0				
	50	1 : 10	−0.3				

cations studied, the greatest interference was caused by beryllium, but amounts equal to that of magnesium did not interfere.

The presence of triethanolamine and potassium cyanide prevents the reaction of many metal ions with chromotrope 2R, so that this method becomes one of the most selective available for determination of magnesium. It was shown that up to 20 ml of 20% triethanolamine solution and up to 10 ml of 5% potassium cyanide solution had no effect on the colour development of the magnesium complex. Triethanolamine was used to mask large amounts of aluminum, manganese and iron, as well as other ions (Table IV).

The results show that although the tolerated amounts of aluminum, manganese and iron are increased on addition of ethanolamine, the tolerances for some other metal ions, *e.g.*, copper, nickel and zinc, are slightly decreased owing to the formation of a coloured complex with triethanolamine and other reactions.

TABLE III

DETERMINATION OF 5.0 μg OF MAGNESIUM IN THE PRESENCE OF FOREIGN ANIONS
(Added as their sodium, potassium or ammonium salts)

Foreign ions added (mg)		*Error caused (μg Mg)*	*Foreign ions added (mg)*		*Error caused (μg Mg)*
F^-	3.0	± 0.0	CO_3^{2-}	5.0	± 0.0
	5.0	-0.4		10.0	-0.2
PO_4^{3-}	1.0	± 0.0	CH_3COO^-	10.0	± 0.0
	2.5	-0.5	SCN^-	50.0	-0.5
	5.0	-1.4		50.0	± 0.0
SO_4^{2-}	30.0	± 0.0		70.0	-0.8
	50.0	-1.0			
NO_3^-	10.0	± 0.0			
	50.0	-0.2			

TABLE IV

DETERMINATION OF 20.0 μg OF MAGNESIUM IN THE PRESENCE OF FOREIGN CATIONS
(TRIETHANOLAMINE USED)

Foreign ions added (mg)		*Error caused (μg Mg)*	*Foreign ions added (mg)*		*Error caused (μg Mg)*
Al^{3+}	7.0	± 0.0	Ni^{2+}	0.02	± 0.0
	10.0	-2.0		0.05	$+4.0$
Cd^{2+}	1.0	± 0.0	Pb^{2+}	0.7	± 0.0
	1.5	-2.0		1.0	-3.0
Cu^{2+}	1.0	± 0.0	Sn^{4+}	0.5	± 0.0
	1.5	$+3.0$		0.7	-2.0
Fe^{3+}	20.0	± 0.0	Zn^{2+}	200.0	± 0.0
				500.0	-2.0
Mn^{2+}	1.0	± 0.0			
	1.5	-2.0			

Nature of complex

The empirical formula of the complex was studied by the continuous variations and mole ratio methods. Typical plots showed quite unequivocally that a 1:1 complex is formed. Continuous variations plots are shown in Fig. 3 for aqueous and partly acetonic media. The enhanced sensitivity and the increased stability of the complex resulting from the use of acetone, are clearly demonstrated. Similar results were obtained from mole ratio plots.

Stability constant of the complex

The combining ratio of magnesium and chromotrope 2R is 1:1, hence the apparent overall stability constant of the complex can be estimated in the usual way from the spectrophotometric data. The apparent stability constant of the complex at room temperature in aqueous and aqueous 40% acetone solution were thus found to be 0.44 and 0.7 respectively. Generally, the values of the stability constants of metal–*o*-hydroxazo compounds are much lower than those of *o,o'*-dihydroxyazo compounds, but this often helps to improve selectivity.

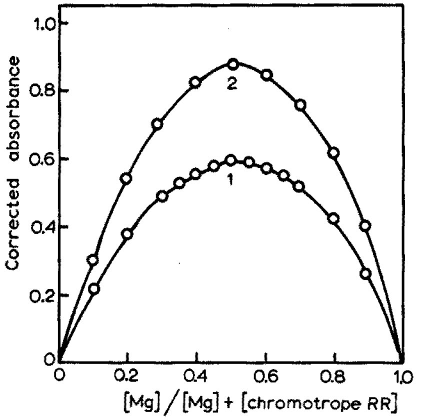


Fig. 3. Continuous variations method. [Mg] + [Chromotrope 2R] $= 4.0 \cdot 10^{-4} M$, pH 10.6, 570 nm. (1) in aqueous solution; (2) in aqueous 40% acetone solution.

DETERMINATION OF MAGNESIUM IN ZINC AND ALUMINUM ALLOY DIE CASTING

Recommended procedure

Dissolve 0.500 g of sample with 5 ml of hydrochloric acid (1 + 1) and 2 ml of nitric acid (1 + 1). Dilute to a known volume with water and transfer an aliquot which contains 0–20 μg of magnesium to a 50-ml beaker. Add 4 ml of aqueous 0.1% chromotrope 2R and 10 ml of 20% triethanolamine solution, and adjust the pH to 10.5 with dilute ammonia and hydrochloric acid (1 + 100), and add 5 ml of buffer pH 10.8. Transfer to a 50-ml volumetric flask, add 20 ml of acetone and dilute to the mark with water. After few minutes, measure the absorbance in a 1-cm cell at 570 nm against a reagent blank.

Results

The results of the determination of magnesium in standard samples are given in Table V. The results are in excellent agreement over a wide range of magnesium contents, the average difference being about ±0.2%.

TABLE V

DETERMINATION OF MAGNESIUM IN ZINC[a] OR ALUMINUM[b] ALLOY DIE CASTING

Sample	*Composition (%)*									*Mg found*
	Al	*Cu*	*Mg*	*Zn*	*Pb*	*Fe*	*Cd*	*Sn*		
ZDC 1[c]	3.5	1.0	0.03	Balance	0.007	0.1	0.005	0.005		0.031 0.032 0.030
ZDC 2[c]	4.0	0.5	0.01	Balance	0.005	0.1	0.005	0.005		0.012 0.011 0.013
	Cu	*Si*	*Mg*	*Zn*	*Fe*	*Mn*	*Ni*	*Sn*	*Al*	
ADC 1[d]	0.6	11.0	0.3	0.5	1.5	0.3	0.5	0.1	Balance	0.31 0.33 0.32
ADC 5[d]	0.2	0.5	4.0	0.1	1.5	0.3	0.1	0.1	Balance	4.0 4.1 4.1

[a] Japanese Industrial Standard H 5301.
[b] Japanese Industrial Standard H 5302.
[c] Zinc alloy.
[d] Aluminum alloy.

SUMMARY

Chromotrope 2R forms a pink complex ($\lambda_{max}=570$ nm) with magnesium in aqueous acetone medium at pH 10.8; down to 0.01 p.p.m. of magnesium can be determined spectrophotometrically. The method is sensitive ($\varepsilon=37,000$) and relatively selective. The colour is formed immediately, and is stable for 90 min. Zinc (200 mg), aluminum (10 mg), iron(III) (20 mg), manganese (1.5 mg), copper (1 mg), lead (0.7 mg), cadmium (1 mg), tin (0.5 mg) and nickel (0.02 mg) do not interfere in the presence of triethanolamine and many other metals can be tolerated; large amounts of beryllium interfere. The method is applicable to the direct determination of magnesium (0.01–4%) in zinc and aluminum alloy die castings.

RÉSUMÉ

Le Chromotrope 2R forme un complexe rose ($\lambda_{max}=570$ nm) avec le magnésium en milieu acétone–eau à un pH de 10.8; on peut déterminer jusqu'à 0.01 p.p.m. de magnésium spectrophotométriquement. La méthode est sensible ($\varepsilon=37,000$) et relativement sélective. La couleur se forme immédiatement et est stable pendant 90 minutes. Le zinc (200 mg), l'aluminium (10 mg), le fer(III) (20 mg), le manganèse (1.5 mg), le cuivre (1 mg), le plomb (0.7 mg), le cadmium (1 mg), l'étain (0.5 mg) et le nickel (0.02 mg) n'interfèrent pas en présence de triéthanolamine; beaucoup d'autres métaux peuvent être tolérés. De grandes quantités de béryllium provoquent des interférences. La méthode peut s'appliquer pour la détermination directe du magnésium (0.01–4%) dans le zinc et dans les alliages d'aluminium obtenus par injection.

ZUSAMMENFASSUNG

Die spektralphotometrische Bestimmung von 0.01 bis 4% Magnesium mit Chromotrop 2R in Zink- und Aluminiumlegierungen wird beschrieben. Das Magnesium bildet mit dem Reagenz in wässrigem acetonischen Medium beim pH 10.8 einen stabilen Komplex mit einem Maximum bei 570 nm. Die molare Extinktion beträgt 37000. In Gegenwart von Triäthanolamin stören Milligrammengen von Zn, Al, Fe(III), Mn, Cu, Pb, Cd, Sn und Ni nicht. Grössere Mengen Beryllium stören.

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THE DETERMINATION OF VANADIUM IN SILICATE MATERIALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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Very few methods are available for the determination of vanadium in the p.p.m. range. Sensitive colorimetric methods, such as thiooxine and nicotinohydroxamic acid are available[1], but these are not selective. Oxidation–reduction titrations with reagents such as hexacyanoferrate(III) and EDTA have been used successfully but are of low sensitivity. The gravimetric cupferron method is well known and widely used, but as in other gravimetric methods[2], many elements interfere, and the method is tedious and is not recommended for microgram quantities.

A sensitive method was required for the determination of vanadium down to 5 p.p.m. in silicate materials. The technique of atomic absorption spectroscopy had proved satisfactory for the determination of a large number of metals, at levels of a few parts per million in silicates. The methods usually are quick, simple, relatively accurate, and free from interference by other elements. Accordingly, attention was directed to atomic absorption spectroscopy for determining vanadium in silicate materials.

Very little work has been published on the determination of vanadium by atomic absorption methods. ROBINSON[3] observed a very weak absorption signal when an oxy–cyanogen flame was used. SLAVIN AND MANNING[4] reported sensitivities of 7 μg/ml with the oxy–acetylene flame. WILLIS[5] demonstrated the advantages of the nitrous oxide–acetylene flame and reported a sensitivity of 1.5 μg/ml. The determination of vanadium and the effect of various solvents has been studied in detail by SACHDEV *et al.*[6,7].

Determination in aqueous media

Synthetic vanadium solutions, prepared by the dissolution of ammonium metavanadate in 4% (v/v) nitric acid, were aspirated directly into the nitrous oxide–acetylene flame. A calibration graph was plotted for the range 80–800 p.p.m. V. However, the presence of iron, titanium, or aluminium caused a large enhancement of the vanadium readings.

SACHDEV *et al.*[6] stated that the enhancement of vanadium readings in the presence of aluminium is constant for ratios of Al:V greater than 2:1. Synthetic aluminium–vanadium solutions were prepared, and readings on these showed that the enhancement of the vanadium readings became constant for ratios of Al:V greater than 25:1. In the presence of this relative concentration of aluminium, 10,000 p.p.m. Fe and 600 p.p.m. Ti no longer caused enhancement nor did 400 p.p.m. Zr, 400 p.p.m. Sn, 400 p.p.m. Sb, 400 p.p.m. Mo or 600 p.p.m. Ni cause any interference. However, the calibration range was 20–400 p.p.m. V. As this was not sensitive enough, methods of extraction were investigated.

Extractions with various organic reagents

Extractions were performed with the following reagents: sodium diethyl dithiocarbamate, Alamine 336, ferron, oxine, and N-benzoyl-N-phenylhydroxylamine. Of these only the last proved to be moderately successful, but the reagent finally selected was cupferron.

SACHDEV *et al.*[6,7] state that absorption readings on extractions of vanadium cupferrate can be improved by the use of mixed solvents. They claim that 25% of oleic acid in MIBK improves the readings of absorption from 12% with MIBK alone to 32% with MIBK and oleic acid. In their work they used the oxy–acetylene flame.

As it was intended to aspirate the organic extract into a nitrous oxide and acetylene flame, the effect of mixed solvents was retested under the conditions described by SACHDEV *et al.* With a mixture of *n*-butyl acetate and oleic acid, the reverse effect was apparent: the oleic acid caused suppression of the readings. The same suppression was observed when a mixture of oleic acid and MIBK was used for the cupferron extraction.

The same authors[6,7] also state that many ions interfere with the extraction, but, if enough cupferron is present, these interferences are negligible up to a ratio of 10:1. Again these results were obtained with the oxy–acetylene flame. When the nitrous oxide and acetylene flame was used, many other elements were found to interfere, but excess of cupferron did not prevent this interference. A possible explanation of these different findings is the behaviour of the vanadium compound in the oxy–acetylene flame, which differs from that in the nitrous oxide and acetylene flame.

EXPERIMENTAL

Apparatus

All measurements were taken on a Techtron atomic absorption spectrophotometer, model AA3, with an 'Atomic Spectral Lamp' hollow-cathode lamp run at 14 mA as the vanadium source. The power supply for the lamp of the spectrophotometer was altered[8] to modulate at 472 c/s, instead of at 50 c/s, to obviate the pick-up of noise from the mains, and a detector incorporating scale expansion, tuned to 472 c/s, replaced the normal AA3 detector. These modifications reduce the amount of flame emission picked up by the instrument. The wavelength was set at 3184 Å, and a slit width of 200 μ was used. This means that vanadium lines at 3183 Å, 3183.4 Å, 3183.9 Å, and 3185.4 Å were admitted. The burner used was the Techtron nitrous oxide and acetylene burner, and, for maximum sensitivity, a fuel-rich flame was used for which the acetylene supply was set almost to maximum on the flowmeter.

Reagents

Analytical-grade reagents were used without further purification.

Standard vanadium solution. To prepare a stock solution (1 ml $\equiv$ 1 mg V) dissolve 2.2966 g of ammonium metavanadate and 1 g of sodium carbonate in 75 ml of water, boiling if necessary to obtain a clear solution, and dilute to 1 l with water. Prepare solutions A (1 ml ≡ 20 μg V) and B (1 ml ≡ 5 μg V) by appropriate dilution of the stock solution with 4% (v/v) nitric acid.

Molybdate–sulphuric acid reagent. Dissolve 1.85 g of ammonium molybdate (A. R.) in 1:1 sulphuric acid, and dilute to 200 ml with 1:1 sulphuric acid (1 ml ≡ 5 mg of Mo).

Cupferron reagent, 5% (w/v). Dissolve 5 g of cupferron in 100 ml of cold water. If kept in a refrigerator, the solution is stable for 1 week.

Procedure

Dissolution of samples. Weigh out accurately 1 g of the sample into a platinum dish, add 10 ml of hydrofluoric acid, 10 ml of nitric acid, and 3 ml of perchloric acid, and evaporate to dense fumes of perchloric acid. If the siliceous material has not been completely attacked, add a further 5 ml of hydrofluoric acid and evaporate to a moist paste (see Note 1). Add 2 ml of nitric acid and 15 ml of water, and heat slowly on a water bath to bring the salts into solution. If there is a large residue, filter the solution and fuse the residue with a minimum of sodium carbonate. Leach the melt with dilute nitric acid, and combine it with the original solution. If the residue is small, it can be filtered off and discarded. Dilute the solution to volume with water, adding nitric acid where necessary to obtain a 4% solution. Transfer a suitable aliquot portion, containing between 50 μg and 200 μg of vanadium, to a 100-ml Phillips beaker, and proceed as in *Extraction of vanadium* below.

Preparation of standard solutions. Transfer 0-, 2-, 4-, 7-, 12-, and 18-ml portions of Solution A to 100-ml Phillips beakers. For scale expansion, use 0-, 0.5-, 1-, 2-, 5-ml portions of Solution B. In each case, proceed as in *Extraction of vanadium* below.

Extraction of vanadium. To the aliquot (or standard solution) in the Phillips beaker, add 10 ml of molybdate solution, and dilute to about 40 ml with water. Add a few drops of aqueous 0.5 *M* manganese(II) sulphate solution and 0.25 g of potassium periodate, and heat gently, without boiling. If the permanganate colour does not form, vanadium is not oxidized, and a further 0.25 g of potassium periodate must be added and the solution heated gently.

Cool the solution, and transfer the oxidized vanadium solutions to 100-ml separating funnels calibrated to the 100-ml mark. Add ice to bring the temperature to below 10°, and dilute to about 80 ml (see Note 2). Add 10 ml of 5% cupferron solution, dilute to 100 ml with distilled water, and shake well. After 5 min, add 10 ml of *n*-butyl acetate and shake for 2 min. After the layers have settled, run off the aqueous layer, and filter the organic layer through a small Whatman No. 40 filter paper. Measure the percentage transmission of the organic phase. With each series of determinations, perform a blank determination, by going through all the above steps but omitting the sample.

Notes

(*1*) If hydrochloric acid must be used in the dissolution process, the concentration in the aliquot portion used for extraction must be below 2% (v/v).

(*2*) For samples high in iron, add 2 g of sodium phosphate and shake the solution well.

DISCUSSION

Oxidation state of vanadium

The manganese(II) sulphate is used as an indicator for complete oxidation, the manganese being oxidized to permanganate after all the vanadium has been oxidized. This oxidation step is necessary because vanadium is not completely precipitated by cupferron unless it is present as vanadium(V).

Study of specific interferences

Molybdenum (5 mg as ammonium molybdate) caused a large enhancement of absorption readings. The enhancement appeared to be constant beyond 20 mg of molybdenum, and so a constant amount of 50 mg was added to the vanadium solutions before extraction.

The vanadium readings were enhanced by 0.3 mg of aluminium, but if the acid concentration before extraction was adjusted to 5% (v/v) of sulphuric acid, little or no aluminium was precipitated by the cupferron, and there was no enhancement of the vanadium readings.

Iron is readily extracted as the cupferron complex, and interferes with vanadium determinations by causing a large suppression of the absorption readings. Masking agents were tried to suppress the effect of iron, and 2 g of phosphate, added before extraction, masked up to 200 mg of iron. Iron in larger quantities can be extracted as the chloro-complex from 1:1 hydrochloric acid with methyl isobutyl ketone, after a complex between vanadium and oxalic acid has been formed. The aqueous layer is evaporated to dryness, and vanadium is determined in the residue.

Effect of other elements. A systematic programme of testing for interfering elements was carried out under the following conditions. Various amounts of selected elements were added to a solution of 20 p.p.m. of vanadium, and extraction was carried out on these solutions. As a control, 20 p.p.m. of vanadium was extracted without the addition of other elements. The results obtained from readings of these solutions appear in Table I.

Organic acids such as oxalic and tartaric, which form strong vanadium complexes, compete with cupferron; reducing agents such as ascorbic acid and tin(II)

TABLE I

ELEMENTS THAT DO NOT INTERFERE IN THE EXTRACTION BY CUPFERRON AND *n*-BUTYL ACETATE OF 20 P.P.M. OF VANADIUM IN THE PRESENCE OF 5000 P.P.M. OF Mo

Element	*Form*	*Concentration range tested (p.p.m.)*	*Element*	*Form*	*Concentration range tested (p.p.m.)*
Fe	$FeCl_3$[a]	5 000–20 000	Mn	$MnCl_2$	500– 5 000
Ti	$Ti(SO_4)_2$[b]	1 000– 3 000	Na	Na_2SO_4	50 000–300 000
Al	$AlCl_3$	5 000–50 000	Cu	$CuSO_4$	1 000– 10 000
Ca	$CaCl_2$	5 000–50 000	Zn	$ZnSO_4$	1 000– 10 000
Cr	$CrCl_3$	1 000– 7 500	Zr	$ZrOCl_2$	100– 1 000
Co	$CoSO_4$	1 000–10 000	Bi	$BiONO_3$	200– 2 000
W	Na_2WO_4	200– 2 000	Sb	$SbCl_3$	200– 2 000
Ni	$NiSO_4$	200– 2 000			

[a] Plus phosphate.
[b] In tartaric acid.

give low results but both these types of interferences are nullified by the oxidation process. Strong oxidizing agents, such as dichromate in acid solution, oxidize the cupferron.

RESULTS

Three standard samples were analysed by this method. These were B.C.S. 174/1 (1.20% V_2O_5), N.B.S. 69A (0.03% V_2O_5), and N.B.S. 76 (0.02% V_2O_5). The results (Table II) show very good agreement with one another and are well within the accepted range for these particular standards.

TABLE II

RESULTS OBTAINED ON STANDARD SAMPLES

Standard	*Expected value* V_2O_5 (%)	*Results obtained* V_2O_5 (%)
B.C.S. 174/1	1.06–1.37	1.19–1.30 (8 detns.) Mean = 1.25% V_2O_5 Coefficient of variation = 3.3%
N.B.S. 69A (Bauxite)	0.03	0.037–0.036 (2 detns.)
N.B.S. 76 (Burnt refractory)	0.014–0.03	0.033 (2 detns.)

TABLE III

COEFFICIENTS OF VARIATION OBTAINED ON SYNTHETIC STANDARDS

Standard	100 μg of V in 0.25 g of sample (0.4% V)	30 μg of V in 1 g of sample (0.003% V)
No. of detns.	10	9
Coeff. of variation (%)	1.86	3.08

The recoveries for three spiked samples, each of 20 μg of vanadium, were found to be 101, 101 and 107%, respectively, which suggests that the results obtained are accurate.

Because there was not enough standard sample, standard deviations were determined for synthetic standards. For these tests, granite and syenite containing little or no vanadium were spiked with known volumes of standard vanadium solutions, and coefficients of variation were calculated from the readings obtained. The results (Table III) show that the reproducibility of the method, even at a level of 30 p.p.m. V, is entirely satisfactory.

CONCLUSION

The atomic absorption method for the determination of vanadium is subject to many interferences from other elements, even when the nitrous oxide and acetylene flame is used. The extraction by *n*-butyl acetate and cupferron from 5% (v/v) sulphuric acid solution, in the presence of 50 mg of molybdenum as molybdate, and with oxidation of the vanadium, can eliminate, or at least diminish, these interferences.

At the levels tested, none of the elements considered in Table I caused any serious interference in the determination of vanadium. Iron above 200 mg must first be removed; it can conveniently be extracted as the chloro-complex into MIBK. Reducing agents cause suppression of the absorption readings, but their effect becomes negligible after strong oxidation of the solutions before the vanadium is extracted.

When applied to silicate materials, the extraction method yielded results that were completely acceptable, and the method should have a wide application. The sensitivity of the method, taken as the concentration that will give a transmittance reading of 99% when 1 g of sample is used and the vanadium is extracted into 10 ml of *n*-butyl acetate, is 3 p.p.m. of the solid sample. Scale expansion has been used with success, in which event the sensitivity of the method can be improved.

On 5 × scale expansion, the fluctuation caused by flame noise is approximately 1% transmittance. The detection limit, which can be taken as twice the background noise, is 0.3 p.p.m. in the *n*-butyl acetate phase.

Although in this investigation a modified Techtron AA3 spectrophotometer was used, the same sensitivities should be possible when a Techtron AA4 with built-in scale expansion, or any comparable atomic absorption spectrophotometer is used.

SUMMARY

A method was developed for the determination of vanadium down to 5 p.p.m. in silicate materials on the basis of a 1-g sample. The absorption of the vanadium was measured after aspiration of a solution of the vanadium–cupferron complex in *n*-butyl acetate. Vanadium(V) was extracted, after oxidation with potassium periodate, from an aqueous solution containing 5% (v/v) of sulphuric acid and 50 mg of molybdenum (as molybdate), to avoid serious interference by other elements. Sodium phosphate was added to mask any iron, which can be tolerated in amounts up to 200 mg in the aqueous solution being extracted.

RÉSUMÉ

Une méthode a été développée pour la détermination du vanadium jusqu'à 5 p.p.m. dans des silicates, sur la base d'un échantillon de 1 gramme. L'absorption du vanadium a été mesurée après extraction de la solution du complexe vanadium–cupferron dans l'acétate de butyle normal. Après oxydation avec du periodate de potassium, le vanadium a été extrait d'une solution aqueuse contenant 5% en volume d'acide sulfurique et 50 mg de molybdène (sous forme de molybdate), afin d'éviter des interférences importantes avec d'autres éléments. Du phosphate de sodium a été ajouté pour masquer le fer que l'on peut tolérer jusqu'à 200 mg dans la solution aqueuse d'où l'on fait l'extraction.

ZUSAMMENFASSUNG

Mit Hilfe der Flammenabsorptionsspektralanalyse wurde Vanadin in Silikatproben von 1 g bis hinab zu 5 p.p.m. bestimmt. Vanadin(V) wurde nach Oxydation

mit Perjodat aus wässriger 5 Vol-%iger Schwefelsäure, die 50 mg Molybdän als Molybdat enthielt mit *n*-butylacetat als Cupferronkomplex extrahiert und in der Flamme zerstäubt. Bis zu 200 mg Eisen sind in der wässrigen Lösung zulässig, wenn sie durch Natriumphosphat maskiert werden.

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ANALYTICAL APPLICATIONS OF THE PHOSPHATASE ENZYME SYSTEM

DETERMINATION OF BISMUTH, BERYLLIUM AND PESTICIDES

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In a recent publication, GUILBAULT, SADAR AND ARCENEAUX[1] described a simple, rapid procedure for the assay of lipase activity in the presence of other esterases based on the hydrolysis of 4-methylumbelliferone heptanoate catalyzed by lipase. A complete study of 12 substrates for lipase indicated this to be the best substrate for the analysis of this enzyme.

Preliminary observations revealed that this ester and other 4-methylumbelliferone esters are catalytically cleaved by acid phosphatase. An optimum rate of hydrolysis was obtained with 4-methylumbelliferone nonanoate at pH 7.0, citrate buffer. This hydrolysis was shown to be catalyzed by phosphatase and not lipase impurities in phosphatase, since Systox, a potent lipase inhibitor[2], did not affect the hydrolysis. Although the sensitivity of detection of acid phosphatase was not quite as good as that obtained with umbelliferone phosphate (10^{-5} units)[3], as little as $6 \cdot 10^{-5}$ units of phosphatase were detectable. Moreover, 4-methylumbelliferone nonanoate is cleaved by acid phosphatase in the presence of large amounts of phosphate with little inhibition, unlike umbelliferone phosphate. Alkaline phosphatase did not hydrolyze any of the 4-methylumbelliferone esters.

A study of the inhibition of acid and alkaline phosphatase by various pesticides (organophosphonates, carbamates, chlorinated insecticides, herbicides) revealed that acid phosphatase was inhibited only by parathion, whereas alkaline phosphatase was inhibited only by Aldrin and Heptachlor. A complete study of the effect of cations and anions on alkaline phosphatase revealed that only beryllium and bismuth inhibit this enzyme. Selective methods were developed for these inhibitors in the micro- and submicrogram concentration range with an accuracy and precision of about 2%.

EXPERIMENTAL

Enzymes

Phosphatase, acid. A 1 mg/ml stock solution was prepared from Type II acid phosphatase (potato, activity 2.0 unit/mg, Calbiochem); one unit hydrolyzes[4] 1 µmole of *p*-nitrophenyl phosphate per min at pH 4.8 and 37°.

Phosphatase, alkaline. A stock 1 mg/ml solution was prepared from Type IV enzyme (hog intestinal Mucosa, 1 unit/mg, Sigma); one unit represents 1 µmole of *p*-nitrophenyl phosphate hydrolyzed per mg of enzyme per min at pH 10.4 and 37°.

Pesticides

Stock solutions of Heptachlor, Aldrin and methyl parathion were prepared in methyl cellosolve. The pesticides were all of 99% purity (Polyscience Corp., Evanston, Ill.).

Metal ions

Stock solutions of all metal ions used (including Be and Bi) were prepared by dissolving the C.P. nitrate salts in triply distilled water, or in 1 *M* nitric acid (Bi).

Substrates

Umbelliferone phosphate was prepared as described in a previous paper[3]. The 4-methylumbelliferone heptanoate, nonanoate and caproate esters were obtained from Dr. T. J. JACKS of the Southern Regional Research Labs. Stock 10^{-2} *M* solutions of all substrates were prepared in methyl cellosolve.

Buffers

TRIS buffer, 0.1 *M*, pH 8.0, was prepared by dissolving tris(hydroxymethyl)-aminomethane (Sigma) in triply distilled water. The pH was adjusted to 8.0 with 0.1 *N* hydrochloric acid.

Citrate and phosphate buffers, 0.1 *M*, pH 5–7, were prepared by dissolving sodium citrate and/or sodium dihydrogen phosphate in triply distilled water. The pH was adjusted to the desired level with either 0.1 *N* hydrochloric acid or sodium hydroxide.

Apparatus

All fluorescence measurements were made with either an Aminco Bowman spectrophotofluorimeter (SPF) grating instrument or an Aminco filter fluorimeter. A constant temperature of 25° was maintained either with a thermoelectric cooler (SPF) or a constant temperature water bath. Wavelengths used were: umbelliferone, λ_{ex} of 346 nm (pH 5) and 365 nm (pH 8), λ_{em} of 450 nm; 4-methylumbelliferone, $\lambda_{ex} = 330$ nm, $\lambda_{em} = 450$ nm. A Corning 7-60 primary filter and a 65-A secondary filter were used for experiments on the filter fluorimeter.

Determination or acid phosphatase

Place 3.0 ml of 0.1 *M* citrate buffer pH 7.0, and 0.1 ml of a 10^{-3} *M* solution of 4-methylumbelliferone nonanoate in a fluorescence cell in the SPF, and adjust the instrument to read zero. At zero time add 0.1 ml of the phosphatase to be assayed and record the change in fluorescence with time, ΔF/min, automatically. Prepare a calibration plot of ΔF/min *vs.* enzyme concentration and use it for all enzyme analyses.

Determination of beryllium or bismuth

To 3.0 ml of TRIS buffer pH 8.0, and 0.1 ml of 10^{-3} *M* umbelliferone phosphate, and 0.1 ml of a solution of beryllium or bismuth to be determined. Adjust the fluorescence to zero, and add 0.1 ml of a 0.1 mg/ml solution of alkaline phosphatase. Record the rate of change in fluorescence with time, ΔF/min. Record a blank rate with no beryllium or bismuth present. The % inhibition is calculated as below:

$$\% \text{ Inhibition} = \frac{(\Delta F/\text{min})_{\text{Blank}} - (\Delta F/\text{min})_{\text{Inh}}}{(\Delta F/\text{min})_{\text{Blank}}} \times 100$$

The concentration of beryllium or bismuth is determined from a calibration plot of % inhibition *vs.* concentration of metal ion.

In addition to the blank (non-inhibited enzymic) rate, the rate of spontaneous (non-enzymic) hydrolysis of substrate should be measured and all rates corrected for spontaneous hydrolysis, if necessary. The non-enzymic hydrolysis of umbelliferone phosphate was found to be zero.

Determination of Aldrin or Heptachlor

Mix 3.0 ml of TRIS buffer pH 8.0, 0.1 ml of a 0.1 mg/ml solution of alkaline phosphatase and 0.1 ml of a methyl cellosolve solution of Aldrin or Heptachlor, and leave the resulting solution for 15 min. After this incubation, adjust the fluorescence of the solution to zero, add 0.1 ml of 10^{-3} M umbelliferone phosphate, and record the rate of change in fluorescence with time. Run a blank (uninhibited) rate with 0.1 ml of solvent incubated with enzyme and buffer, but with no pesticide present. Calculate the % inhibition as above and determine the concentration of Aldrin or Heptachlor from a calibration plot of % inhibition *vs.* pesticide concentration.

Determination of methyl parathion

To 3.0 ml of 0.1 M citrate buffer pH 5.0, add 0.1 ml of a 0.1 mg/ml solution of acid phosphatase and 0.1 ml of a methyl cellosolve solution of methyl parathion, mix and leave the resulting solution for 15 min. Adjust the fluorescence to zero, add 0.1 ml of 10^{-2} M umbelliferone phosphate and record the rate of change in fluorescence with time. Calculate the concentration of methyl parathion as described above.

DISCUSSION AND RESULTS

4-Methylumbelliferone nonanoate as substrate for phosphatase

JACKS AND KIRCHER[5] synthesized and tested the butyryl, hexanoyl, heptanoyl, nonanoyl, palmitoyl and oleoyl esters of 4-methylumbelliferone as substrates for 5 preparations of lipase. GUILBAULT *et al.*[1], in a study of 12 different substrates for lipase, found that 4-methylumbelliferone heptanoate was the best substrate for porcine pancreas lipase, and 4-methylumbelliferone octanoate was best for fungal lipase.

Preliminary observations showed that the 4-methylumbelliferone esters were

TABLE I

EFFECT OF pH AND BUFFER ON ACID PHOSPHATASE HYDROLYSIS OF 4-METHYLUMBELLIFERONE ESTERS

(Substrates = $3 \cdot 10^{-5}$ M, AP = 0.00624 units/ml)

pH, Buffer	*Ester*	$\Delta F/min$
6.0, Phosphate	Nonanoate	5.0
6.0, Citrate	Nonanoate	13.2
7.0, Phosphate	Nonanoate	18.0
7.0, Citrate	Nonanoate	29.0
7.5, Citrate	Nonanoate	18.0
5.0, Citrate	Nonanoate	7.1
7.0, Citrate	Acetate	0.07
7.0, Citrate	Butyrate	1.28
7.0, Citrate	Heptanoate	11.6
7.0, Citrate	Caproate	6.5

also catalytically cleaved by acid phosphatase. The maximum rate of hydrolysis was observed with the nonanoate ester at a pH of 7.0 in citrate buffer (Table I).

As little as 0.00006 units of enzyme could be determined, and good precision and accuracy was obtained in the analysis of acid phosphatase over the concentration range 0.00006 to 0.010 unit/ml (Table II).

TABLE II

DETERMINATION OF ACID PHOSPHATASE WITH 4-METHYLUMBELLIFERONE NONANOATE

(4-MeUm = $3 \cdot 10^{-5}$ *M*; 0.1 *M* citrate buffer, pH 7.0)

Acid phosphatase (units/ml)		*Rel. error*
Added	*Found*[a]	*(%)*
0.0000624	0.0000604	+ 3.0
0.000187	0.000190	+ 1.5
0.000312	0.000304	− 2.5
0.000624	0.000624	0.0
0.00187	0.00190	+ 1.5
0.00312	0.00321	+ 3.0
	Av. rel. error	± 2.0

[a] Results of 3 or more determinations with a standard deviation of 2%.

TABLE III

EFFECT OF SYSTOX AND PHOSPHATE ION ON ACID PHOSPHATASE ACTIVITY

(Substrate = $3 \cdot 10^{-5}$ *M* 4-MeUm)

Concn. of diverse substance	*ΔF/min (AP)*	*ΔF/min (lipase)*
Phosphate, 0.01 *M*	29.0	8.2
Phosphate, 0.1 *M*	26.0	10.5
Phosphate, 1.0 *M*	22.0	10.5
Systox, 10^{-4} *M*	29.0	1.0
Systox, 10^{-3} *M*	15.0	0

Although umbelliferone phosphate is a better substrate, in terms of sensitivity, than the nonanoate ester (as little as 10^{-5} unit of enzyme being detectable[3]), the 4-methylumbelliferone nonanoate is cleaved by phosphatase in the presence of up to 1.0 *M* concentrations of phosphate (Table III). As little as 10^{-3} *M* phosphate ion causes a 50% decrease in the activity of acid phosphatase with umbelliferone phosphate[3].

Alkaline phosphatase was not found to have any activity with any of the 4-methylumbelliferone esters, at any pH, or under any conditions. Thus, 4-methylumbelliferone nonanoate can be used for the detection of acid phosphatase, in the presence of alkaline phosphatase and phosphate ion.

Since lipase also effects the hydrolysis of 4-methylumbelliferone nonanoate, studies were undertaken to prove that true acid phosphatase, and not lipolytic, activity was being measured. Systox, shown to be a strong lipase activity by GUILBAULT AND KRAMER[2], had little effect on acid phosphatase. A 10^{-4} *M* solution caused a 90% inhibition of porcine pancrease lipase but no decrease in acid phosphatase activity. As much as 10^{-3} *M* systox only caused a 50% decrease in the activity of acid phosphatase. Furthermore, an increase in the concentration of phosphate ion effects an increase in the lipase activity, as predicted from an ionic strength consideration[6]; acid phosphatase activity is depressed, however, as expected (Table III).

Effect of inhibitors

A thorough study of the effect of pesticides on acid and alkaline phosphatase revealed that very few of the insecticides or herbicides had any effect on either of these enzymes. Of all the pesticides tested (the organophosphorus insecticides, Systox, methyl parathion and malathion; the carbamate, Sevin; the chlorinated insecticides, Heptachlor, Aldrin, Lindane and DDT; and the herbicide, 2,4-D-(2,4-dichlorophenoxyacetic acid)), only methyl parathion had any appreciable effect on acid phosphatase, and only Aldrin and Heptachlor had effect on alkaline phosphatase (Table IV).

Methyl parathion in the range 5–60 μg/ml can be determined in the presence of

TABLE IV

COMPARISON OF I_{50} FOR VARIOUS INHIBITORS OF ALKALINE PHOSPHATASE

(Substrate = $3 \cdot 10^{-5}$ *M*; enzyme = 0.033 mg/ml)

Inhibitor	$I_{50}(M)$	*Incubation time (min)*
Be^{2+}	$1.65 \cdot 10^{-5}$	0
Bi^{3+}	$1.5 \cdot 10^{-4}$	0
Aldrin	$1.37 \cdot 10^{-4}$	15
Heptachlor	$1.2 \cdot 10^{-3}$	15

TABLE V

RESULTS OF DETERMINATION OF INHIBITORS

(Substrate = $3 \cdot 10^{-5}$ *M* umbelliferone phosphate, pH 7 (acid phosphatase) or pH 8 (alkaline phosphatase))

Bismuth (μg/ml)[a]			*Beryllium (μg/ml)*[a]		
Added	*Found*[c]	*Error (%)*	*Added*	*Found*[c]	*Error (%)*
3.00	3.03	+ 1.0	0.0120	0.0117	− 2.5
6.50	6.50	0.0	0.0280	0.0290	+ 3.5
19.0	18.0	− 5.0	0.0800	0.0800	0.0
32.0	32.1	+ 0.3	0.200	0.195	− 2.5
45.0	44.8	− 0.4	0.270	0.270	0.0
63.0	63.4	+ 0.6	0.130	0.131	+ 0.7
Av. rel. error		± 1.3	Av. rel. error		± 1.5

Aldrin (μg/ml)[a]			*Methyl parathion (μg/ml)*[b]		
Added	*Found*[c]	*Error (%)*	*Added*	*Found*[c]	*Error (%)*
5.0	5.05	+ 1.0	8.00	7.90	− 1.2
10.0	9.92	− 0.8	20.0	21.0	+ 5.0
21.0	20.3	+ 3.5	30.0	29.0	− 3.3
52.0	50.5	− 3.0	45.0	47.0	+ 4.4
100.0	100.3	+ 0.3	60.0	57.0	− 5.0
Av. rel. error		± 1.7	Av. rel. error		± 3.8

[a] Alkaline phosphatase system.
[b] Acid phosphatase system.
[c] Average of 3 determinations with deviation of ±1.5%.

other pesticides (except ethyl parathion) with a relative error of about 3.8% (Table V). Concentrations of Systox greater than 10^{-3} M interfere.

With alkaline phosphatase, 5–100 µg/ml of Aldrin and 50–700 µg/ml of Heptachlor are determinable (Table V) in the presence of large amounts of the organophosphorus pesticides and up to 500 µg of Sevin and 1 mg of 2,4-D. DDT and lindane do not interfere, even in large concentrations.

Finally, the effect of various cations and anions on the activity of alkaline phosphatase was tested. Beryllium and bismuth were found to be strong inhibitors of this enzyme, and were determinable in the 0.01–10 µg/ml and 3–100 µg/ml concentration range, respectively, with a relative error of about 1.5%. The anions sulfate, chloride, bromide, iodide and phosphate do not interfere. Neither do the cations Na^+, K^+, Li^+, Cu^{2+}, Mg^{2+}, Ni^{2+} and Mn^{2+}. The following ions may be tolerated in the overall concentrations listed: fluoride (150 µg), dichromate (15 µg), aluminum (15 µg), lead (150 µg), zinc (30 µg), copper (30 µg), silver (10 µg), mercury (20 µg) and cadmium (1 mg). No interference is observed in the determination of beryllium or bismuth with these concentrations of diverse ions present. Larger concentrations will cause some decrease in the rate, dichromate and zinc being the most serious interferences.

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SUMMARY

A fluorimetric method is described for the determination of bismuth and beryllium, and the pesticides methyl parathion, Aldrin and Heptachlor. The procedure is based on the inhibition of acid and alkaline phosphatase by these substances. The substrate umbelliferone phosphate is used, which is cleaved by phosphatase to the highly fluorescent umbelliferone ($\lambda_{ex} = 346$ nm at pH 5, and $\lambda_{ex} = 365$ nm at pH 8; $\lambda_{em} = 450$ nm). Beryllium (0.01–0.30 µg/ml), bismuth (1–70 µg/ml), Aldrin (5–100 µg/ml) and Heptachlor (50–700 µg/ml) inhibit the hydrolysis catalyzed by alkaline phosphatase, and methyl parathion (5–500 µg/ml) that catalyzed by acid phosphatase, causing a decrease in the slopes of the fluorescence–time curves. This decrease is a direct measure of the concentration of inhibitor.

4-Methylumbelliferone nonanoate was found to be a good substrate for acid phosphatase in the presence of large amounts of phosphate (1.0 M). As little as 0.00006 units of acid phosphatase can be assayed with an accuracy and precision of 2%.

RÉSUMÉ

On décrit une méthode fluorimétrique pour la détermination du bismuth et du béryllium ainsi que celle des pesticides méthylparathion, Aldrin et Heptachlore. Le procédé est basé sur l'inhibition des phosphatases acide et alcaline par ces substances. Le substrat employé est le phosphate d'umbelliferone, lequel est rattaché par la phosphatase à l'umbelliferone très fluorescente. ($\lambda_{ex} = 346$ nm à un pH = 5 et $\lambda_{ex} = 365$ nm à un pH = 8; $\lambda_{em} = 450$ nm). Le béryllium (0.01–0.30 µg/ml), le bismuth (1–70 µg/ml), l'Aldrin (5–100 µg/ml) et l'Heptachlore (50–700 µg/ml) inhibent l'hydrolyse catalysée par la phosphatase alcaline; le méthyl-parathion (5–500 μg/ml) inhibe l'hydrolyse catalysée par la phosphatase acide et provoque, sur les courbes de fluorescence en fonction du temps, une diminution des pentes. Cette diminution est une mesure directe de la concentration de l'inhibiteur.

Le nonanoate de la 4-méthylumbelliferone est considéré comme un bon substrat par la phosphatase acide en présence de grandes quantités de phosphate (1.0 *M*). On a également essayé des quantités très faibles (de l'ordre de 0.00006 unités) de phosphatase acide avec une précision de 2%.

ZUSAMMENFASSUNG

Es wird eine fluorimetrische Methode zur Bestimmung von Wismut, Beryllium und den Pestiziden Methylparathion, Aldrin und Heptachlor beschrieben. Das Verfahren beruht auf der Blockierung der sauren und alkalischen Phosphatase durch diese Substanzen. Das Substrat Umbelliferonphosphat wird verwendet, welches durch die Phosphatase zu dem stark fluoreszierenden Umbelliferon gespalten wird ($\lambda_{ex}=346$ nm beim pH 5 und $\lambda_{ex}=365$ nm beim pH 8; $\lambda_{em}=450$ nm). Beryllium, Wismuth, Aldrin und Heptachlor in μg-Mengen blockieren die durch alkalische Phosphatase katalysierte Hydrolyse. Methylparathion, das durch saure Phosphatase katalysiert wird, verursacht eine Verringerung der Steigung in den Fluoreszenzzeitkurven. Diese Verringerung ist ein direktes Mass für die Konzentration des Inhibitors. 4-Methylumbelliferonnonanoat zeigte sich als eine gutes Substrat für die saure Phosphatase in Gegenwart grosser Mengen Phosphat. 0.00006 Einheiten saurer Phosphatase können mit einer Genauigkeit von 2% bestimmt werden.

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AN AUTOMATED COULOMETRIC TITRATOR AND ITS APPLICATION TO THE DETERMINATION OF WATER

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The development of many recent processes has made it necessary to determine the trace water content (0–10 p.p.m.) in various petrochemical and refinery streams. In this laboratory, all previous low-level water work had involved either the direct conventional Karl Fischer titration technique or a glycol extraction of the water-containing stream followed by a conventional Karl Fischer titration. These techniques were plagued with difficulties, primarily water contamination, and were, at best, only approximations of the water level.

A survey of the literature revealed many papers describing methods for low-level water determination. Some of the methods described included direct and indirect infrared spectroscopy[1], gas chromatography[2], P_2O_5 absorption[3], and the use of diethyl aluminum hydride[4]. Several papers on coulometric generation of iodine for a Karl Fischer-type reaction looked promising[5–7].

Coulometric titration, invented by SZEBELLEDY AND SOMOGYI[8], employs electrolysis to generate a reagent which reacts stoichiometrically with the substance to be determined. The quantity of substance reacted is computed via Faraday's Law from the number of coulombs rather than from the volume of a standard solution as in an ordinary titration. By performing the electrolysis with constant current the quantity of electricity passed can be determined simply by timing the electrolysis. The coulometric approach had several advantages. The coulometric generation of small amounts of iodine for the Karl Fischer reaction had been studied and the stoichiometry was known[5]. Coulometric generators were available which produce precise small currents for timed intervals, thereby avoiding the problem of standardizing and protecting the very dilute and highly moisture-sensitive Karl Fischer reagent. Although coulometric generation of iodine for the Karl Fischer reaction had been previously described[5] and applied to water concentrations below 10 p.p.m.[6], it was decided to examine this approach, to improve the titration cell design, and to attempt to develop an automated end-point detector and coulometer controller.

"Karl Fischer Reagent" has been widely used for the determination of water in a variety of organic and inorganic compounds since 1935[9]. Generally, the reagent contains excesses of pyridine and sulfur dioxide, so that the iodine is the limiting constituent. Therefore, a depleted solution of this reagent can be regenerated by the addition of iodine. If the iodine is introduced by electrolysis of iodide in the depleted solution, then fresh Karl Fischer reagent can be generated *in situ* coulometrically.

EXPERIMENTAL

Apparatus

Coulometric source. A Sargent Model IV coulometric generator (E. H. Sargent Co., Chicago, Ill., Catalog No. 30974) was used. This unit is a constant-current coulometer with six range settings which allow accurate generation of 0.05–2 µeq/sec. An internally mounted timer is calibrated so that the product of the timer reading and the multiplier setting equals the number of microequivalents of compound generated. The instrument is capable of ±0.1% relative error as long as external resistances do not exceed 1700 ohms on the lower 5 ranges and 850 ohms on the highest range.

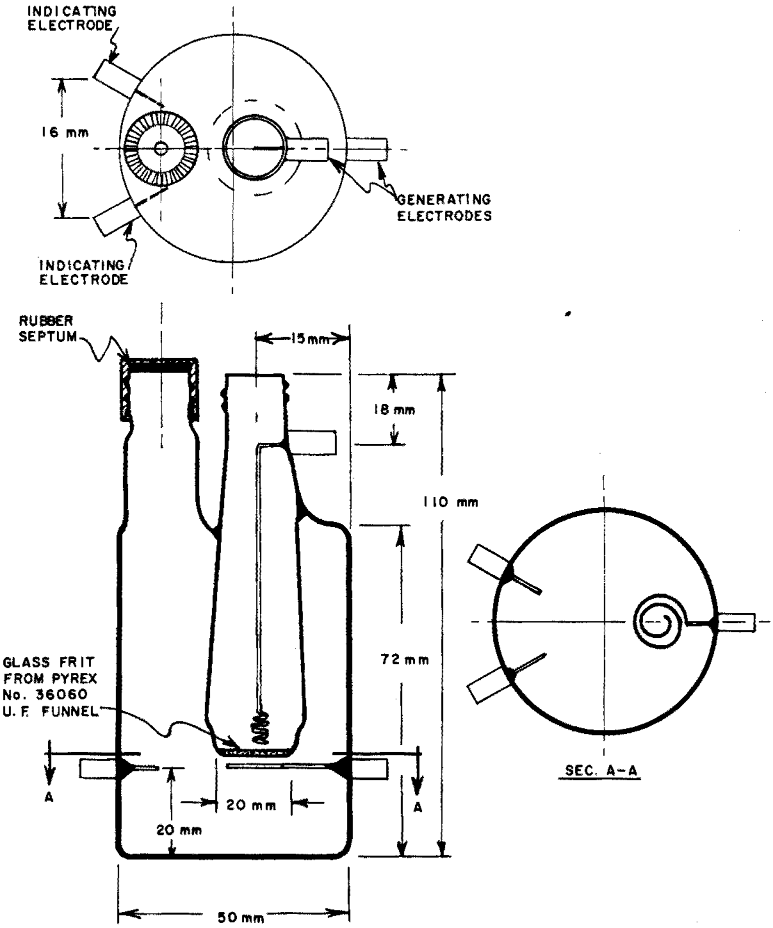

Fig. 1. Reaction cell of coulometric water titrator. Electrodes: 20 gauge platinum wire; glass frit: ultra-fine porosity from Corning serial no. 36060 funnel; electrode connections are made with 1/4 in grid caps; screw cap tops on cell made from ≃ 15 mm pyrex culture tubes.

Cell assembly. The titration vessel consisted of the two-compartment cell shown in Fig. 1. The larger outside compartment contains the generator anode, the large platinum spiral under the glass frit, and the two platinum indicating electrodes, as shown in Fig. 1, Sec. A-A. The smaller inner compartment contains the generator cathode, and is isolated from the anode compartment by a Corning *ultra-fine* porosity glass frit. Both compartments may be sealed with rubber septum-lined screw caps. During titration, the solution in the anode compartment is stirred magnetically with a Teflon-covered bar.

End-point detector and coulometer controller. Amperometric end-point detection was used. A wiring diagram of the unit is shown in Fig. 2. A small potential difference is maintained between the two platinum-indicating electrodes. When excess of water is present, the cathode is polarized so that no current flows, but as the end-point is reached, the free iodine present depolarizes the electrode allowing current to flow. This current is measured on the micro-ammeter and the built-in relay automatically switches off the coulometric current source as the end-point is reached. A built-in timer checks the end-point every 30 sec. If the end-point has drifted, that is, if the indicator current has dropped below the setpoint, the unit will switch the coulometer "on" to supply the necessary current to return to the end-point conditions.

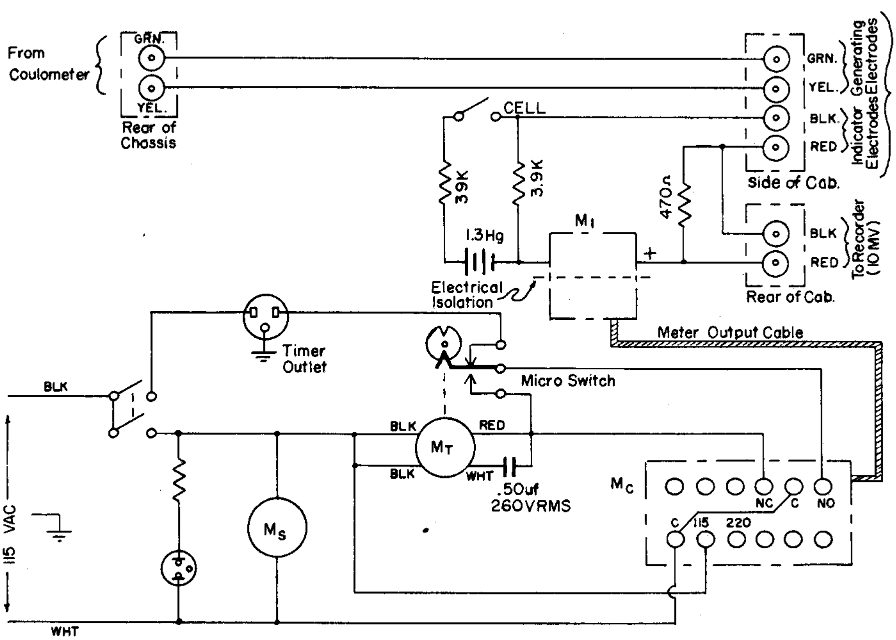

Fig. 2. Wiring diagram of amperometric end-point detector. M$_1$: API Optical Meter Relay Mod. No. 302L-0-20uA single setpoint upper.
M$_C$: Module-API Mod. No. 901 A; on-off type single setpoint.
M$_S$: motor-stirring-Magni-Mix cat. no. 65904
M$_T$: motor-timing-Haydon Model C-1RPM.

Reagents

Karl Fischer reagent (Fisher Scientific Company, Catalog No. SO-K-2). This reagent comes in two solutions: sulfur dioxide in pyridine, and iodine in methanol.

Pyridine, methanol and benzene or xylene were of reagent grade.

Titration solvent. Mix equal volumes of pyridine, Karl Fischer Solution No. 1 (SO_2), Karl Fischer Solution No. 2 (iodine), methanol and benzene or xylene, in the order listed.

Methanol–water solution. Add 1 ml of water to 100 ml of methanol.

Procedure

Add *ca.* 50 ml of titration solvent to the large outer compartment and *ca.* 5 ml of titration solvent to the small inner compartment of the coulometric cell. Switch on the power and cell switches on the coulometric controller and adjust the magnetic stirrer speed to give good mixing with a minimum of entrained air. Set the meter relay cut-off point to the 10 μA position and add methanol–water solution dropwise to the large cell compartment until the indicator current just falls below 10 μA. Set the coulometer "multiplier" switch to the proper range and switch the cell current switch to the "remote" position. Allow the coulometer to generate until the 10 μA end-point is reached. Turn the current switch "off" and shake the cell gently. Set the current switch to "remote" and allow the cell to reach a stable end-point. After a stable end-point is reached, set the timer on the coulometer to zero and introduce a measured amount of sample into the large compartment of the cell. Turn the cell current switch to the "remote" position and allow the coulometer to generate to the 10 μA cut-off. Shake the cell as before and allow to reach a stable end-point. Record the amount of sample, the current multiplier setting, and the timer reading, and calculate the water content calculated as follows:

$$\%\ \text{water} = \frac{A \times B \times 9.01 \times 100}{W \times 1000}$$

where A = timer reading from coulometer (timer units); B = multiplier setting (μeq/timer unit); W = sample weight in mg; 9.01 = equivalent weight of water.

RESULTS AND DISCUSSION

Other workers in coulometry have used both amperometric and potentiometric end-point detection techniques. The equipment for the amperometric technique is simpler than that used in the potentiometric technique, but cell geometry (electrode placement) and stirring rate are critical in the amperometric method. The potentiometric method is more sensitive, and somewhat more precise at very low concentrations; also, it is less dependent on cell geometry and stirring conditions. The amperometric method was chosen here because of its simplicity. Also, the cell geometry and stirring rate could be controlled, thus minimizing these disadvantages. Under the conditions described, the sensitivity is also adequate.

Since the geometry of the titration cell is very important when the amperometric end-point detection method is used, the optimum electrode placement was experimentally determined. The two generating electrodes were set up and then the proper indicator electrode location was established by a "trial and error" procedure. The indicator electrode should be positioned outside the electrical field (current path) between the generating electrodes. If the indicator electrodes are in the generating current field, the voltage drop produced by the generating current acts like a change in voltage applied across the indicator electrodes and causes a spurious indicator current. The elimination of this spurious current or "kick" is very important when one is designing an automatic switching type instrument such as the one described in this paper.

MEYERS AND SWIFT found that when the hydrogen produced at the generator cathode was allowed to enter the body of the solution, it produced an anomalous behavior of the indicator circuit at the end-point[10]. For this reason, it was necessary to isolate the generator cathode from the main body of the solution.

The isolation of the generating anode from the generating cathode was accomplished by use of an ultra-fine glass fritted disc. The junction material must give good electrical conduction, but minimize solvent leakage between the cathode and anode compartments; coarse material would permit a liquid flow which would interfere with end-points condition, whereas fine material would cause excessive cell resistance (above 1700 ohms). The Corning *ultra-fine* frit was found to be a satisfactory compromise.

One of the important features of the coulometric controller end-point detector described is its ability not only to detect and maintain a pre-set end-point, but to check it periodically, *i.e.* every 30 sec. If the indicator current has drifted below the pre-set end-point, the controller turns the coulometer "on" to give the current needed to bring the reaction back to the end-point. The 30-sec interval was chosen because many industrial standard procedures such as ASTM, AOCS, and AOAC methods use an end-point which will hold for this length of time. This feature is especially important in slow reactions such as the Karl Fischer, iodination, and bromination reactions. The end-point checking feature allows high-speed coulometric generation of titrant without the possibility of end-point over-shoot. It also enabled the instrument to be made semi-automatic; after sample addition, no further operator time is required until the final timer reading is taken and the results calculated.

The accuracy of the titrator was checked at the higher water levels by two techniques: direct titration of known weights of water, and a standard addition technique. A 0.5-ml hypodermic syringe was used to transfer small amounts of water directly into the titration cell. The weight of water added was obtained on a semi-micro analytical balance. These data are shown at the top of Table I. The good agreement

TABLE I

ACCURACY OF THE COULOMETRIC TITRATOR

Sample	*Added (mg)*	*Found (mg)*	*Recovered (%)*	*Error (%)*
Water weighed into titration cell	6.78	6.87	101.3	1.3
	9.60	9.62	100.2	0.2
	10.8	10.8	100.0	—
	20.8	20.3	97.6	2.4
				Avg. 1.0

	Added (%)	*Expected (%)*	*Found (%)*	*Recovered (%)*
Isopropanol	—	—	0.070	—
Isopropanol + water	0.027	0.097	0.098	103.7
Isopropanol + water	1.10	1.17	1.19	101.8
Isopropanol + water	4.35	4.42	4.47	101.1

between the added and found data shows that the generating efficiency is near 100% as required for a workable coulometric method. As a secondary accuracy check, a standard addition technique was used. Isopropyl alcohol (reagent grade) was analyzed to determine its initial water content. Standard blends were prepared by addition of weighed amounts of water and these blends were analyzed by the coulometric method. The resulting data are also shown in Table I.

Table II shows a comparison of coulometric titration with the conventional volumetric method and with a commercial stream analyzer.

TABLE II

COMPARISON OF METHODS

Sample	*Coulometric*	*Karl Fischer*[a]	*"MEECO"*[b]
Paraffin	11 p.p.m.		8.0 p.p.m.
Paraffin	0.9 p.p.m.		0.9 p.p.m.
Chloroparaffin	8.4 p.p.m.		6.5 p.p.m.
Alcohol A	3.5%	3.6%	
Alcohol B	4.6	4.6	
Alcohol C	0.39	0.45	

[a] Standard KF procedure—back-titration of excess KF reagent with water–methanol. Dead-stop end-point.

[b] Commercial Model W electrolytic moisture stream analyzer (MEECO, Warrington, Pa.) based on gas stripping of water onto P_2O_5 and coulometric regeneration of P_2O_5.

The coulometric titrator was used to determine the water content of a variety of sample types. Examples of some of the types analyzed and the precision obtained are shown in Table III. The precision of the technique was also demonstrated by ten analyses of reformer naphtha. The mean of the results was found to be 20.5 ± 0.76 p.p.m. with a range of 2.4 p.p.m., the standard deviation being 0.89 and the relative standard deviation 4.3%.

TABLE III

EXAMPLES OF SAMPLE TYPE AND PRECISION OF THE COULOMETRIC TITRATOR

	Replicates	*Average*
Isopropanol	972, 971, 974, 991, 995, 993	983 p.p.m. ± 10
Isopropanol	0.397, 0.391, 0.390, 0.389	0.392% ± 0.003
Isopropanol + water	684, 718, 701, 704	702 p.p.m. ± 9
Isopropanol + water	1.19, 1.20, 1.19	1.19% ± 0.003
Isopropanol + water	4.46, 4.51, 4.43	4.47% ± 0.03
Methanol	458, 463, 471, 456	462 p.p.m. ± 5
Paraffin	0.6, 1.0	0.8 p.p.m. ± 0.2
Paraffin	5.7, 6.7, 4.2 ,5.7	5.6 p.p.m. ± 0.7
Chloroparaffin	5.3, 5.6, 4.6	5.1 p.p.m. ± 0.4
Benzene	480, 482, 483, 481, 487	482 p.p.m. ± 2

The automated coulometric titrator is applicable to all levels of water, from hydrocarbons containing a few parts-per-million water to samples consisting of pure water.

SUMMARY

An automated coulometric titrator and its successful application to the determination of water *via* a Karl Fischer-type reaction is described. Coulometric *in situ* generation of the highly moisture-sensitive Karl Fischer reagent is used to determine accurately the water content of a variety of compounds. The titrator is applicable to all levels of water, from hydrocarbons containing a few parts-per-million water to samples consisting of pure water.

RÉSUMÉ

On décrit un appareil pour la titration automatique par coulométrie. Cette méthode s'applique avec succès à la détermination de l'eau selon le type de réaction de Karl Fischer. La formation coulométrique *in situ* du réactif très sensible à l'humidité de Karl Fischer est employée pour déterminer avec précision la teneur en eau d'un certain nombre de composés. L'appareil est utilisable pour la titration de toutes les teneurs en eau en partant d'hydrocarbures contenant quelques p.p.m. d'eau jusqu'à des échantillons d'eau pure.

ZUSAMMENFASSUNG

Es wird ein automatischer coulometrischer Titrator und seine erfolgreiche Anwendung bei der Bestimmung von Wasser nach K. FISCHER beschrieben. Die coulometrische Erzeugung des K-Fischer-Reagenzes *in situ* wird zur genauen Bestimmung des Wassergehaltes in verschiedensten Verbindungen verwendet. Der Titrator ist für alle Konzentrationsbereiche des Wassers anwendbar. Von Kohlenwasserstoffen, die nur wenige p.p.m. enthalten bis zu Proben aus reinem Wasser.

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THE DETERMINATION OF STABILITY CONSTANTS FROM CONTINUOUS VARIATION DATA

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The method of continuous variation has widely been used for the determination of the composition of metal complexes in solution. Several authors[1-6] have calculated theoretical curves, and have discussed the form of these curves for different compositions and stabilities.

For the calculation of the stability constant SCHWARZENBACH[2] and FOLEY AND ANDERSON[7] used data from the continuous variation method for relatively weak complexes. SCHAEPPI AND TREADWELL[8] and BUDĚŠÍNSKÝ[9] determined the stability constant of very stable complexes. All these applications are limited to cases when only the complex to be studied is present in the solutions, and data from the end branches of the curves are involved. It happens very often, however, that other complexes are formed, at least in small amounts, at mole fractions deviating from that of the maximum.

The first and most important step in the use of the continuous variation curves is—by the abscissa of the maximum—to determine $n/(m+n)$ in the complex A_mB_n. The present paper describes an investigation of the variation of the ordinate of the maximum with the stability of the complex, when only one complex is formed. The limits within which it is possible to determine the stability constant from such data are established. A method for the determination of the stability constant of complexes with moderate strength is suggested. This method uses data exclusively from the maximum of the curves. At the same time the method can be used for differentiating between monomer and dimer complexes A_mB_n, where $m = n$.

THEORY

Theoretically, a curve of continuous variation for a system where only one complex A_mB_n is formed between the components A and B, is described by the following equation[5,6]:

$$(1 - x - my)^m(x - ny)^n - (1/Kc^{m+n-1})y = 0 \qquad (1)$$

In this equation $y = [A_mB_n]/c$, and c represents the sum of the total molar concentrations of the components ($c = c_A + c_B$), which is held constant in the method of continuous variation. x denotes the mole fraction ($x = c_B/c$), and K the stability constant ($K = [A_mB_n]/[A]^m[B]^n$). In spectrophotometric measurements, the measured extinction is usually proportional to y, following the familiar Lambert–Beer law:

$$E = \varepsilon l[A_mB_n] = \varepsilon lcy \tag{2}$$

where ε represents the effective extinction coefficient[*], and l the light path.

In a recent paper[6] theoretical curves for y as a function of x are plotted for the complexes AB, A_2B_2, AB_2 and AB_3, for different values of the parameter $1/Kc^{m+n-1}$. It was shown that the maximum value of y ($= y_{max}$) at $x = n/(m+n)$ increases as the value of $1/Kc^{m+n-1}$ decreases, approaching $1/(m+n)$ as a limit, corresponding to the infinitely stable complex.

By means of a computer program, the maximum value of y as a function of the parameter $1/Kc^{m+n-1}$ was calculated from eqn. (1), putting $x = n/(m+n)$. For each value of $1/Kc^{m+n-1}$ in the calculations, different concentration sums $c = c_1/q$ were substituted for c in this parameter, q being an integer, *i.e.* for each value of $1/Kc^{m+n-1}$, the multiple values $(1/Kc^{m+n-1})\quad q^{m+n-1}$ were chosen. In this way a set of values of y_{max} was obtained, representing the same value of K, but different fractions of the concentration sum c. The values of y_{max} were denoted $y_{c/q}$, *e.g.*, y_c, $y_{c/2}$, $y_{c/3}$, etc. On the basis of these sets the ratios

$$f(c/q,c) = \frac{y_{c/q}}{y_c} \tag{3}$$

were calculated as a function of $1/Kc^{m+n-1}$[**].

In Figs. 1 and 2 $f(c/q,c)$ is plotted as a function of $\log(Kc^{m+n-1})$ for $q = 2, 3, 4, 5, 10$ for the complexes AB and A_2B_2. In Tables I–IV the corresponding numerical values are given both for the complexes AB and A_2B_2 above, and for the complexes AB_2 and

TABLE I

CALCULATED EXTINCTION RATIOS (COMPLEX AB, MOLE FRACTION $\frac{1}{2}$)

log(Kc)	y_c	*f(c/2,c)*	*f(c/3,c)*	*f(c/4,c)*	*f(c/5,c)*	*f(c/10,c)*
−1.477	0.0080	0.5081	0.3408	0.2565	0.2057	0.1035
−1.000	0.0228	0.5232	0.3543	0.2678	0.2154	0.1089
−0.477	0.0635	0.5653	0.3947	0.3033	0.2463	0.1271
0.000	0.1340	0.6403	0.4740	0.3771	0.3132	0.1700
0.523	0.2347	0.7479	0.6061	0.5122	0.4447	0.2706
1.000	0.3209	0.8363	0.7313	0.6548	0.5952	0.4175
1.523	0.3916	0.9045	0.8379	0.7860	0.7432	0.5992
2.000	0.4341	0.9433	0.9021	0.8688	0.8406	0.7391
2.523	0.4628	0.9685	0.9450	0.9256	0.9089	0.8463
3.000	0.4781	0.9817	0.9678	0.9563	0.9463	0.9079
3.523	0.4879	0.9899	0.9822	0.9758	0.9702	0.9484
4.000	0.4930		0.9897	0.9860	0.9827	0.9699
5.000	0.4978				0.9945	0.9904

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[*] If the components themselves absorb light at the actual wavelength, the measured total extinctions are corrected as usual by the extinctions caused by the total amount of the components present. In that case the effective extinction coefficient is $\varepsilon = \varepsilon_{A_mB_n} - m\varepsilon_A - n\varepsilon_B$.

[**] The computer program (the same as was used earlier[6]) is written in FORTRAN IV and can be used for the calculation of complete theoretical continuous variation curves or values of y_{max} and $f(c/q,c)$ for any complex A_mB_n with any value of $1/Kc^{m+n-1}$. On request, a copy of the program can be obtained from the author. The program uses a variation procedure for solving the involved equations of $(m+n)$-th degree and checks finally the y-values by inserting them into eqn. (I).

AB_3. Because it is possible to determine f($c/q,c$) experimentally—as will be seen below—diagrams like those in Figs. 1 and 2 can be used to find the values of log (Kc^{m+n-1}), and then the stability constant, if m and n are known.

It can be seen that f($c/q,c$) approaches unity as a limit for increasing stability constant of the complexes, and that the opposite limit, *viz.* for decreasing stability, is $1/q^{m+n-1}$.

The ratios f($c/q,c$) can be measured experimentally as follows. The extinction E_c is measured for a solution with total molar concentration c_1, in a cell with light

TABLE II

CALCULATED EXTINCTION RATIOS (COMPLEX A_2B_2, MOLE FRACTION $\frac{1}{2}$)

$\log(Kc^3)$	y_c	$f(c/2,c)$	$f(c/3,c)$	$f(c/4,c)$	$f(c/5,c)$	$f(c/10,c)$
−1.000	0.0057	0.1355				
−0.477	0.0160	0.1565	0.0477	0.0203		
0.000	0.0345	0.2022	0.0648	0.0279	0.0144	
0.523	0.0639	0.2970	0.1079	0.0485	0.0254	
1.000	0.0942	0.4178	0.1842	0.0903	0.0493	0.0066
1.523	0.1260	0.5554	0.3102	0.1776	0.1062	0.0160
2.000	0.1514	0.6629	0.4412	0.2943	0.1981	0.0377
2.523	0.1744	0.7541	0.5735	0.4366	0.3326	0.0917
3.000	0.1912	0.8160	0.6727	0.5564	0.4605	0.1805
3.523	0.2057	0.8659	0.7573	0.6651	0.5853	0.3108
4.000	0.2159	0.8993	0.8159	0.7433	0.6788	0.4364
4.523	0.2245	0.9263	0.8641	0.8091	0.7593	0.5613
5.000	0.2305	0.9444	0.8970	0.8547	0.8159	0.6567
5.523	0.2355	0.9591	0.9240	0.8924	0.8632	0.7405
6.000	0.2390	0.9691	0.9424	0.9182	0.8958	0.8002
7.000	0.2438	0.9827	0.9677	0.9540	0.9412	0.8858
8.000	0.2465		0.9818	0.9741	0.9669	0.9353
9.000	0.2480				0.9814	0.9634

TABLE III

CALCULATED EXTINCTION RATIOS (COMPLEX AB_2, MOLE FRACTION 2/3)

$\log(Kc^2)$	y_c	$f(c/2,c)$	$f(c/3,c)$	$f(c/4,c)$	$f(c/5,c)$	$f(c/10,c)$
−1.477	0.0047	0.2583	0.1157			
−1.000	0.0131	0.2732	0.1236	0.0701	0.0449	
−0.477	0.0353	0.3159	0.1483	0.0851	0.0550	
0.000	0.0717	0.3958	0.2012	0.1195	0.0786	0.0204
0.523	0.1234	0.5240	0.3089	0.1989	0.1370	0.0384
1.000	0.1710	0.6465	0.4436	0.3176	0.2355	0.0768
1.523	0.2159	0.7570	0.5933	0.4748	0.3860	0.1635
2.000	0.2481	0.8308	0.7068	0.6094	0.5302	0.2889
2.523	0.2743	0.8870	0.7997	0.7275	0.6657	0.4498
3.000	0.2916	0.9219	0.8599	0.8071	0.7608	0.5866
3.523	0.3050	0.9479	0.9058	0.8692	0.8366	0.7080
4.000	0.3135	0.9640	0.9345	0.9087	0.8854	0.7913
4.523	0.3200	0.9760	0.9561	0.9386	0.9227	0.8573
5.000	0.3240	0.9834	0.9695	0.9573	0.9462	0.8999
5.523	0.3271		0.9796	0.9714	0.9639	0.9324
6.000	0.3290			0.9801	0.9749	0.9529
7.000	0.3313				0.9883	0.9780

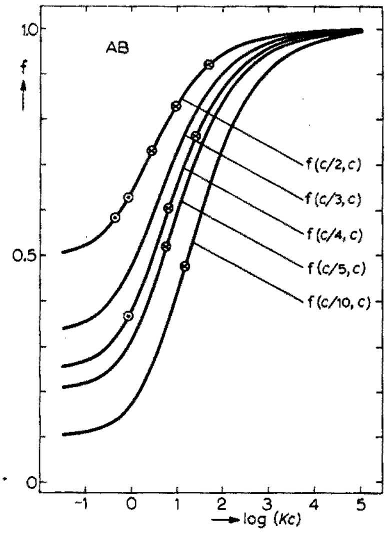
path l_1. Then different solutions with $c = c_1/q$ in cells with $l = l_1 \cdot q$ are measured, where q is a whole number depending on the light path of the available cells.

The extinction of the latter solutions is designated $E_{c/q}$. In all the solutions the components are present in the stoichiometric molar ratios ($x = n/(m+n)$). Of course, the reference and sample cells must be identical within each measurement. The reference solution must be a reagent blank if the latter solution has an absorption at

TABLE IV

CALCULATED EXTINCTION RATIOS (COMPLEX AB_3, MOLE FRACTION $\frac{3}{4}$)

$\log(Kc^3)$	y_c	$f(c/2,c)$	$f(c/3,c)$	$f(c/4,c)$	$f(c/5,c)$	$f(c/10,c)$
−1.000	0.0091	0.1420	0.0427			
−0.477	0.0236	0.1741	0.0540	0.0231		
0.000	0.0464	0.2373	0.0794	0.0346	0.0180	
0.523	0.0783	0.3520	0.1392	0.0647	0.0344	
1.000	0.1084	0.4790	0.2346	0.1222	0.0689	0.0096
1.523	0.1386	0.6094	0.3725	0.2298	0.1451	0.0241
2.000	0.1620	0.7058	0.5012	0.3562	0.2538	0.0561
2.523	0.1829	0.7858	0.6235	0.4958	0.3943	0.1292
3.000	0.1980	0.8397	0.7124	0.6067	0.5174	0.2344
3.523	0.2109	0.8831	0.7872	0.7047	0.6323	0.3712
4.000	0.2200	0.9121	0.8386	0.7742	0.7164	0.4930
4.523	0.2276	0.9355	0.8809	0.8323	0.7881	0.6090
5.000	0.2329	0.9514	0.9098	0.8724	0.8382	0.6957
5.523	0.2373	0.9642	0.9334	0.9055	0.8798	0.7707
6.000	0.2403	0.9729	0.9495	0.9282	0.9085	0.8239
7.000	0.2445	0.9849	0.9717	0.9596	0.9484	0.8996
8.000	0.2469			0.9773	0.9710	0.9431
9.000	0.2483				0.9837	0.9679



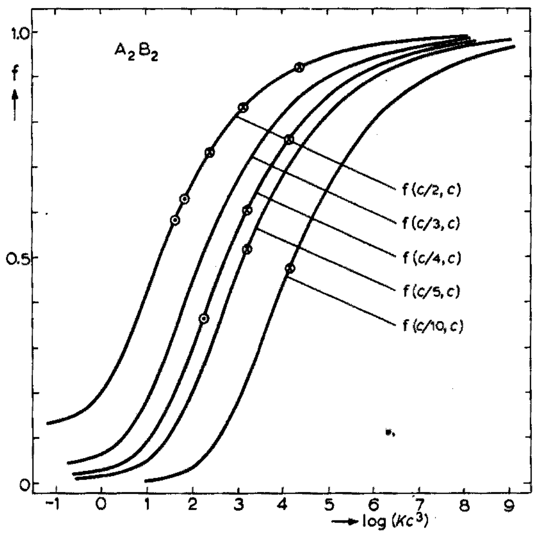


Fig. 1. Theoretical extinction ratios. Complex AB. ⊙ Measured ratios for the iron(III)–tiron system at pH 1.15. ⊗ Measured ratios for the iron(III)–chrome azurol S system at pH 3.40.

Fig. 2. Theoretical extinction ratios. Complex A_2B_2. ⊙ Measured ratios for the iron(III)–tiron system at pH 1.15. ⊗ Measured ratios for the iron(III)–chrome azurol S system at pH 3.40.

the actual wavelength, or the measured extinction must be corrected in the usual way for the absorption caused by the total amount of reagent present in the sample solution.

From eqns. (2) and (3) it follows that

$$f(c/q,c)=\frac{y_{c/q}}{y_c}=\frac{E_{c/q}}{E_c} \tag{4}$$

With the use of "the extinction ratio" $f/c/q,c)$ the corresponding value of log (Kc^{m+n-1}) can be found from a diagram like Fig. 1 or 2 corresponding to the proper complex A_mB_n.

At this stage two criteria, which the obtained log (Kc^{m+n-1}) values must satisfy, should be mentioned. Firstly, two extinction ratios $f(c/q,c)$ and $f(c/2q,c/2)$ must give two log (Kc^{m+n-1}) values theoretically differing by $(m+n-1)$ log 2. Generally, $f(c/q,c)$ and $f(c/pq,c/p)$ must give log (Kc^{m+n-1}) values differing by $(m+n-1)\log p$ (p is a whole number). Secondly, the two extinction ratios $f(c/q_1,c)$ and $f(c/q_2,c)$ must give the same values of log (Kc^{m+n-1}) within experimental error if the correct (m,n) value is used. In the practical application of the method, different extinction ratios should be measured, and the resultant log (Kc^{m+n-1}) values checked against these two criteria. In addition, the criteria can be used to determine the true values of m and n for complexes with $m=n$, because only the use of the diagram for the correct complex A_mB_n will give a consistent set of log (Kc^{m+n-1}) values.

The range of log (Kc^{m+n-1}) for the best application of the method was estimated from the Figures as follows:

log (Kc^{m+n-1}) for	1:1	2:2	1:2	1:3
Higher limit	3.0	6.0	4.5	6.0
Lower limit	−1.0	−0.5	−1.0	−0.5

With the use of high values of q, *viz.* $q = 10$, the range can be extended by roughly 2 log-units in the direction of higher values of log (Kc^{m+n-1}) (1 log-unit for 1:1). Accordingly, the method is applicable to the determination of the stability constant of complexes of intermediate and low stability, *i.e.* to complexes having curves of continuous variation deviating appreciably from the hypothetical curve for the infinitely stable complex[6].

THE IRON(III)–TIRON SYSTEM

The system iron(III)–tiron* at pH 1.15 was chosen as an example of the application of the method. This system has previously been investigated by several authors. SCHWARZENBACH[2] has published a continuous variation curve measured at pH 1.15, which shows the formation of a monomeric 1:1 complex, and the stability constant determined by his own method[2].

In the present experiments three iron(III)–tiron solutions at pH 1.15 were made, all with mole fraction $x = \frac{1}{2}$ and ionic strength 0.1 M (KCl). The extinctions were measured with a Zeiss PMQ II spectrophotometer at 660 nm against distilled water. Neither iron(III) nor tiron solutions absorbed light at this wavelength. The results are given in Table V.

The extinction ratios were calculated, and the values of $f(c/q,c)$ in Table VI were

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* Tiron = 1,2-dihydroxy-benzene-3,5-disulfonic acid, disodium salt.

plotted on the proper curves both on Fig. 1 (AB complex) and on Fig. 2 (A_2B_2 complex). It can be seen that the values corresponding to the AB complex fit the two criteria mentioned in the theoretical part very well, *viz.*, the two former values are identical, and the difference between the latter value and the two former ones is very near to log 2 = 0.30. From the third column of Table VI it can be seen that the extinction ratios do not fit the criteria when an A_2B_2 complex is tried, which demonstrates the well-known fact that the iron(III)–tiron complex is 1:1, and not 2:2.

The value $\log (Kc) = -0.05$ gives $K = 0.45 \cdot 10^3$.

TABLE V

MEASURED EXTINCTIONS AT 660 nm FOR EQUIMOLAR SOLUTIONS OF IRON(III) AND TIRON AT pH 1.15

Solution no.	*Concentration sum*	*Light path*	*Extinction*
1	$c = 2 \cdot 10^{-3}\ M$	$l = 1$ cm	$E_c = 0.467$
2	$c/2 = 1 \cdot 10^{-3}\ M$	$2l = 2$ cm	$E_{c/2} = 0.293$
3	$c/4 = 5 \cdot 10^{-4}\ M$	$4l = 4$ cm	$E_{c/4} = 0.170$

TABLE VI

EXTINCTION RATIOS AND LOG (Kc^{m+n-1}) VALUES FOR THE IRON(III)–TIRON SYSTEM

Extinction ratio	*log(Kc) AB complex (Fig. 1)*	*log(Kc^3) A_2B_2 complex (Fig. 2)*
$f(c/2,c) = 0.627$	−0.05	1.84
$f(c/4,c) = 0.364$	−0.05	1.64
$f(c/4,c/2) = 0.580$	−0.34	2.25

An experimental continuous variation curve at the same pH, using the method of SCHWARZENBACH[2], in which tangents to the curve at the end-points are drawn, gave values of K equal to $1.1 \cdot 10^3$ and $0.66 \cdot 10^3$. The values were calculated from the extinction at the maximum of the curve, together with the slope of the tangent at the end branches with excess of tiron and excess of iron(III), respectively. These values of K were, however, very sensitive to small deviations in the slope of the tangents. The curve was slightly asymmetrical, probably because of the formation of small amounts of $FeTi_2$ complex, so that the value $0.66 \cdot 10^3$ is probably the more reliable one. At this point the great advantage of the "extinction ratio method" appears to be demonstrated fully, *i.e.* that only data for solutions with the components present in the stoichiometric molar ratio are used. These solutions contain the maximum amounts of the complex in question, and the minimum amounts of complexes with different composition.

THE IRON(III)–CHROME AZUROL S SYSTEM

This system has previously been investigated by LANGMYHR AND KLAUSEN[5,10]. In the present experiments, the conditions for the formation of the 2:2 complex were established, *i.e.* pH 3.40, room temperature and ionic strength 0.1 M (KCl). The curve of continuous variation has been given previously[5]. The experiments were carried out in the following way. Five different concentration sums (and light paths) were used. In each solution iron(III) and chrome azurol S were mixed in equimolar amounts. For each concentration sum, reagent blank solutions were made, which contained the same amount of all the reagents as in the test solution, but not iron(III). The extinctions were measured with a Zeiss PMQ II spectrophotometer against distilled water at 570 nm. The extinctions for the reagent blank solutions were subtracted from those of the test solutions. The results are given in Table VII. The extinctions are mean values for several parallel solutions.

TABLE VII

MEASURED EXTINCTIONS AT 570 nm EQUIMOLAR SOLUTIONS OF IRON(III) AND CHROME AZUROL S AT pH 3.40

Solution no.	*Concentration sum*	*Light path*	*Extinctions*		
			Complex	*R. blank*	*Difference*
1	$2c = 8\cdot10^{-5}\,M$	$l/2 = 0.5$ cm	0.537	0.126	0.411
2	$c = 4\cdot10^{-5}\,M$	$l = 1$ cm	0.515	0.137	0.378
3	$c/2 = 2\cdot10^{-5}\,M$	$2l = 2$ cm	0.458	0.145	0.313
4	$c/4 = 1\cdot10^{-5}\,M$	$4l = 4$ cm	0.375	0.146	0.229
5	$c/5 = 8\cdot10^{-6}\,M$	$5l = 5$ cm	0.342	0.146	0.196

TABLE VIII

EXTINCTION RATIOS AND LOG (Kc^{m+n-1}) VALUES FOR THE IRON(III)–CHROME AZUROL S SYSTEM

No.	*Extinction ratio*	*A_2B_2 complex*		*AB complex*	
		log(Kc^3) (Fig. 2)	*corrected 0.90*	*log (Kc) (Fig. 1)*	*corrected 0.30*
1	f($c/2,c$) = 0.829	3.15	3.15	0.96	0.96
2	f($c/4,c$) = 0.605	3.20	3.20	0.85	0.85
3	f($c/5,c$) = 0.519	3.22	3.22	0.76	0.76
4	f($c,2c$) = 0.920	4.35	3.45	1.70	1.40
5	f($c/2,2c$) = 0.761	4.13	3.23	1.42	1.12
6	f($c/5,2c$) = 0.476	4.15	3.25	1.18	0.88
7	f($c/4,c/2$) = 0.731	2.40	3.30	0.45	0.75

As in the previous example the calculated extinction ratios were plotted on both of the Figs. 1 and 2. The results are shown in Table VIII. In Table VIII the check of the first criterion is executed by adding or subtracting $(m + n - 1)$ log 2 to the log(Kc^{m+n-1}) values from the ratios f(..,$c/2$) and f(..,$2c$), respectively, no correction being made on the f(..,c) ratio values. The value of $(m+n-1)$ log 2 is given in the heading of the columns for the corrected values.

The corrected values obtained when the A_2B_2 complex is tried, are equal within experimental error. The difference is 0.30 between the highest and the lowest value. Further, it can be seen that the values do not fit the trial AB complex; the difference here is 0.65 between the highest and the lowest value, and for a 1:1 complex a smaller variation is tolerated than for a 2:2 complex.

The mean value log(Kc^3) = 3.25 gives the conditional constant (pH 3.40) of the complex equal to $2.8\cdot10^{16}$. From this value the logarithm of the absolute stability constant of the 2:2 complex[10] can be calculated to be 37.6.

SUMMARY

A method for the determination of stability constants of complexes in solution is described. It is based on the method of continuous variation and on computer calculated values of the maximum complex concentrations for different total molar concentrations. The measurements are carried out in cells of different light paths, and the molar concentration sum is chosen so that the product of the light path and the concentration sum is constant. The method can be used to differentiate between monomeric and dimeric complexes A_mB_n, with $m = n$.

RÉSUMÉ

On décrit une méthode pour la détermination des constantes de stabilité de complexes en solution. Elle est basée sur la méthode de variation continue et sur les valeurs, obtenues au moyen d'une calculatrice, des concentrations maximales des complexes par rapport aux différentes concentrations molaires totales. Les mesures sont effectuées dans des cellules de différentes épaisseurs et la somme des concentrations molaires est choisie de telle sorte que le produit du chemin lumineux par la somme des concentrations soit constant. La méthode peut être utilisée pour différencier des complexes monomère et dimère — (A_mB_n) avec $m=n$.

ZUSAMMENFASSUNG

Eine Methode zur Bestimmung von Stabilitätskonstanten von Komplexen in Lösung wird beschrieben. Sie beruht auf der Methode der kontinuierlichen Variation und auf Computer-Berechnungen für die maximalen Komplexkonzentrationen von verschiedenen totalen Molkonzentrationen. Die Messungen werden in Zellen mit verschiedenen Lichtwegen durchgeführt und die Summe der molaren Konzentration so gewählt, dass das Produkt aus dem Lichtweg und der Summe der Konzentration konstant ist. Die Methode kann zur Unterscheidung zwischen monomeren und binären Komplexen A_mB_n mit $m=n$ verwendet werden.

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FLUORESCENCE AND METALLIC VALENCY STATES

PART I. DETERMINATION OF SILVER WITH OXINE-5-SULPHONIC ACID

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Differences in the fluorescent (and phosphorescent) lifetimes of some metal complexes have been explained on the basis of varying degrees of interaction between the electrons responsible for fluorescence and the field of the metal ion[1]. STEVENS[2] has discussed the relationship between electronic structures of metal ions and their relative abilities to form fluorescent species with oxine; he concluded that only those ions which are diamagnetic when coordinated and which are not capable of possessing more than one stable valency can be expected to form fluorescent metal chelate compounds. Thus, zinc and cadmium, which form ions of one stable valency, fluoresce, but copper, gold, and mercury possess two relatively stable valencies, energy is dissipated internally, and their complexes are consequently non-fluorescent. Although metals capable of possessing more than one stable valency may not normally form fluorescent chelates, coordination of a chelating molecule does alter the oxidizing or reducing power of a metal ion and states normally unstable in aqueous solution may be stabilized; there seems to be no reason why $\pi \rightarrow \pi^*$ transitions in such chelates should not lead to fluorescence if the complexes are diamagnetic. Alternatively, metals might be determined fluorimetrically by using variable valency to produce fluorescent reagent products (from normally non- or weakly-fluorescent organic molecules) through oxidation–reduction reactions.

A program has therefore been initiated to investigate the possible use of normally unstable valencies to form fluorescent species useful in the analysis of metals through either (*a*) the formation of stable, fluorescent diamagnetic chelates or (*b*) the specific oxidative reaction of higher valent metal ions upon selected organic molecules to give fluorescent reagent products. The present paper describes one such investigation which permits the determination of traces of silver; the fluorescence developed on treatment of silver(I) solutions with persulphate and oxine-5-sulphonic acid, is measured at 485 nm after excitation at 375 nm.

Oxine has been used by a number of workers for the fluorimetric determination of metal ions[3–10], and the potentialities of some oxine derivatives have been explored; none is superior to oxine but the 5-sulphonic acid is effective in aqueous solution[11–14]. The reported major influence of polar constituents (like OH, NH_2, CO_2H, SO_3H) in the 5-position is to form species soluble in water or other polar solvents[12]. Most determinations have been made at a pH greater than 5 where selectivity is generally poor. For oxine, close pH control, masking agents, and solvent extraction are combined to give more selectivity; for oxine-5-sulphonic acid, which forms water-soluble species, improvement in selectivity is limited to pH control and the use of masking agents. It is evident that fluorimetric determination in acid solution with these reagents would automatically eliminate the interference of many metals that fluoresce only at higher pH values; the procedure described for silver involves measurement in the pH range 1.5 to 3.5 where many metals do not react to form oxine complexes.

EXPERIMENTAL

Apparatus, reagents and solutions

An Aminco Bowman Spectrophotofluorimeter with corrected spectrum attachment was used for obtaining excitation and emission spectra. Intensity measurements at 485–90 nm were uncorrected.

8-Hydroxyquinoline-5-sulphonic acid was recrystallized several times from water and dried at 110°; the melting point was 320–323° with decomposition. Reagent solutions (10^{-4} M) were freshly prepared in doubly distilled water.

Stock silver solutions (0.1 M) were prepared from Analar silver nitrate and were standardized by FAJAN's method using dichlorofluorescein as indicator.

Potassium persulphate solutions (0.1 M) were freshly prepared from Analar potassium persulphate.

Procedure

To a solution containing 0.1–10 μg of silver, add a 10–25-fold molar excess of oxine-5-sulphonic acid and adjust the pH between 1.5 and 3.5. Add 5 ml of 0.1 M potassium persulphate solution and dilute to 10 ml in a volumetric flask. Measure the fluorescence intensity at 485 nm between 60 and 90 min after addition of persulphate; the excitation wavelength is 375 nm. A reagent blank should be run concurrently.

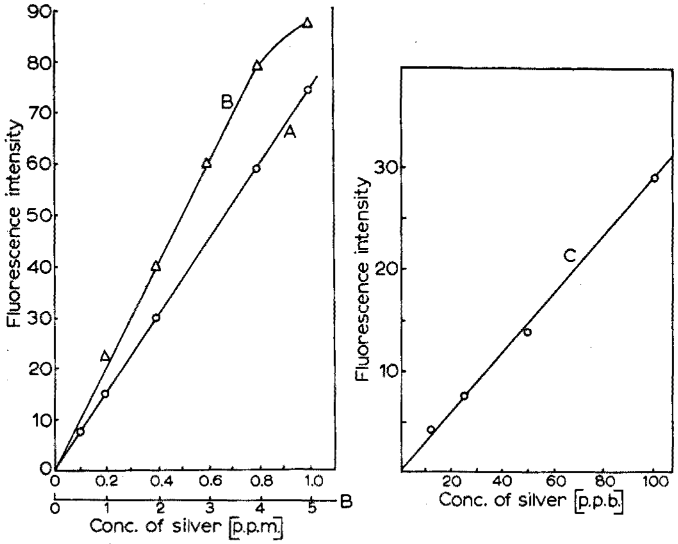

Fig. 1. Calibration curves. (A) 0.1–1.0 p.p.m. Ag at meter multiplier (MM) setting 0.001 and sensitivity (S) 0; (B) 1.0–5.0 p.p.m. Ag at MM 003 and (S) 0; (C) 12.5–100 p.p.b. Ag at MM 0.001 and (S) 30.

Typical results (corrected for reagent emission) are shown in Fig. 1. Excitation and emission spectra obtained using the corrected spectra attachment are shown in Fig. 2. Except in Fig. 2, all results are corrected for reagent emission.

Factors affecting fluorescence intensity

The fluorescence intensity is linear between 12.5 p.p.b. and 5 p.p.m. of silver. Lower concentrations of silver may be estimated but, at maximum instrument sensitivity, the noise level becomes significant and reproducibility is poor.

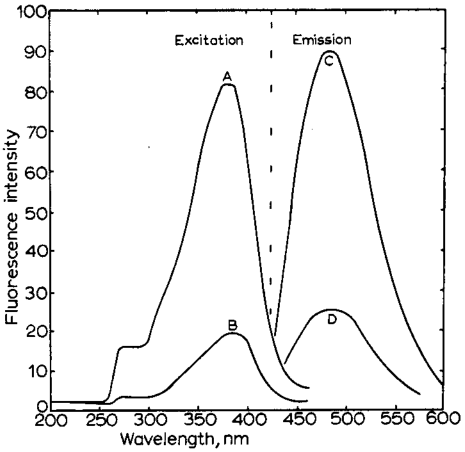

Fig. 2. Corrected spectra. A and B are excitation spectra of complex (1 p.p.m. Ag) and reagent respectively (emission λ, 485 nm); C and D are corresponding emission spectra (excitation λ, 375 nm).

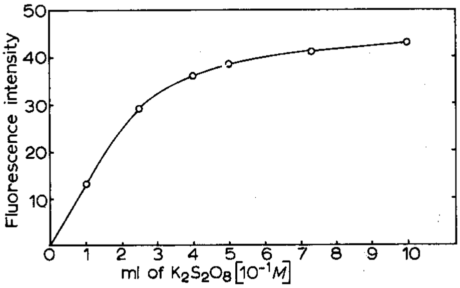

Fig. 3. Variation in fluorescence intensity with persulphate concentration (0.5 p.p.m. Ag at MM 0.001 and (S) 0).

Constant maximum intensity is obtained in the pH range 1.5–3.5. The intensity decreases at lower and higher pH values; no fluorescence is observed in 1 *N* acid and, at pH values greater than 5, a shift of emission maxima to a higher wavelength occurs.

The fluorescence intensity reaches a maximum after 1 h, remains constant for 1 h, and then slowly increases. All analytical measurements were therefore made between 60 and 90 min after the addition of persulphate.

Intensities are maximum and constant when reagent to metal mole ratios exceed 10:1; low results are obtained at lesser reagent concentrations and ratios higher than 100:1 were not tried.

Persulphate plays a vital role in producing and enhancing fluorescence. Figure 3 shows the rapid intensity increase as the persulphate concentration increases; there is little change in intensity after 5 ml of 0.1 *M* persulphate are added and this amount is recommended.

The fluorescence is quenched by prolonged heating but heating at 70° for 5 min speeds up the reaction rate and a maximum is obtained which gradually diminishes with time. Results, however, were not as reproducible as those obtained at room temperature by the recommended procedure.

RESULTS

Twelve samples, each containing 0.4 p.p.m. of silver, were analyzed by the above procedure; the percent standard deviation was 2.1. As expected, several hundred p.p.m. of normally fluorescent metal–oxine-5-sulphonic acid chelates did not interfere at the pH of measurement; 500 p.p.m. of Ca^{2+}, Cd^{2+}, Mg^{2+}, Mn^{2+}, NH_4^+, Pb^{2+}, Zn^{2+}, and 200 p.p.m. of Be^{2+} and Th^{4+} did not interfere. Results were also satisfactory in the presence of 100 p.p.m. Li^+, 75 p.p.m. Al^{3+}, 50 p.p.m. La^{3+}, 20 p.p.m. Co^{2+}, 10 p.p.m. Ni^{2+} and Fe^{3+}. However, more than 1 p.p.m. of Cu^{2+}, Hg^{2+} and Pd^{2+} caused quenching of the fluorescence whilst similar amounts of Zr^{4+} and Hf^{4+} caused a large increase in the fluorescence intensity.

Large amounts (10,000 p.p.m.) of sodium, potassium, sulphate, nitrate, perchlorate and chlorate had no effect on the results obtained but only 10 p.p.m. of chloride could be tolerated. Results in the presence of chloride were improved on the addition of mercury(II) sulphate but, since close control of mercury(II) ion concentration is also necessary, such addition was not very practicable. No fluorescence was observed when EDTA was present (1 ml 0.01 *M*) and fluorescence was also destroyed in solutions containing 20% of ethanol, acetone, or dioxane.

Nature of reaction

Whether the fluorescent product used for determining silver is a stable silver-(III)–oxine-5-sulphonic acid chelate or an oxidized product of oxine-5-sulphonic acid is not completely clear; present evidence would suggest that an oxidized reagent product is formed. It has been shown by various workers[15–18] that silver(I) is undoubtedly oxidized to silver(III) by persulphate; the process, though slow, is definite and measurable. The silver(III) thus produced is a strong oxidizing agent which may oxidize the reagent to give a fluorescent species. At pH 2, oxine-5-sulphonic acid gives only a slight greenish fluorescence in the presence of persulphate but the intensity is markedly increased if trace amounts of silver(I) are added; a similar fluorescence is obtained at pH 2 with other oxidizing agents such as permanganate, manganese dioxide or lead dioxide. Direct supporting evidence for the formation of an oxidized reagent product is difficult because of the aqueous solubility and non-extractability of the fluorescent species; it is clear, however, that formation of the fluorescent product which permits the spectrofluorimetric determination of silver is dependent upon the presence of higher valency states of silver (presumably silver(III)). A detailed investigation of the nature of the fluorescent species is in progress.

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SUMMARY

Small amounts (0.1–10 μg) of silver can be determined by measurement of the fluorescent intensity (at 485 nm) obtained on addition of persulphate to aqueous solutions (pH 1.5–3.5) containing silver(I) and oxine-5-sulphonic acid. Fluorescence intensity is linear from 12.5 p.p.b. to 5 p.p.m. and most metal ions do not interfere;

1 p.p.m. of copper, mercury or palladium, causes fluorescence quenching whilst similar amounts of zirconium and hafnium form strongly fluorescent chelates and cause high results. The reaction involves formation of silver(III) which then reacts with the oxine-5-sulphonic acid to give the fluorescent product.

RÉSUMÉ

On peut déterminer de petites quantités d'argent (0.1 à 10 μg) par mesure de l'intensité de la fluorescence (à 485 nm) obtenue par addition de persulfate dans des solutions aqueuses de pH compris entre 1.5 et 3.5 contenant de l'argent(I) et de l'acide oxine-5-sulfonique. La loi de Beer est suivie de 12.5 p.p.b. à 5 p.p.m. et la plupart des ions métalliques n'interfèrent pas; 1 p.p.m. de cuivre, de mercure ou de palladium provoque la disparition de la fluorescence alors que des quantités semblables de zirconium et d'hafnium forment des chélates très fluorescents et sont la cause de résultats trop forts lors de l'analyse. La réaction comprend la formation d'argent(III) qui réagit alors avec l'acide oxine-5-sulfonique en donnant le produit fluorescent.

ZUSAMMENFASSUNG

Kleine Mengen (0.1 bis 10 μg) Silber können durch Messung der Fluoreszenzintensität (485 nm) bestimmt werden. Gemessen wird eine wässrige Lösung (pH 1.5–3.5) die Silber(I) und Oxin-5-sulfonsäure enthält und zu der Persulfat gegeben wurde. Das Beersche Gesetz wird von 12.5 p.p.b. bis 5 p.p.m. befolgt; Metallionen stören nicht. 1 p.p.m. Kupfer, Quecksilber oder Palladium verursachen eine Auslöschung Fluoreszenz, während ähnliche Mengen von Zirkonium und Hafnium stark fluoreszierende Chelate und damit eine Erhöhung der Ergebnisse verursachen. Bei der Reaktion wird Silber(III) gebildet, das mit der Oxin-5-sulfonsäure ein fluoreszierendes Produkt ergibt.

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THE QUANTITATIVE ANALYSIS OF HYDRAZINE MIXTURES BY PROTON MAGNETIC RESONANCE SPECTROMETRY

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Various mixtures of hydrazine, monomethylhydrazine and asymmetrical dimethylhydrazine are important as fuels in rocket systems and in fuel cells. The mixtures, blended in certain proportions, possess certain properties superior to the individual fuels. Investigation of these systems requires analytical methods and several such methods have been developed: gas chromatography[1], iodate titration in an aqueous system[2], selective reaction of hydrazine with salicylaldehyde followed by non-aqueous titration with standard acid[3], and differential reaction rates with acetic anhydride[4]. Although electrometric methods have yet to be applied to mixtures of the above hydrazines, anodic chronopotentiometry has been used to analyze mixtures of hydrazine and hydroxylamine[5]. These methods have various disadvantages among which are standard solution requirements, necessity of calibration data, and lack of speed. Proton magnetic resonance spectrometry (PMR) requires no standard solutions or calibration data, and is a rapid method of quantitative analysis. The application of PMR to analysis of hydrazine mixtures is herein reported.

EXPERIMENTAL

The experiments were performed using the Varian Model A-60 PMR spectrometer at ambient temperatures. The frequency response was 4 c.p.s. The r.f. power setting was 0.16 milligauss for spectral recording, and 0.60 milligauss for integral recording; sweep rates were 2 and 20 c.p.s., respectively.

The hydrazine, methylhydrazine and asymmetrical dimethylhydrazine were commercial products (Matheson, Coleman and Bell) and were used without further purification. Titration with standard acid showed all three compounds to be better than 99% pure and no contamination was observed when the PMR spectrometer was used.

DISCUSSION

PMR in analytical chemistry is concerned mainly with qualitative analysis, but experimental conditions for quantitative analysis have been investigated intensively[6,7]. It was concluded from such research that quantitative analysis by PMR should involve the use of internal reference standards and of peak area integration at experimentally determined r.f. power level and scan rate.

Here, in the analysis of hydrazine mixtures containing no other species, reference standards are not necessary. The components of the hydrazine mixture serve as reciprocating reference standards. The experimental determination of r.f. power level and scan rate is indeed desirable, but here was deemed too time-consuming to be done on a routine basis. The difficulty is that each change of the r.f. power level requires a readjustment of the r.f. phase sensitive detector which is very time-consuming. In this work, instrument settings found reasonable by previous workers[6,7], were used without further investigation, and the results justify this selection of experimental conditions.

The experimentally determined PMR peak positions of hydrazine, methylhydrazine and asymmetrical dimethylhydrazine are listed in Table I for tetramethylsilane as the internal standard. The values in brackets in Table I are for 100% hydrazines[8] and agreement is within experimental error except for the amine protons of hydrazine. The disagreement in the case of hydrazine probably results from a trace of water in the commercial hydrazine. Proton exchange between the hydrazines and trace water is sufficiently rapid to yield a single peak[9] between the amine peak position of 100% hydrazine and the peak position of water run neat. The frequency position of this exchange peak is critically dependent upon trace water concentration and, if the analyst required the determination of trace water in hydrazines, a calibration plot of peak position *versus* water content of hydrazine would yield a rapid and simple chemical analysis.

TABLE I

PROTON ABSORPTIONS OF HYDRAZINES (p.p.m. *versus* tetramethylsilane)

	Methyl	*Amine*
Hydrazine		4.25 (3.65)
Methylhydrazine	2.52 (2.52)	3.57 (3.56)
Dimethylhydrazine	2.35 (2.34)	3.23 (3.21)

The amine protons of the different hydrazines also interchange rapidly and a single amine proton absorption is observed, the chemical shift of this amine peak being also dependent upon the hydrazine mole fractions. However, the separation of the single amine and the methyl peaks allows the integration of the area under these peaks. The relative areas, corrected statistically to area per proton, are then used to calculate the hydrazine mole fractions assuming only hydrazines to be present. The simultaneous equations necessary for the three possible binary mixtures and the ternary mixture are given as eqns. 1–4, where the units of hydrazine concentrations are mole fractions and A, B, C are integrated amine, methyl, and dimethyl absorptions respectively, H, MMH and DMH being hydrazine, monomethylhydrazine and dimethylhydrazine, respectively.

$$\begin{aligned} 4\times \mathrm{H}+3\times \mathrm{MMH}&=\mathrm{A} \\ 3\times \mathrm{MMH}&=\mathrm{B} \end{aligned} \qquad (1)$$

$$\begin{aligned} 4\times \mathrm{H}\quad 2\times \mathrm{DMH}&=\mathrm{A} \\ 6\times \mathrm{DMH}&=\mathrm{B} \end{aligned} \qquad (2)$$

$$\begin{aligned} 3 \times \mathrm{MMH} + 2 \times \mathrm{DMH} &= \mathrm{A} \\ 3 \times \mathrm{MMH} + 6 \times \mathrm{DMH} &= \mathrm{B} \end{aligned} \tag{3}$$

$$\begin{aligned} 4 \times \mathrm{H} + 3 \times \mathrm{MMH} + 2 \times \mathrm{DMH} &= \mathrm{A} \\ 3 \times \mathrm{MMH} &= \mathrm{B} \\ 6 \times \mathrm{DMH} &= \mathrm{C} \end{aligned} \tag{4}$$

Results obtained by means of eqns. 1–4 are shown in Tables II–V. The observed average deviations in the mole fractions determined by means of PMR were 0.008, 0.003, 0.018, respectively, for the 24 binary mixtures of hydrazine–methylhydrazine,

TABLE II

ANALYSIS OF HYDRAZINE–METHYLHYDRAZINE MIXTURES

Mole fraction hydrazine		
Added	*Found*	*Difference*
0.053	0.046	−0.007
0.153	0.146	−0.007
0.156	0.159	+0.003
0.354	0.368	+0.014
0.492	0.495	+0.003
0.532	0.522	−0.010
0.747	0.734	−0.013

TABLE III

ANALYSIS OF HYDRAZINE–ASYMMETRICAL DIMETHYLHYDRAZINE MIXTURES

Mole fraction dimethylhydrazine		
Added	*Found*	*Difference*
0.024	0.021	−0.003
0.092	0.095	+0.003
0.101	0.104	+0.003
0.244	0.244	0.000
0.500	0.502	+0.002
0.757	0.762	+0.005

TABLE IV

ANALYSIS OF METHYLHYDRAZINE–ASYMMETRICAL DIMETHYLHYDRAZINE MIXTURES

Mole fraction methylhydrazine		
Added	*Found*	*Difference*
0.088	0.109	+0.021
0.367	0.365	−0.002
0.397	0.374	−0.023
0.500	0.546	−0.004
0.565	0.548	−0.017
0.601	0.616	+0.015
0.607	0.619	+0.012
0.750	0.777	+0.027
0.790	0.808	+0.018
0.863	0.883	+0.020
0.941	0.979	+0.038

TABLE V

ANALYSIS OF TERNARY MIXTURES

Hydrazine[a]			*Methylhydrazine*[a]			*Dimethylhydrazine*[a]		
Added	*Found*	*Diff.*	*Added*	*Found*	*Diff.*	*Added*	*Found*	*Diff.*
0.493	0.502	+0.009	0.389	0.391	+0.002	0.118	0.106	−0.012
0.693	0.704	+0.011	0.174	0.172	−0.002	0.133	0.124	−0.009
0.748	0.759	+0.011	0.117	0.113	−0.004	0.134	0.128	−0.006

[a] Expressed as mole fractions.

hydrazine–dimethylhydrazine, and methylhydrazine–dimethylhydrazine, and 0.008 for the 3 ternary mixtures. Proton magnetic resonance spectrometry in the integral recording mode requires less than 10 sec and is thus a rapid and convenient method for the quantitative determination of all four possible hydrazine mixtures. Moreover, it is the only analytical technique so applicable to all four mixtures.

SUMMARY

The application of proton magnetic resonance spectrometry to the quantitative analysis of binary and ternary mixtures of hydrazine, monomethylhydrazine, and asymmetrical dimethylhydrazine is described. The methyl absorptions and the amine exchange absorption serve as reciprocating internal reference standards. The integrated absorptions, corrected statistically to area per proton, are used in simultaneous equations. The solution of the equations yields the analytical result expressed as mole fraction. Twenty seven hydrazine mixtures were analyzed; the average deviation in mole fraction was less than 0.01.

RÉSUMÉ

On décrit l'application de la spectrométrie de résonance magnétique du proton à l'analyse quantitative de mélanges binaire et ternaire d'hydrazine, de monométhylhydrazine et de diméthylhydrazine asymétrique. Les absorptions dues au groupe méthyle et les absorptions d'échange dues aux amines servent réciproquement de références internes standards. Les absorptions intégrées, corrigées statistiquement par rapport à la surface par proton, sont utilisées dans des équations simultanées. La résolution des équations fournit un résultat analytique exprimé en fraction de mole. Vingt-sept mélanges d'hydrazine ont été analysés; la déviation moyenne en fraction de mole fut inférieure à 0.01.

ZUSAMMENFASSUNG

Die Anwendung der protonenmagnetischen Resonanz zur quantitativen Analyse binärer und ternärer Mischungen von Hydrazin, Monomethylhydrazin und asymmetrischem Dimethylhydrazin wird beschrieben. Die Methylabsorptionen und die Aminaustauschabsorption dienen als wechselseitiger innerer Standard. Die integrierten Absorptionen welche statistisch auf den Raum pro Proton korrigiert

wurden, werden in den Simultangleichungen verwendet. Die Lösung dieser Gleichungen führt zum Molenbruch als analytisches Ergebnis. 27 Hydrazinmischungen wurden analysiert. Die durchschnittliche Abweichung der Molfraktion betrug weniger als 0.01.

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FLUORIMETRIC DETERMINATION OF OXALATE ION

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The only fluorimetric method that seems to be available for measuring oxalate ion was published in this journal in 1966[1]. The method is based on the principle that non-fluorescent cerium(IV) may be reduced to fluorescent cerium(III) by oxalate ion in the presence of a catalyst, and is applicable to 8.8–44.0 μg of oxalate per 100 ml of sample solution. ZAREMSKI AND HODGKINSON[2] developed a fluorimetric method for oxalic acid in which the acid is reduced to glyoxalic acid and coupled with resorcinol to form a colored fluorescent complex; the maximum sensitivity of this method is 8 μg of oxalic acid per 100 ml of sample solution.

ALFORD *et al.*[3] described a fluorimetric method for the determination of zirconium by reaction with flavonol (3-hydroxyflavone). This paper presents an approach to the determination of oxalate ion based on the quenching of zirconium–flavonol fluorescence by oxalate. The method is simple, and subject to few interferences. This technique is more sensitive than the two methods described previously. As little as 0.5 μg or 5 p.p.b. of oxalate ion can be determined.

EXPERIMENTAL

Apparatus

Fluorescence intensity measurements were made with a Beckman Model DU spectrophotometer equipped with a Beckman Model 73500 fluorescence attachment. A F4T5/BL mercury lamp providing radiation in the range of 310 to 390 nm, with maximum intensity at 365 nm, is satisfactory for excitation. A Beckman Zeromatic II pH meter was used for all pH measurements.

Reagents

Zirconium solution. A standard solution was prepared by dissolving zirconyl chloride octahydrate in 7.2 *N* sulfuric acid. This solution was analyzed gravimetrically by precipitation as the phosphate and ignition to the pyrophosphate. This standard solution contained 10.417 mg of zirconium per ml. The stock solution of 1 mg of zirconium per ml was prepared by combining 24 ml of the original standard solution with 26 ml of 7.2 *N* sulfuric acid and diluting to 250 ml with water. The 20 μg zirconium per ml solution was prepared by diluting 2 ml of the 1 mg/ml solution to 100 ml with 3.24 *N* sulfuric acid.

Flavonol (3-hydroxyflavone) solution. A 0.10% solution was prepared by dissolving 250 mg of flavonol in 250 ml of 95% ethanol. The 70 μg/ml solution was prepared by diluting 7 ml of the standard solution to 100 ml with 95% ethanol.

Oxalate solution. A stock solution of oxalate was prepared by dissolving 20.932 g of potassium oxalate monohydrate in 1 l of water. More dilute oxalate solutions were prepared by suitable dilution.

All other reagents (analytical grade) were used without further purification. Flavonol was obtained from Eastman Kodak Company, lot No. 3A. The 95% ethanol was redistilled, and water was deionized.

Recommended procedure

Prepare a calibration curve by adding up to 10 μg of oxalate ion to 100-ml volumetric flasks and bringing to a total volume of 10 ml with deionized water. To each flask add 1 ml of 20 μg/ml zirconium solution and 1 ml of 70 μg/ml flavonol solution. Dilute to 100 ml with water and mix. Measure the fluorescence intensity at 460 nm for each solution at any predetermined time within 7 h.

A sample containing oxalate in the concentration range 0.5–10 μg may be analyzed by placing a solution containing the ion in a 100-ml volumetric flask. The sample volume should be adjusted to 10 ml and the above procedure followed.

RESULTS AND DISCUSSION

Optimum wavelength for fluorescence

The maximum fluorescence emission for the zirconium–flavonol chelate occurs at 460 nm as reported by WHITE *et al.*[4]. The wavelength of maximum fluorescence is not altered by the presence of oxalate.

Effect of pH

Figure 1 shows the effect of the amount of sulfuric acid present on the fluorescence of two solutions. One solution contained only the fluorescent zirconium–flavonol chelate, while the other contained 5 μg of oxalate in addition to the chelate. The fluorescence maximum, and the largest decrease in fluorescence caused by oxalate, occurred at pH 1.80, which corresponded to the addition of 3.0 ml of 0.8 *N* sulfuric acid. The percentage quenching by 5 μg of oxalate was very nearly the same for the range 3–10 ml of 0.8 *N* sulfuric acid added. This corresponded to a pH range of 1.80 to 1.38. A pH of 1.69, which corresponded to 4 ml of sulfuric acid, is obtained if the recommended procedure is followed with the reagents as described.

Effect of concentration and ratio of zirconium and flavonol

To determine the mole-ratio of the zirconium–flavonol chelate and to determine the best ratio of flavonol to zirconium for quenching by oxalate, the method of continuous variations was used. A plot of the mole fraction of flavonol *vs.* fluorescence intensity resulted in a maximum at a 1:1 mole ratio. The mole ratio was not altered by the presence of oxalate, and the percentage quenching by oxalate was somewhat higher with a slight excess of flavonol present.

To determine the optimum amounts of flavonol and zirconium, studies were conducted with constant amounts of zirconium and increasing amounts of flavonol, and constant amounts of flavonol with increasing amounts of zirconium. Maximum percentage quenching by oxalate in amounts of 0.5 to 20 μg occurred with 0.22 μmoles of zirconium and 0.29 μmoles of flavonol in 100-ml volumes.

Effect of ethanol

Ethanol in excess of the 1 ml introduced with the flavonol solution caused a decrease in the fluorescence intensity of zirconium–flavonol solutions, both with and without 5 μg of oxalate present. The percentage quenching by oxalate was also reduced by the presence of additional ethanol.

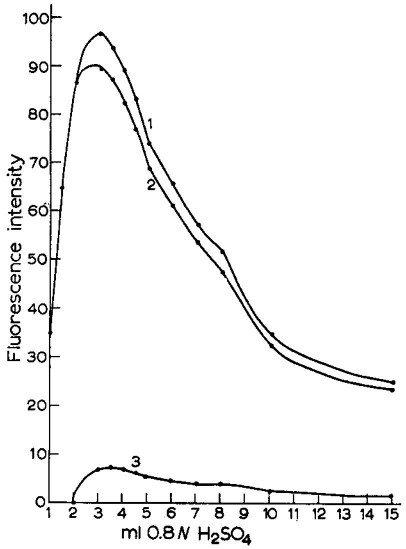

Fig. 1. Effect of amount of 0.8 *N* sulfuric acid. (1) No added oxalate; (2) 5 μg oxalate present; (3) Fluorescence intensity increment, 1 — 2.

Effect of time

The fluorescence intensity of a zirconium–flavonol solution was equally as stable as a solution containing 5 μg of oxalate in addition to the chelate. There was no change in the fluorescence intensity of either solution for 7 h following an initial fluorescence measurement 10 min after the solutions were prepared.

Effect of temperature

The temperature at which the sample solutions were maintained before the fluorescence intensity measurements did not affect the fluorescence or the percentage quenching. Solution temperatures above room temperature during the fluorescence measurement caused a decrease in both fluorescence intensity and percentage quenching.

Calibration curves

A linear calibration curve was obtained for 0–10 μg of oxalate ion when the recommended procedure was used. There was a linear decrease in fluorescence intensity with an increase in the amount of oxalate from 0.5 to 10 μg.

Effect of diverse ions

Several ions were added to the system with 5 μg of oxalate present in order to study interferences. The results of this investigation are shown in Table I and Table II. Of the 41 ions tested, 27 did not interfere at the 100 p.p.m. level, while only four could not be tolerated in at least a ten-fold excess.

TABLE I

INTERFERING IONS

(With 5 μg of $C_2O_4^{2-}$ in 100 ml of sample solution)

Ions	*Amount permitted*[a] *(μg)*	*Ions*	*Amount permitted (μg)*
UO_2^{2+}	6000	$Cr_2O_7^{2-}$	200
BrO_3^-	5000	Fe^{3+}	100
SiO_3^{2-}	4000	WO_4^{2-}	80
IO_3^-	1000	MoO_4^{2-}	20
Al^{3+}	500	IO_4^-	20
NO_2^-	400	Citrate	20
PO_4^{3-}	200	F^-	1

[a] 3% error considered tolerable.

TABLE II

TOLERATED IONS

(Ions which do not interfere at 10 mg per 100 ml of sample solution)[a]

Ions[b]	*Ions*	*Ions*
Na^+	Mg^{2+}	ClO_3^-
K^+	Ni^{2+}	SO_4^{2-}
NH_4^+	Cu^{2+}	$S_2O_3^{2-}$
Ca^{2+}	Cd^{2+}	SO_3^{2-}
Sr^{2+}	Co^{2+}	SCN^-
Hg^{2+}	Cr^{3+}	$C_2H_3O_2^-$
Zn^{2+}	CO_3^{2-}	Cl^-
La^{3+}	NO_3^-	Br^-
Mn^{2+}	ClO_4^-	I^-

[a] 5 μg of oxalate present.
[b] 3% error considered tolerable.

SUMMARY

A very selective, simple, sensitive fluorimetric method for the determination of oxalate ion is described. The method is based on the quenching by oxalate of the fluorescence of a 1:1 zirconium–flavonol chelate in dilute sulfuric acid solution. The fluorescence is measured at 460 nm. A linear calibration curve is obtained for 0–10 μg of oxalate ion; there are very few interferences.

RÉSUMÉ

Une méthode fluorimétrique très sélective, simple et sensible est décrite pour la détermination de l'ion oxalate. La méthode est basée sur l'arrêt, au moyen de l'oxalate, de la fluorescence du chélate zirconium–flavonol (1:1) en solution diluée d'acide sulfurique. La fluorescence est mesurée à 460 nm. Une courbe de calibration linéaire est obtenue pour des quantités de l'ion oxalate allant de 0 à 10 μg; il y a très peu d'interférences.

ZUSAMMENFASSUNG

Eine sehr selektive einfache empfindliche fluorimetrische Methode zur Bestimmung von Oxalationen wird beschrieben. Die Methode beruht auf der Auslöschung der Fluoreszenz des 1:1 Zirkonium–Flavonol-Chelats in verdünnter Schwefelsäure durch Oxalat. Die Fluoreszenz wird bei 460 nm gemessen. Eine lineare Eichkurve wurde für 0–10 μg Oxalation erhalten. Es treten nur wenige Störungen auf.

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AN IMPROVED FLUORIMETRIC DETERMINATION OF HISTAMINE BY STABILIZING THE *o*-PHTHALALDEHYDE REAGENT

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The reaction between histamine and *o*-phthalaldehyde (OPT) to give a fluorophore was first adapted by SHORE *et al.*[1] to the determination of histamine in aqueous solution. The fluorimetric methods had been widely used, and it has been extended to the resolution of histamine in chromatograms[2,3]. BEALL[4], however, reported that OPT consisted of more than one active component so that its use could cause inaccuracies. Modifications of the method have indicated a need to improve the separation procedure to eliminate interferences[5,6]. Moreover, the likelihood that the extraction of histamine from natural sources can involve interferences is indicated by the numerous fluorophores made by reacting OPT with amines[3,7,8] and with a tripeptide[9].

In order that the analysis of histamine may be capable of determining the slight concentration changes which occur in physiological tissues and fluids, the method of assay should not only be precise and accurate but also it should detect interferences. The present report describes a more precise and reliable assay by keeping recrystallized OPT completely anhydrous before the condensation reaction, even though the histamine–OPT fluorophore is prepared in aqueous solution.

EXPERIMENTAL

Reagents

Anhydrous OPT. The reagent as received (see Table I for suppliers) was recrystallized from petroleum ether (dried over anhydrous sodium sulfate). For filtration of the hot solution (35 ml for 0.5 g of OPT), which contains undissolved residue, filter paper covered with a slurry of Celite Analytical Filter Aid was used. The filtration was performed in a pre-heated oven flushed with nitrogen at a temperature just below the boiling point of the solvent to provide an inert atmosphere and prevent crystallization. After the filtrate had cooled for 30 min, almost all of the supernatant liquid was decanted to leave the solid OPT wet with solvent. Portions of the OPT slurry were placed in previously dried and weighed screw-cap vials (moistened with petroleum ether). For an exact weight, the volatile solvent was removed by allowing the vials to remain in the nitrogen-flushed oven. OPT was dissolved in sufficient *p*-xylene (dry, see below) to give a 0.1% solution[6]. The 0.1% OPT solution, stable in *p*-xylene over 3 weeks, was stored in a desiccator over sodium hydroxide.

p-*Xylene*[2,3]. The *p*-xylene (reagent grade) was dried by direct addition of pressed sodium wire.

Apparatus

A Turner fluorimeter was used for the determination of histamine with a 7-60 Corning filter (360 nm) for the activating light, and both a 450-nm interference filter (Bausch and Lomb) and a Turner 2A (No. 110-816) for the fluorescent light. This combination of exit filters has a maximum transmission at 452 nm. The single-hole opening on the range selector (designated 1X) was used. Fluorescence readings are reported in arbitrary units.

To adapt the fluorimeter for the small volumes of liquid, the cuvets (12 × 75 mm test tubes, Corning No. 9820) were used with the Turner High Sensitivity Conversion Kit (No. 110-865). The opening of the cuvet holder was partly closed with black tape to mask the upper 23 mm of the 35 mm opening, thus leaving 12 mm at the bottom for light to enter the cuvet tube.

As the Turner fluorimeter is not thermostatted, fluorescence intensities were determined rapidly (*ca.* 10 sec) after temporarily withdrawing the cuvets from the constant temperature bath.

Procedure

Prepare a histamine solution (253 μg/ml) by dissolving 70 mg of histamine diphosphate (U.S.P., Fisher) in 100 ml of 6 *N* hydrochloric acid; immediately before use, dilute to 0.4 μg/ml water. Before the final dilution, add aqueous sodium hydroxide solution to the test tubes so that the very dilute aqueous histamine solution is made alkaline immediately.

To 1.8 ml of water in small test tubes (slightly larger than the cuvets specified) add 0.4 ml of 0.5 *N* aqueous sodium hydroxide, 0.2 ml of histamine solution (0.4 μg/ml) and 0.1 ml of 0.1% OPT in *p*-xylene. Ensure a constant temperature of 23°, and mild agitation during the condensation, with a suitable incubator. Remove the test tubes from the incubator for each addition, after which they are mixed (see below). Then replace the test tubes in the incubator where gentle shaking is maintained. After alkaline condensation of histamine and OPT has proceeded for 5.5 min, add 0.2 ml of a solution containing 0.1 *M* citric acid and 0.5 *M* phosphoric acid, which stabilizes the fluorophore at a pH of 3 or above[5]. To mix the small volumes of liquids efficiently, the test tubes were held, after each addition, against a rubber stopper eccentrically positioned on a stirrer for about 10 sec.

Pour the stabilized fluorophore solution, containing 0.03 μg histamine/ml, into cuvets and place them in the 23° bath with gentle shaking for 15 min. Temporarily withdraw the cuvets, dry the outer sufaces, and measure the fluorescence intensities immediately. Intensities remained stable for several hours after acidification.

The final concentration of histamine in the aqueous fluorophore solution varies depending on the solvent chosen. If methanol is used, a homogeneous solution of 2.7 ml is obtained and the histamine concentration is 0.030 μg/ml. If *p*-xylene is used, a layer of 0.1 ml remains on the surface. The aqueous fluorophore solution, now reduced to 2.6 ml, has a histamine concentration of 0.31 μg/ml.

"Fluorescence" blank

To prepare a blank, use 2 ml of water in the *Procedure* and omit the histamine solution. This procedure, which permits condensation with OPT in alkaline solution, provides for the development of all interfering fluorescences except that of histamine (see below).

RESULTS AND DISCUSSION

Initial experiments in this laboratory with the histamine–OPT fluorophore resulted in variable fluorescence intensities. Slight or inappreciable improvements occurred after consideration of factors such as the purity and age of solutions, the method of mixing before condensation of histamine and OPT, the time and temperature of the condensation reaction, and the recrystallization of the OPT. A major source of variability remained which was exhibited as both an increase and a decrease of fluorescence.

By analogy with benzaldehyde, it was suspected that OPT, $C_6H_4(CHO)_2$, might be sensitive to air oxidation. This seemed unlikely since OPT did not develop appreciable acidity on storage. In accord with BEALL's findings[4], inhomogeneity of the OPT was indicated by the presence of varying amounts of insoluble residue in the petroleum ether solution of OPT.

Attention was concentrated on OPT as the principal source of variability in the assay, because of the observation that the fluorescence intensity of the fluorophore varied with the age of the recrystallyzed OPT. The possibility of an internal oxidation–reduction of the aldehyde groups of OPT, due to irradiation of OPT solutions by sunlight, was indicated by SHONBERG AND MUSTAFA[10]. The insoluble residue obtained during the recrystallization of OPT had the appearance of a polymer. These considerations led KAGAN[11] to study the irradiation of solid OPT with ultraviolet light in order to account for the variable fluorescences observed. However, these irradiation products, on condensation with histamine, exhibited no appreciable fluorescence, as tested by KAGAN[12] and in this laboratory.

It was then shown that atmospheric humidity caused a considerable variation in the action of OPT. The reagent was recrystallized from petroleum ether under conditions which excluded atmospheric humidity. Six samples in one group were then exposed to the atmosphere for 15 min. Fluorophore prepared from these samples exhibited a 15% increase in fluorescence, on the average, compared to a second group (6 samples also) in which fluorophore was prepared from OPT which was kept anhydrous. There was no overlap of the fluorescence intensities of the two groups.

The variability attending an ordinary recrystallization of OPT, followed by air drying, is seen in Fig. 1. Before crystallization, the hot petroleum ether solution of OPT was decanted from a small amount of insoluble residue; filtration of the solution, a more demending technique for so volatile a solvent, is less likely to be employed. Aging followed 15 min of air drying. Samples aged less then a day were kept in brown screw-cap vials on the bench top; those aged a day or more were stored in the refrigerator immediately after air drying. After the OPT was dissolved in methanol, solutions were immediately used to prepare fluorophore. Two variables, which are usually not precisely controlled, are the cyrstal size of the OPT and atmospheric humidity. Thus, the variations of Fig. 1 are figurative or representative only.

Irregular fluorescences persist if the recrystallized OPT (air dried or anhydrous) is dissolved in methanol, as is shown in Fig. 2, curves 1, 2, and 3. For the three methanolic solutions, the OPT was obtained as follows: for curves 1 and 2, recrystallized OPT (dried in air and stored in the refrigerator), aged two and four days respectively, was used; for curve 3, freshly crystallized OPT (anhydrous) was used.

The largest positive deviation in Fig. 2 (43.2), almost a 25% increase above the average fluorescence (34.7), resulted from the use of anhydrous freshly recrystallized OPT (whith no evaporation of petroleum ether), a precaution frequently taken to improve purity of a product; the amount of petroleum ether used to keep recrystallized OPT wet has a negligible effect on the fluorescence of the final fluorophore solution.

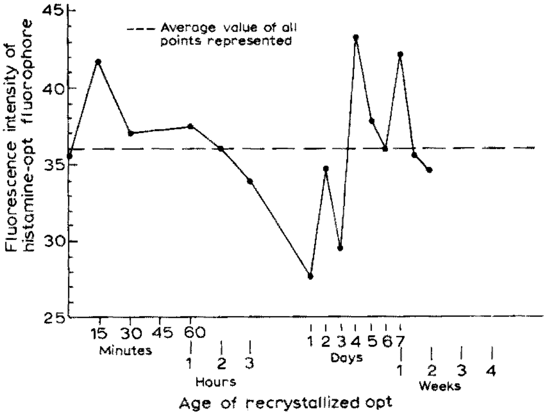

Fig. 1. Fluorescence variability of recrystallized OPT after air drying and aging (or storage in the refrigerator). Fluorescence intensities qere corrected for a blank which was in the range 2–8 when methanol was used as the solvent for OPT. To prepare fluorophore solutions, 0.2 ml of dilute histamine solution (0.4 μg/ml) was used.

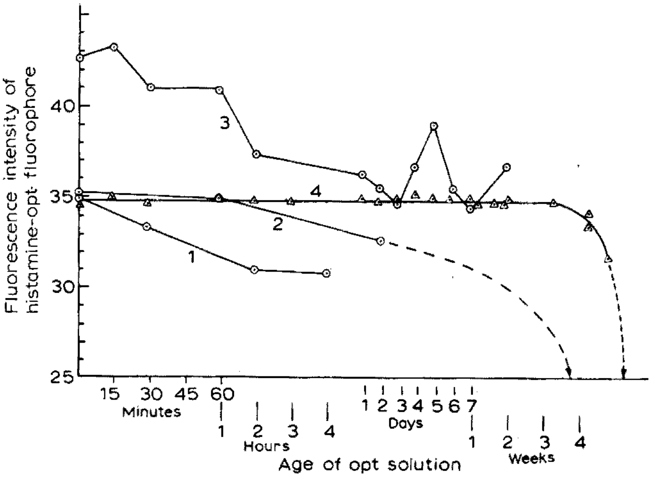

Fig. 2. Stability of p-xylene solutions of recrystallized OPT; variability of methanol solutions (26-day old methanol solution gave no fluorescence). △ Average (OPT–p-xylene) for 2 weeks = 34.7.

However, the irregular fluctuations (again the plots of curves 1, 2, and 3 are representative only) are largely eliminated by the use of p-xylene as a solvent for the anhydrous OPT, as seen by the almost horizontal line, 4, of Fig. 2. Freshly crystallized, anhydrous OPT was used to prepare the OPT p-xylene solution; solutions retain stability over 3 weeks. Blanks obtained from the p-xylene solutions were in the range 2–4.

Evidence for the improvement provided by keeping the recrystallized OPT *dry* was secured in three ways. First, the (single) *p*-xylene solution of OPT, seen in Fig. 2, exhibited a relative standard deviation of 0.007 for 37 aliquots taken from it over a 2-week period to prepare fluorophore solutions. Second, relatively constant fluorescences were also obtained from 4 different *p*-xylene solutions of dry OPT. Sixteen fluorophore solutions, prepared from the four OPT solutions, resulted in a relative standard deviation of 0.014. Third, the advantage of recrystallized dry OPT, compared to suppliers' products, is clearly seen in Table I. Customarily, OPT is used as received from the supplier for the histamine determination.

TABLE I

COMPARISON OF RECRYSTALLIZED DRY OPT AND SUPPLIERS' PRODUCTS BASED ON FLUORESCENCE INTENSITY OF HISTAMINE–OPT FLUOROPHORE

(Three methods of drying were used: A, one to three days in vacuum desiccator over $CaCl_2$; B, in desiccator over NaOH at least 30 days; C, overnight under vacuum (1 to 2 mm) at 42° to 48°. All OPT samples were dissolved in *p*-xylene)

OPT source	*Method of drying*	*Av. fluor. intensity (corr.)*	*S.D. rel.*	*No. of samples*
Recryst., dry		34.7	0.011	8
Mann[a]		33.8	0.044	8
Mann, dry	A	34.1	0.023	4
Calbiochem[b] (Lot No. 1)		33.8	0.071	10
Calbiochem, dry (Lot No. 1)	B	30.8	0.032	5
Calbiochem (Lot No. 2)		33.7	0.097	8
Calbiochem, dry (Lot No. 2)	B	30.8	0.039	4
Calbiochem (Lot No. 3)		33.8	0.032	4
Calbiochem, dry (Lot No. 3)	C	31.0	0.027	4
Aldrich[c]		34.0	0.031	4
Aldrich, dry	B	30.2	0.023	4
Gallard–Schlesinger[a]		31.5	0.018	4
Gallard–Schlesinger, dry	C	31.3	0.074	4
Gallard–Schlesinger, dry	B	27.3	0.051	5

[a] New York.
[b] California.
[c] Wisconsin.

Comparisons between recrystallized dry OPT and suppliers' products are given in Table I. The variability of one of the products, used as received, was indicated by a relative standard deviation almost nine times that obtained from the use of recrystallized dry OPT dissolved in *p*-xylene. The method presumed most efficient for drying the supplier's product, B of Table I, had two apparent effects; a lower fluorescence intensity of the fluorophore resulted, and a lower relative standard deviation was obtained, with one exception, which was still not comparable with the relative standard deviation using recrystallized dry OPT. These findings indicate that it would not only be questionable to use OPT as received with an internal standard of histamine but in addition, improved precision may be needed to determine many physiological changes in histamine concentration.

A calibration curve of fluorescence intensity of the fluorophore *versus* histamine concentration, with recrystallized dry OPT in *p*-xylene, is shown in Fig. 3. The lowest point on the curve, which represents less than 10 ng histamine, exhibits a fluorescence intensity approx. twice the value of the blank.

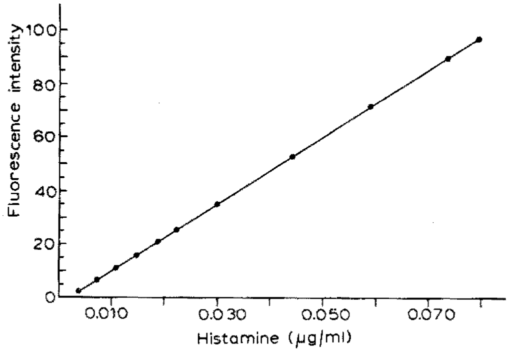

Fig. 3. Calibration curve of authentic histamine assayed by the procedure described.

For comparison, a standard curve obtained by the method of SHORE *et al.*[1] showed that some of the points deviated appreciably from a fitted line. The relative standard deviation was 0.061, compared to 0.011 in Table I (8 fluorophores of the same concentration were used in each case), and the absolute value of the fluorescence intensity, corresponding to 0.03 μg histamine per ml, was 33.9 (compared to 34.7 in Table I). The lowest point on the linear portion of the curve corresponded to over 20 ng of histamine, about three times the average blank (6.1) determined as specified[1].

"Fluorescence" blank

A blank, in a procedure which depends on fluorescence as a basis of measurement, should allow for the development of all fluorescences other than that due to histamine. In securing a sample from tissues or fluids, only the histamine should be destroyed in the solution prepared for blank analysis, *e.g.* a histaminase can selectively accomplish this, followed by removal of the enzyme. This histamine-free sample would then be appropriate for a blank. The determination of glutathione[9], a tripeptide, which is also based on condensation with OPT, emphasizes the likelihood that interfering constituents may be present in tissues or that they may be formed by the procedure used to isolate proteins. Thus, a "fluorescence" blank which permits condensation in alkaline solution with OPT would serve as an indication of components other than histamine which are likely to develop fluorescence. The magnitude of the blank above that of water would then indicate the extent to which such interferences were present, and a valid correction would be provided by subtraction of such a blank from the sample fluorophore intensity.

We thank the Department of Chemistry of the College of Pharmacy, University of Illinois, for facilities afforded us for much of this research. This investigation was supported in part by Public Health Service Grant AM-07587.

SUMMARY

An improved fluorimetric determination of histamine, based on the formation of a fluorophore between histamine and *o*-phthalaldehyde (OPT), is obtained if conditions are maintained anhydrous during recrystallization of the OPT and for the preparation and storage of the OPT solution in *p*-xylene. The increased precision of the method is reflected by a relative standard deviation of 0.007, for 37 aliquots of a *p*-xylene solution of OPT removed over a 2-week period. The calibration curve is linear above 10 ng of histamine, at which lower limit the fluorescence intensity of the fluorophore is almost twice that of the blank.

RÉSUMÉ

Une détermination fluorimétrique améliorée de l'histamine, basée sur la formation d'un fluorophore entre l'histamine et l'orthophthalaldéhyde (OPT), est obtenue si des conditions anhydres sont maintenues durant les recristallisations de l'OPT et pendant la préparation et le stockage de la solution d'OPT dans le *p*-xylène; la précision de la méthode a été augmentée, ce qui se traduit par un écart type relatif de l'ordre de 0.007 pour 37 prélèvements de la solution d'OPT dans le *p*-xylène agitée durant 2 semaines. La courbe d'étalonnage est linéaire au-dessus de 10 ng d'histamine; pour cette limite inférieure, l'intensité de la fluorescence du fluorophore est presque deux fois celle du témoin.

ZUSAMMENFASSUNG

Die fluorimetrische Bestimmung von Histamin, welche auf der Bildung eines Fluorophors zwischen Histamin und *o*-Phthalaldehyd (OPT) beruht, lässt sich verbessern, wenn man während der Rekristallisation von OPT und für die Herstellung und Aufbewahrung der OPT-Lösung in *p*-Xylol für Wasserfreiheit sorgt. Die gestiegene Genauigkeit dieser Methode spiegelt sich in einer relativen Standardabweichung von 0.007. Die Eichkurve ist oberhalb von 10 ng Histamin linear.

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PRECISION POLAROGRAPHY BY TIME-INTEGRATION OF THE DIFFUSION CURRENT

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Ordinarily the errors involved in quantitative polarographic analyses are regarded as being of the order of 1–2 relative percent, and this is true by the common technique of measuring the diffusion current from the wave heights on recorded polarograms. However, this error reflects the uncertainty of this particular measuring technique and not any inherent lack of reproducibility of polarographic diffusion currents.

As was demonstrated long ago[1] the current measurement itself can easily be performed with a precision of ±0.1% by placing a known resistance in series with the polarographic cell and measuring the iR drop across it with a potentiometer. Today there is no lack of elegant instrumentation for performing this measurement less tediously. The reproducibility of the dropping electrode, and control of the factors which govern the diffusion current, ultimately determine whether or not an accuracy commensurate with the precision of current measurement is obtained. Thanks to the efforts of many investigators, whose achievements are well documented[2,3], the effect of each of the many factors which influence the diffusion-controlled limiting current are now known sufficiently well that, if one is motivated enough to take the pains to learn and control them, a precision and accuracy of the order of ±0.1% is well within reach.

This degree of precision was reported by SHALGOSKY AND WATLING[4] and by ROONEY[5] using a differential cathode-ray polarograph and two matched dropping electrodes. Most recently SHULTS, FISHER AND SCHAAP[6] demonstrated that the elegant, sophisticated polarograph developed at the Oak Ridge National Laboratory is capable of a precision and accuracy near ±0.1% when operated in the mode of comparative polarography by measuring the difference in diffusion currents of unknown and standard solutions.

In the present study a new method of measuring the diffusion current to ±0.1% has been developed, based on integrating it over an exactly known time which includes 50 or more mercury drops. The averaging effect of this time-integration minimizes the perturbations caused by small random variations of drop time, or other accidental factors which influence the diffusion current. A conventional dropping mercury electrode was used, but to eliminate the effect of fluctuations in ambient temperature the mercury in the stand tube was kept at the same temperature as the solution.

EXPERIMENTAL TECHNIQUE

Instrumentation

As shown in Fig. 1, a constant voltage is applied to the polarographic cell circuit from potentiometer R-4, and the voltage drop across the input resistor R-1 produced by the resulting current is amplified by a Keithley Model 140 d.c. amplifier whose output is integrated over an exactly measured time interval.

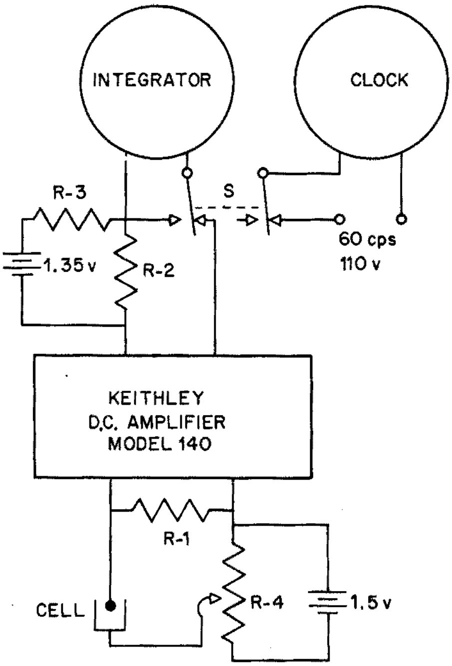

Fig. 1. Electrical circuit.

The Model 140 amplifier (Keithley Instruments, Inc., 28775 Aurora Road, Cleveland, Ohio 44139) is excellent for the present purpose. Its gain accuracy is ±0.01 % (stable to better than ±0.005% for a 3-month period) and its zero stability is within ±0.001% over an 8-h period. There is a choice of four gain settings (100, 1000, 10,000, and 100,000) with a full-scale output in each case of 10 V at up to 1 mA. Three rise times of 0.05, 0.5, and 5 sec (10%–90% full scale) are selectable. When the output is to be integrated, it is best to employ the slowest rise time (5 sec) and thus obtain a well averaged value. This was done in all the measurements reported herein.

Not the least of this amplifier's virtues is that it can be operated either from the 110 V a.c. line or from an internal nickel–cadmium battery (automatically rechargeable). Battery operation was used because it insures minimum pickup of stray signals. Our environment is teeming full of a vast number and variety of electrical signals, and line-operated instruments have an exasperating proclivity to respond to extraneous ones.

To minimize the voltage withdrawn from the cell circuit most measurements were made with the amplifier gain at 10,000, so that a voltage drop of only 1 mV across R-1 produced a full-scale, 10-V output. Under this condition the potential of the dropping electrode varies by only 1 mV during the drop life, provided that the cell resistance is small. The input resistance R-1 was a decade resistance box, and ordinarily it was adjusted to provide an amplifier output of 9–10 V (nearly full scale).

The value of R-1 required to produce a 1-mV input is relatively small; *e.g.*, only about 25 ohms when the concentration of the electroactive species is 5 m*M*. At this relatively small value, and when R-1 is selected to keep the output near its maximal value in comparing an unknown and standard solution, one must be sure that the switch contact resistances do not cause the actual resistance to differ significantly from the nominal value. Therefore, the resistance box was calibrated against a certified Leeds and Northrup 100-ohm resistor, so that R-1 was known to ±0.01% at all settings.

With an input signal of only 1 mV, care must be taken to avoid pickup of extraneous signals. To this end all the leads were kept as short as possible and close together to minimize electrical loops. For the same reason the constant voltage applied to the cell was taken from the simple potentiometer R-4 (200-ohm Beckman Helipot) powered by a large 1.5-V dry cell rather than from a polarograph. Although a battery powered polarograph is satisfactory, it was observed that an a.c. line-operated polarograph introduced disturbing extraneous signals.

The output of R-4 was adjusted so that the potential of the dropping electrode was on the diffusion current plateau, and it was controlled to ±1 mV by measurement with a potentiometer. Close control of the potential of the dropping electrode is important because of its effect on $m^{\frac{2}{3}}t_d^{\frac{1}{6}}$, especially at potentials more negative than the electrocapillary maximum. For instance, at −0.9 V *vs.* S.C.E. in 1 *M* potassium chloride the rate of change of $m^{\frac{2}{3}}t_d^{\frac{1}{6}}$ (and hence the diffusion current) is −0.004%/mV. At −1.2 V it increases to −0.006%/mV, and rapidly becomes larger at more negative potentials.

Integrator

The integrator was the fixed-field motor-counter type manufactured by Ether Ltd. (formerly Electro Methods Ltd., Stevenage, Herts, England; available in the U.S.A. from Acromag Inc., 30765 Wixom Road, Wixom, Michigan 48096). The characteristics of this instrument have been discussed in detail elsewhere[7,8]. It was recently demonstrated[8] that when the decay of the counting rate with decreasing input voltage is properly counteracted by a small, constant input voltage the integration error is as small as ±0.04% over a 20-fold range of input voltage. The combination of R-2, R-3, and the 1.35-V mercury battery supplies this compensating voltage. For the particular 24-V model of the Electro Methods integrator used, the optimum value of the compensation voltage was 0.031 V. Since R-2 was fixed at 20 ohms, the optimum value of R-3 was 850 ohms.

In comparative measurements of the diffusion currents of unknown and standard solutions, the input resistance R-1 can be adjusted to keep the output voltage of the amplifier nearly the same, and when this is done the compensating voltage is not strictly necessary. However, to simplify the computation of the result, it is more convenient to keep R-1 fixed, and since the output voltage may then vary considerably, the compensating voltage should be used.

A double pole–double throw 110-V a.c. relay S was used to activate the integrator and timing clock simultaneously. Note (Fig. 1) that in the left-hand off position the integrator terminals are short-circuited, so that the instrument self-damps to an instantaneous stop. It is a simple matter to operate this relay by a manual switch, and this is done when the integration is performed over a fixed number of drops. However, provided that the integration included 50 or more drops, there was no detectable difference in precision in integrating over a discrete number of drops or over a fixed time. It is most convenient to integrate over a fixed time, and this can be done automatically by using a timer-switch to open the relay after a pre-set time interval. The Gralab timer-switch (Dimco-Gray Co., 207 E. Sixth St., Dayton, Ohio 45402, or Fisher Cat. No. 6-656 V1) served very satisfactorily.

The timing clock was a Standard Electric Time Co. Model S-10, precise to ±0.02 sec, but whose accuracy is no better than the constancy of the frequency of its 110-V supply voltage. Because the frequency of commercial line voltage undergoes short term variation of as much as ±0.15%, the clock was driven from a frequency-regulated power supply (American Time Products Inc., Type 2005).

With the amplifier set at 5-sec rise time (the time required for the output to go from 10 to 90% of its final value after application of the signal) the output voltage does not attain a constant value until at least 30 sec after the cell circuit is closed. Therefore, the measurements were made by first closing the cell circuit and then waiting for 30–60 sec before closing the relay S to start the integration.

The averaged input current (diffusion current) is given by

$$i = \frac{N}{GRtk} \tag{1}$$

where N is the integrator reading after t sec, G is the gain of the amplifier, R is the input resistance (R-1 in Fig. 1), and k is the counting rate of the integrator with exactly 1 V across its terminals. For the particular integrator used, k was 0.11615 counts/sec/V, with an uncertainty of ±0.04% when the proper compensation voltage was used[8]. Thus, when the input resistance and gain were selected to produce an amplifier output of 9–10 V, the counting rate was close to 1 count/sec. Since the integrator is readable to ±0.1 count, an integration time of at least 100 sec is necessary for ±0.1% or better precision of reading. Usually an integration time of 300 sec was employed to obtain about 300 counts readable to ±0.03%.

When the concentration of an unknown solution is determined by comparing its diffusion current with that of a standard solution, it is, of course, unnecessary to convert the integrator readings to current, and the values of N/GRt can be compared directly (after correction for the counting rate observed with the supporting electrolyte alone). When G, R, and t are constant, the N values themselves are directly comparable.

No doubt, some of the electronic integrators now available (particularly those that employ voltage-to-frequency conversion followed by a frequency counter) could be used instead of the Electro Methods (Ether) integrator. However, the cost of instruments of this type of equal performance capability is much greater than that (about $150) of the Electro Methods instrument.

Reproducibility and assembly of the dropping mercury electrode

The most critical factor in precision polarography is not the electrical instrumentation, but rather the reproducibility of the dropping electrode itself. The Ilkovic equation and its modifications delineate the factors that govern the diffusion current and indicate how to control them[2,3]. The two cardinal factors are the nature and concentration of the supporting electrolyte (including maximum suppressors) and the temperature, because both the diffusion coefficient of the electroactive species and the $m^{\frac{2}{3}}t_d^{\frac{1}{6}}$ value of the dropping electrode depend on them. The temperature coefficient of the diffusion current is 1.5 to 2.0% per degree, and therefore temperature control to at least ±0.05° is essential when a precision of ±0.1% is sought.

The common practice is to immerse the cell in a thermostatically controlled water bath (usually at 25°), which does indeed control the temperature of the bulk of the solution. It has been tacitly assumed that when the dropping electrode capillary is immersed in the solution that the temperature of the mercury drop will be the same as that of the solution, *but this will be true only if the mercury that enters the top of the capillary is originally at the same temperature as the solution.* The mercury flows through the capillary much too fast for the attainment of temperature equalization.

The volume of mercury in the lumen of a capillary of the usual dimensions (10 cm length and 0.03 mm internal diameter) is only $2.8 \cdot 10^{-4}$ cc, and its weight is only 3.8 mg. Since the m-value usually is between about 2 and 3 mg/sec, it follows that the linear velocity of mercury flow through the capillary is 5–8 cm per second. Ordinarily less than 5 cm of the capillary tip is immersed in the solution, so that the mercury flows through this portion in only a fraction of a second.

In view of the poor thermal conductivity of glass (only about one-tenth that of mercury and about one-seventh that of water), coupled with the fact that its specific heat per unit of volume is only about one-third that of mercury, the temperature of the mercury just as it emerges from the tip of the capillary must still be much closer to the temperature when it entered the top of the capillary than to the solution temperature. The usual condition is that the mercury that enters the top of the capillary is at ambient temperature, which ordinarily is a few degrees lower than the temperature of the solution. Consequently, the growing mercury drop extracts heat from the solution in contact with it, which produces a temperature gradient in the diffusion layer. Therefore, the diffusion coefficient of the electroactive species decreases as it approaches the drop surface. Because diffusion coefficients are temperature-sensitive by about 2% per degree, only a few tenths of a degree difference between the temperature of the mercury drop surface and the bulk of the solution is enough to change the diffusion current by several tenths of a percent. When the limiting current is kinetically controlled the effect of such a temperature gradient in the diffusion layer will be much greater. This effect does not seem to have been previously recognized.

Furthermore, when the mercury that enters the drop is still close to room temperature, the $m^{\frac{2}{3}}t_d^{\frac{1}{6}}$ value will depend on room temperature, and since its temperature coefficient is about 0.18%/deg significant variation will occur if the room temperature fluctuates.

As shown in Fig. 2, these effects were eliminated by enclosing the entire mercury stand tube in a water jacket through which constant-temperature water from the water bath was circulated continuously. To minimize heat leak to the mercury reservoir the side arm of the stand tube was capillary tubing of 1 mm i.d. Care was taken to position the upper end of the dropping electrode capillary well up into the thermostatted stand tube, and it was sealed rigidly in place with Varno cement at the lower end of the stand tube. This cement (Varniton Co., Los Angeles) is convenient because it melts at only about 80° to a viscous liquid which flows readily into the thin annular space between the dropping electrode capillary and the stand tube, but sets to a hard, varnish-like substance at room temperature.

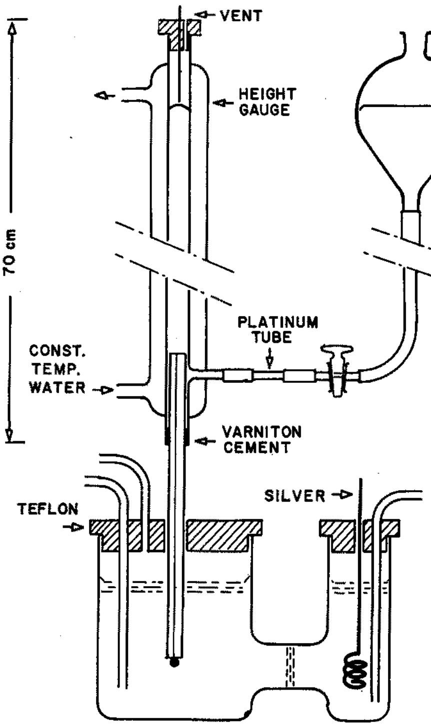

Fig. 2. Dropping mercury electrode cell with thermostatted stand tube. The cell is immersed in a constant temperature water bath and water from the bath is circulated through the water jacket around the stand tube. Electrical connection to the dropping electrode is made via the short platinum tube in the side arm of the stand tube.

Even though the mercury in the stand tube is kept at the same temperature as the solution a temperature gradient must still be present at the mercury–solution interface because of the heat of the electrode reaction. Under polarographic conditions the electrode reaction usually is endothermic. The specific heat of mercury per unit of volume is only 0.45 that of water, and it conducts heat ten times faster, so that the endothermic heat of reaction must cool the mercury side of the mercury–solution interface to a greater degree than the solution side, to produce an asymmetrical temperature gradient at the interface. This temperature gradient must increase as the rate of the electrode reaction (concentration of the electroactive species) increases. Although in principle this could be eliminated by increasing the temperature of the mercury in the stand tube appropriately, this is so obviously impractical that the best that one can do to keep its effect approximately constant in comparative polarography is to employ a standard solution whose concentration is not very different from that of the sample solution.

The familiar blunt-ended capillary of marine barometer tubing (E. H. Sargent Co.) was used. Its total length was about 15 cm, and the drop time was close to 4 sec under a mercury head of about 70 cm. Obviously, the precision attainable in comparing the diffusion currents of an unknown and standard solution can be no better than the constancy of the $m^{\frac{2}{3}}t_d^{\frac{1}{6}}$ value of the dropping electrode. A few simple precautions which maximize the probability of this constancy have been described by KOLTHOFF AND LINGANE[2] and by MEITES[3]. In experienced hands, which do not abuse it, this convenient type of dropping electrode normally retains constant characteristics for months on end.

The height gauge, used to adjust the mercury level in the stand tube precisely, was a stout nickel wire whose lower end was sharpened to a fine conical point. Juxtaposition of this point with its mirror image in the mercury surface is easily discernible to ± 0.1 mm. Because a diffusion-controlled limiting current depends on the square root of the mercury level above the tip of the dropping electrode, which in the present case was about 700 mm, a variation of ±0.1 mm produces an uncertainty in the diffusion current of only about ±0.007%.

The usual method of completing electrical connection to the dropping electrode is by means of a contact in the mercury reservoir. However, this creates a large electrical loop (antennae) which invites pick-up of extraneous signals. To avoid this, electrical contact was made via the short length of platinum tubing inserted close to the stand tube in the gum rubber tubing leading to the reservoir (nickel or stainless steel tubing probably would serve as well).

As the mercury drop nears dead ripeness, it becomes sensitive to short-period vibrations, which if brissant enough to dislodge it prematurely will cause an erratic drop time. Even though the integration technique tends to average out the effect of erratic dropping on the diffusion current, care was taken to mount the entire dropping electrode assembly on a massive (about 20 kg) tripod support. Rubber pads under the legs of this heavy tripod effectively absorbed vibrations.

The stand tube was fastened to a steel rod which was movable up and down through two guides, with a fixed stop in the lowest operating position. The assembly was adjusted (once and for all) against a plumb line so that the dropping electrode capillary was truly vertical. The important condition is that the flat end of the capillary must be within about 5° of the horizontal, otherwise the drop time will be erratic. Within this tolerance, a variation of 1° causes a change of about 0.07% in the diffusion current[9]. It is easy to break off the tip of the capillary so that its flat end is at 90° to its axis within 5°, and to true the vertical angle of the capillary by a plumb line to within 1°.

Cell assembly

The cell was mounted in a movable holder on the rim of the water bath in such a way that it was adjustable in the horizontal plane to accommodate entry of the dropping electrode through the slightly oversize hole in the Teflon cell cover, but its vertical position was fixed. The cell was always filled to the same level against a mark on its side. Thus it was easy always to position the dropping electrode vertically and to the same depth (about 2 cm) below the surface of the solution. Because depth of immersion detracts from the applied pressure of the mercury column it must be kept constant in comparative measurements, but there is considerable tolerance owing to the 13-fold difference between the densities of water and mercury.

With chloride supporting electrolytes a silver electrode is most convenient as the auxiliary electrode. It was placed in the separate compartment of the H-type cell because the solubility of silver chloride is appreciable in the presence of excess of chloride ($1.2 \cdot 10^{-4}$ M in 1 M chloride), and this would increase the background current considerably if the silver electrode were in the dropping electrode compartment. The two compartments are separated by a fine sintered glass disk in the cross arm. Both compartments contained the same solution and they were filled to the same level to minimize interflow. Various other auxiliary electrodes and cell designs can, of course, be used to best suit the conditions extant in a particular analytical situation.

A relatively large volume of solution (100 cc) was used in the dropping electrode compartment in order to minimize the depletion of the concentration of the electroactive species by the electrolysis. This electrolysis error is independent of both n and the concentration, and, expressed in percent, is $100(607\ D^{\frac{1}{2}}m^{\frac{2}{3}}t_d^{\frac{1}{6}})t/VF$, where the term in parenthesis comes from the Ilkovic relation, t is the electrolysis time (sec), F is the faraday constant, and V is the solution volume (cc). For most substances $607D^{\frac{1}{2}}$ has a value close to 1.5, and usually $m^{\frac{2}{3}}t_d^{\frac{1}{6}}$ is about 2 $\text{mg}^{\frac{2}{3}}/\text{sec}^{\frac{1}{2}}$, so that the electrolysis error ordinarily will be close to 0.003 t/V%. For each integration measurement of 300 sec the active electrolysis time is close to 400 sec, because the circuit is closed about 60 sec before the integration is started and a somewhat shorter time elapses before integration is stopped. Therefore, in triplicate measurements the total electrolysis time will be about 1200 sec, and to prevent the electrolysis error from becoming larger than -0.1% the solution volume must be at least 36 cc.

High-purity nitrogen, which first passed through wash bottles containing water and then the supporting electrolyte, was used to remove dissolved air from both compartments of the cell. Deaeration can be greatly accelerated by stirring the solution with a magnetic stirrer vigorously enough so that a considerable quantity of nitrogen bubbles is entrained to furnish a large surface area for oxygen removal. (The submersible magnetic stirrer of Henry Troemner, Inc., Philadelphia, served conveniently.) With this technique it was found that 95% of the dissolved oxygen was removed during the first 2 min, and hence the total deaeration time need not be much longer than 5 min. The dropping electrode must not be in the solution during this vigorous deaeration. After the stirrer has been stopped, the nitrogen stream is deflected over the surface of the solution; care should be taken to wait a minute or so until all the tiny nitrogen bubbles have disappeared before the dropping electrode is immersed, because such bubbles tend to collect on the flat tip of the capillary and cause an erratic drop time. It is best not to bubble nitrogen through the solution when the dropping electrode is immersed, but simply to stir it gently with the magnetic stirrer for only a few seconds between each trial.

PERFORMANCE DATA AND DISCUSSION

For many of the measurements cadmium ion was the electroactive species, and the supporting electrolyte was 1.00 M potassium chloride containing 0.001 M hydrochloric acid and 0.001% Triton X-100. With cadmium ion a maximum suppressor is not really necessary, but it did seem to improve the constancy of the drop time, and it also decreased the background current somewhat. Because it affects the diffusion current, a potent maximum suppressor like Triton X-100 should be used only at a very small concentration, and in comparative measurements its concentration in the two solutions should be the same within a few relative percent. It was observed that 0.001% Triton X-100 decreased the diffusion current of cadmium ion by 2.4% and therefore care was taken to keep its concentration constant to ±1 relative percent. It might have been safer to omit the Triton X-100, but it was used so that the supporting electrolyte would have identically the same composition as that employed by SHULTS, FISHER AND SCHAAP[6], since it was of interest to compare the present results to theirs.

TABLE I

EXAMPLE OF PRECISION OF REPEATED MEASUREMENTS ON THE SAME SOLUTION

(100 cc of 5.00 mM $CdCl_2$ in 1.00 M KCl + 0.001 M HCl + 0.001% Triton X-100 at 25.00 ± 0.05°. Input resistance R-1 was 25.033 ohms and amplifier gain was 10,000. Integration over exactly 75 drops. $E_{d.e.}$ = −0.900 ± 1 V *vs.* Ag/AgCl,1 M KCl)

Integration time (sec)	*N (counts)*	*N/t (counts/sec)*	
		Observed	*Corrected*
300.60	322.5	1.0729	1.0730
300.88	323.0	1.0735	1.0738
300.94	323.3	1.0743	1.0748
300.76	322.7	1.0729	1.0735
301.17	323.3	1.0735	1.0743
301.27	323.1	1.0725	1.0735
301.14	322.4	1.0706	1.0717
301.38	322.7	1.0707	1.0720
301.77	323.8	1.0730	1.0744
301.70	323.3	1.0716	1.0732
	Av.	1.0726	1.0734
	Av. dev.	±0.09%	±0.07%
	Max. diff.	0.34%	0.29%

Table I presents typical data which demonstrate the precision of repeated measurements on the same solution. The constant voltage applied to the cell was 0.900 ±1 V, so the potential of the dropping electrode was −0.900 V *vs.* Ag/AgCl, 1 M KCl, which is nearly 0.3 V more negative than the half-wave potential of cadmium ion and thus well onto the diffusion current plateau. In this case the integration was performed over exactly 75 drops, but it was found that equally precise results are obtained by integrating over a fixed time, which is more convenient.

The observed counting rate of the integrator is shown in the third column. Because the total electrolysis time for these ten successive trials was close to 4000 sec, the cumulative electrolysis error was appreciable. From eqn. (1) the average value of the diffusion current was $1.0726/(0.11615 \cdot 25.033 \cdot 10^4)$ or $36.890 \cdot 10^{-6}$ A, which in 4000 sec corresponds to 0.148 coulombs. Since the total quantity of cadmium ion in the 100 cc of the 5.00 mM solution is equivalent to 96.5 coulombs, the cumulative electrolysis error was −0.15%, or − 0.015% per trial. This correction was applied to the observed counting rates to obtain the corrected values shown in the last column of Table I.

Note that the drop time (1/75 of the integration time) varied from 4.008 to 4.024 sec, or by 0.40%, during these trials, and that the change was progressive toward a larger value. If this change had been caused by a change in m-value, then m would have decreased by 0.40% and $m^{\frac{2}{3}}t_d^{\frac{1}{6}}$ would have decreased by 0.20%, but the N/t

values do not show such a trend. It appears, therefore, that the progressive small increase in drop time was not caused by a decrease in m. With m constant, an increase of 0.40% in the drop time will increase $m^{2/3}t_d^{1/6}$ by 0.07%, and N/t should increase correspondingly. The corrected value of N/t at the longest drop time (1.0744) is indeed larger than the value (1.0730) at the shortest drop time, and the difference of 0.13% agrees with the expected 0.07% within the discriminatory capability (precision) of the data. The use of a "drop knocker" to dislodge the mercury drop artificially after a fixed time might, perhaps, minimize this source of variability. However, the normal drop time variability of the simple free-dropping electrode is so small that it is a moot question whether such an additional instrumental complexity would be worthwhile.

Test solutions containing various concentrations of cadmium ion were compared against a standard cadmium solution with the results shown in Table II. The standard solution was 5.00 mM cadmium chloride in a supporting electrolyte composed of 1.00 M potassium chloride, 0.001 M hydrochloric acid, and 0.00100% Triton X-100. The test solutions were prepared by precise dilutions of this standard solution with the supporting electrolyte. The volumetric manipulations were performed in such a way that the dilution ratio $C_{\text{Test}}/C_{\text{Std}}$ was known to better than ±0.1%.

TABLE II

ACCURACY OF COMPARISONS OF STANDARD AND TEST SOLUTIONS

(Standard solution was 5.00 mM $CdCl_2$ in 1.00 M KCl + 0.001 M HCl + 0.00100% Triton X-100, and test solutions were prepared by diluting the standard solution with the supporting electrolyte. Temp. = 25.00 ± 0.05°)

$C_{\text{Test}}/C_{\text{Std}}$		*Error (%)*
Taken	*Found*	
0.9525	0.9502 ± 12	−0.24
0.9525	0.9525 ± 11	0.00
0.6667	0.6668 ± 5	+0.02
0.5000	0.5013 ± 8	+0.26
0.5000	0.5005 ± 8	+0.10
0.3333	0.3331 ± 2	−0.06
	Av.	±0.11

In all cases the integration time was 300 sec, two to four measurements were made with each solution, and measurement of the standard solution was repeated at the time of each trial. The observed ratio of the concentration of the test solution (simulating an unknown) and the standard solution is given by

$$\frac{C_{\text{Test}}}{C_{\text{Std}}} = \frac{N_{\text{Test}} - N_{\text{Blank}}}{N_{\text{Std}} - N_{\text{Blank}}} \tag{2}$$

when the gain of the amplifier and the input resistance are constant, where N is the integrator reading after a fixed time and N_{Blank} is the value observed with the supporting electrolyte alone corresponding to the background (residual) current. Measurements on the standard and test solutions were made at the same gain setting of the amplifier (10,000), but when the concentration of the test solution was more than about 10% smaller than that of the standard solution, the input resistance R-1 was increased appropriately to maintain the amplifier output between 9 and 10 V, and the observed

N-value (close to 300 counts readable to ±0.1) was computed to the value it would have had with the same input resistance (25.033 ohms) used with the standard solution. Measurement of the background counting rate of the supporting electrolyte was made at a ten-fold larger amplifier gain (100,000) and a relatively large input resistance of 1000 ohms, to produce an amplifier output close to 10 V, and the resulting counting rate was then computed to the values of the input resistance and gain used with the standard solution.

The reader will appreciate that maximal accuracy is favored when the concentration of the electroactive species is sufficiently large so that N_{Blank} is relatively small, and this optimum concentration is within a factor of two either way of 5 mM. Under the ideal conditions used to obtain the data in Table II, N_{Std} was close to 300 counts and N_{Blank} was 0.78 counts, or only 0.26% of N_{Std}. In more familiar terms, this value of N_{Blank} corresponds to 0.096 μA, and the diffusion current of 5 mM cadmium ion was close to 37 μA.

The data in Table II demonstrate that this integration technique is more accurate than the ordinary polarographic method by a factor of ten, and its accuracy is comparable to the better classical analytical methods. The near equality of the summations of positive and negative errors indicates that systematic sources of deviation were under good control. There is no discernible impairment of accuracy when the concentration of the standard solution differs by as much as a factor of three from that of the test solution.

From measurements at 25° and 28° the temperature coefficient of the diffusion current of the cadmium ion was found to be 1.6%/deg. The temperature variation during the measurements of Table II was ±0.05°, which permitted a variation in the diffusion current of ±0.08%. The observed average error of ±0.11% is close to this. In all subsequent measurements quoted herein, a better thermostatic unit, which controlled the temperature to ±0.01°, was used and there was, indeed, a definite improvement of the precision.

However, one cannot expect an average error of less than ±0.04% since this is the precision of the integrator itself[8]. Also, according to its manufacturer, the temperature coefficient of the Electro Methods (Ether) integrator is 0.035%/deg, and since it is at ambient room temperature this must be constant to better than ±3° when a net error of less than ±0.1% is sought.

The most appropriate application of comparative precision polarography is the determination of a single substance under conditions where the background current is relatively small. In principle, it is applicable to determining successively two or more substances of sufficiently different half-wave potentials in a mixture. However, just as in ordinary polarography, the precision of determining each substance after the first inevitably is impaired to a degree that depends on the relative magnitude of the correction that is required for the preceding, cumulative diffusion current.

The correction is complicated by the significant change of $m^{\frac{2}{3}}t_d^{\frac{1}{6}}$, and therefore of the preceding diffusion current, with the potential of the dropping electrode. When a substance B is to be determined in the presence of a more easily reduced substance A, the diffusion current of A is measured at a potential well in advance of the wave of B, and then the sum of the two diffusion currents is measured at a potential well onto the diffusion current plateau of B. To obtain the true diffusion current of B by subtracting that of A, the latter must be corrected for the change it undergoes between the two potentials of measurement, and this change commonly is as large as 1–2%.

Mixtures of cadmium and zinc ions in neutral 1.00 *M* potassium chloride were studied as an example of the analysis of two-component samples. In this supporting electrolyte the half-wave potential of cadmium ion is −0.642 V *vs.* S.C.E. (nearly the same *vs.* Ag/AgCl, 1 *M* KCl) and thus about 0.4 V in advance of that (−1.022 V) of zinc ion, which is an ideal condition. By measurement at −0.820 V the cadmium is determinable as precisely as in the absence of zinc, so that interest focuses on how accurately the zinc can be determined.

When present at a concentration of several millimoles in 1.00 *M* potassium chloride, the limiting current of zinc is distorted by a "maximum of the second kind" which appears as an abnormal broad hump between about −1.1 and −1.4 V on the diffusion current plateau. Although this can be eliminated easily enough by either Triton X-100 or gelatine, the former is unsatisfactory because it produces new abnormalities, including a decreased slope of the rising portion of the zinc wave and abnormal variations of drop time in the diffusion current region. Gelatine, at a concentration of 0.001%, serves well as a maximum suppressor, and in its presence the zinc wave and limiting current are both perfectly normal.

The cadmium diffusion current was measured at −0.820 V *vs.* Ag/AgCl, 1 *M* KCl, and that of zinc at −1.200 V. With the supporting electrolyte alone, the background counting rates at these two potentials were evaluated. They corresponded to residual currents of 0.092 and 0.175 μA, and were measurable with a precision of about ±1%.

With cadmium alone the ratio of its diffusion currents at −1.200 V and −0.820 V (corrected for the background currents) was carefully evaluated, and the average of two trials with 5 and 10 m*M* cadmium ion was 0.9869 ± 13. Thus the diffusion current at −1.200 V is 1.31% smaller than at −0.820 V.

A standard 2.500 m*M* solution of zinc sulfate in 1.00 *M* potassium chloride with 0.001% gelatine was prepared. Test solutions were prepared by mixing known volumes of this standard solution with a 10.00 m*M* solution of cadmium chloride in the same supporting electrolyte. Determination of the zinc in these test solutions is illustrated by the following data obtained in a typical trial.

The counting rate (N/t) of the integrator with the standard 2.500 m*M* zinc solution was first determined at −1.200 V. Triplicate measurements yielded 1.0992, 1.1010, and 1.0997, for an average of 1.1000 ±7 counts/sec when the amplifier input resistance was 53.046 ohms. When the background counting rate (0.0108 counts/sec) is subtracted, this becomes 1.0892±7 counts/sec.

The particular test solution had been prepared by mixing 200.00 cc of the standard zinc solution with 24.95 cc of the cadmium solution, and thus it contained 2.223 m*M* zinc and 1.109 m*M* cadmium. At −0.820 V (cadmium) the counting rate was 1.0522, 1.0519, and 1.0545, for an average of 1.0529±11 counts/sec when the input resistance was 110.08 ohms. Recalculated to what it would have been with the same input resistance used with the standard zinc solution (53.046 ohms), this becomes 0.5074 ± 5 counts/sec. When the background counting rate (0.00568 counts/sec) is subtracted, the corrected value is 0.5017±5 counts/sec at −0.820 V. Multiplication by the factor 0.9869±13, converts this to 0.4951±7 counts/sec at −1.200 V.

At −1.200 V (cadmium plus zinc), the test solution showed a counting rate of

1.0587, 1.0592, and 1.0593, for an average of 1.0591 ± 2 when the input resistance was 38.041 ohms. This corresponds to 1.4769 ± 3 counts/sec at 53.046 ohms, and, after the background counting rate (0.0108 counts/sec) is subtracted, the corrected value corresponding to the sum of cadmium and zinc is 1.4661 ± 3 counts/sec. When the 0.4951 ± 7 counts/sec contributed by the cadmium is subtracted, the counting rate due to the zinc was 0.9710 ± 7 counts/sec. Comparison with the counting rate of the standard zinc solution yields (0.9710 ± 7/1.0892 ± 7)·2.500 or 2.229 ± 2 mM zinc found. This is 0.27% larger than the 2.223 mM that was actually present.

As expected, because the concentration of cadmium was only half that of the zinc, the error in this case was not much larger than it would have been in the absence of cadmium. Naturally, the error is greater when the cadmium concentration exceeds that of the zinc, and when the zinc concentration is smaller than in the preceding case. For example, with another test solution containing 2.5 mM cadmium and only 1 mM zinc the error of the zinc determination was −0.59%.

SUMMARY

A new method of measuring the polarographic limiting current is described, based on integrating it over a precisely known time interval which includes 50 or more mercury drops. The averaging effect of integration minimizes the influence of small random variations in the factors which govern the diffusion current and is conducive to high precision. The electrical instrumentation, which produces the time integral as a direct readout, is relatively simple, and all components are availabe commercially as complete units whose assembly requires only interconnection. Provided that the correction for any preceding diffusion currents is smaller than the one being measured, and by comparison with a standard solution, substances present at concentrations 1–10 mM are determinable with a precision and accuracy of the order of ±0.1%.

RÉSUMÉ

On décrit une nouvelle méthode pour mesurer le courant limite en polarographie, méthode basée sur l'intégration du courant limite dans un intervalle de temps connu avec précision pendant lequel s'écoulent 50 gouttes de mercure, ou plus. L'avantage de la méthode d'intégration est de diminuer l'influence de petites variations dues au hasard, c'est-à-dire aux facteurs qui ont une influence sur le courant de diffusion; on peut donc le déterminer avec une grande précision. L'équipement électrique qui permet de lire directement le temps d'intégration est relativement simple; tous les composants peuvent être obtenus sur le marché sous forme d'unités complètes dont l'assemblage ne nécessite que des interconnections.

En supposant que la correction pour n'importe quels courants de diffusion soit plus faible que celle que l'on calcule, et en comparant avec une solution étalonne, on peut déterminer les substances présentes à des concentrations de 1 à 10 mM avec une précision de l'ordre de ± 0.1%.

ZUSAMMENFASSUNG

Es wird eine neue Methode zur Messung des polarographischen Grenzstroms

beschrieben. Sie beruht darauf, dass für eine genau bekannte Zeit von etwa 50 oder mehr Quecksilbertropfen der Strom integriert wird. Der mittelnde Effekt dieser Integration verringert den Einfluss kleiner Zufallsschwankungen des Diffusionsstroms und ist der Genauigkeit förderlich. Die elektrische Instrumentation ist relativ einfach und kommerziell zugänglich. Konzentrationen von 1 bis 10 m*M* sind mit einer Reproduzierbarkeit und Richtigkeit von ±0.1% bestimmbar.

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ANODIC STRIPPING SQUARE-WAVE VOLTAMMETRIC DETERMINATION OF LEAD IN HIGH-PURITY BISMUTH

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Stripping voltammetric analysis with linearly varying potential has been studied by many workers, but few papers have been published on stripping analysis in conjunction with square-wave voltammetry. BARKER[1] detected 10^{-9}–10^{-8} M cadmium, lead, and copper in potassium chloride–hydrochloric acid base solutions by this technique. STURM AND RESSEL used the method to determine nanogram amounts of 11 elements[2] (Bi, Cu, Sb, Pb, Sn, Tl, Cd, In, Zn, Mn and Ba) and later to analyse As for impurities at the p.p.b. level[3]. Hanging mercury drop electrodes were used in these experiments. The present authors have found that high sensitivity and excellent reproducibility are achieved in the stripping of lead from a mercury-plated platinum electrode[4], and have applied this technique in combination with anion-exchange separation to the determination of lead at the p.p.b. level in high-purity bismuth metal. Various methods have been proposed for the determination of traces of lead in bismuth, *i.e.*, emission spectrography[5-9], voltammetry[10-14], and spectrophotometry[13], mostly combined with separation or preconcentration techniques including volatilization[13], solvent extraction[10], precipitation[6], electrodeposition[11], amalgamation[12], ion-exchange[14], and zone melting[5]. However, the present method has several advantages such as high sensitivity, excellent precision at low levels, and simplicity.

EXPERIMENTAL

Apparatus

A Yanaco PF-501 polarograph (Yanagimoto Mfg. Co., Kyoto, Japan) was used for pre-electrolysis and recording of current–voltage curves. A saturated calomel reference electrode (S.C.E.) was separated from a sample solution by a 3% agar-saturated potassium chloride bridge held in place by a fine-porosity sintered-glass disk.

Preparation of mercury-plated platinum electrodes

A small platinum wire (0.7 mm diam. × 2.2 mm exposed) sealed into a piece of 5-mm soft glass tubing, was washed in hot concentrated nitric acid for 5 min and then in water; it was then used as cathode in a saturated potassium chloride solution at a total applied voltage of 2.5 V for 3 min, a platinum wire (0.5 mm diam. × 10 mm) serving as anode. After rinsing with water, the electrode was plated in 0.25 M

mercury(II) nitrate at 2.6 V for 3 min, rinsed in water, and then conditioned by holding it cathodic in a saturated potassium chloride solution at 2.5 V for 3 min. During the conditioning, the matted gray surface of the electrode turned bright. A large evolution of hydrogen gas from the surface indicates imperfect plating. After each anodic stripping experiment, the electrode was held at −0.2 V *vs.* S.C.E. in a stirred 0.1 *M* potassium chloride–0.01 *M* hydrochloric acid solution for 5 min to remove lead completely for the following experiment.

Reagents

Water was purified by ion-exchange followed by repeated distillation. *Nitric acid* was purified by distillation. *Hydrochloric acid* was purified by isopiestic distillation[15] at room temperature (20°); *ca.* 0.0002 p.p.m. of lead was found in purified 10.5 *M* hydrochloric acid.

Potassium chloride. Potassium chloride solution (100 ml of 3 *M*) was shaken with 4 ml of 0.1% sodium diethyldithiocarbamate and 20 ml of chloroform twice, and then with 20 ml of chloroform. The aqueous phase was evaporated to dryness in a quartz beaker and heated to about 400° to destroy organic matter.

Standard lead solutions. A stock solution (1.00 mg of lead per ml) was prepared by dissolving 100 mg of pure lead (99.99%) in 10 ml of nitric acid (1:1) and diluting to 100 ml with water. This solution was diluted to 0.001–10 μg of lead per ml with water.

Lead-free bismuth solution. High-purity bismuth metal (1 g) was dissolved and adsorbed on anion-exchange resin as described under *Recommended procedure.* After elution of lead with 40 ml of 8 *M* hydrochloric acid, bismuth was eluted with 300 ml of 0.5 *M* nitric acid. The effluent was collected in a quartz beaker and evaporated to dryness. The residue was then dissolved in 5 ml of 5 *M* nitric acid.

Anion-exchange resin. BioRad AG 1-X8, 100–200 mesh, chloride-form.

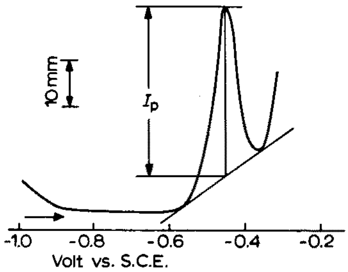
All the reagents used were of reagent grade. A quartz condenser was employed in the distillations. Prepared solutions were stored in polyethylene bottles.

Recommended procedure

Place 1 g of bismuth metal sample in a 50-ml quartz beaker, add 6 ml of nitric acid (1:1), and heat to dissolve completely. Cool the solution, and add water and nitric acid (1:1) to give 5 ml of 5 *M* nitric acid solution. Pour this solution onto a 1-cm diam. × 15-cm column containing 12 g of anion-exchange resin, pretreated with 5 *M* nitric acid, at a flow rate of 0.3 ml per min, and pass 40 ml of 8 *M* hydrochloric acid through the column at the same rate, collecting the effluent in a 100-ml quartz beaker. Evaporate the effluent to dryness on a water bath, moisten the residue with a few ml of water, and evaporate to dryness again. Dissolve the residue in 2 ml each of 0.1 *M* hydrochloric acid and 1 *M* potassium chloride, and dilute to 20 ml with water.

Transfer the solution to a 20-ml electrolysis cell, and deaerate with purified tank nitrogen for 10 min. Pre-electrolyze with stirring at a constant rate (about 800 r.p.m.) onto a mercury-plated platinum electrode at −1.0 V *versus* S.C.E. for 15 or 30 min. Switch the cell out of the electrolysis circuit, and stop the stirring. After 30–60 sec, scan the electrode potential from −1.0 to −0.2 V *versus* S.C.E. and record a current–voltage curve by means of a square-wave polarograph (scan rate: 0.2 V/min; square-wave voltage: 10 mV; amplifier sensitivity: 1/50; recorder sensitivity:

0.1 µA/mm). Measure the peak height (see Fig. 1), and determine the amount of lead by reference to a calibration curve (peak height *versus* lead quantity) prepared with standard lead solutions.



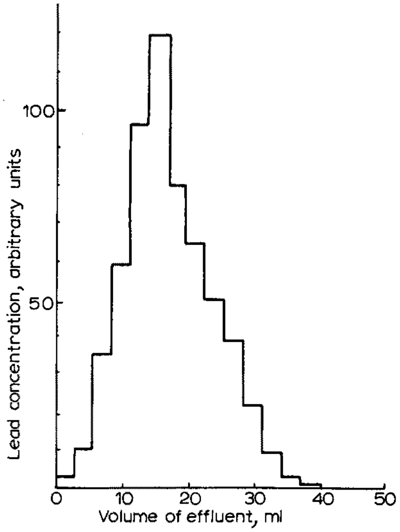


Fig. 1. Typical current–voltage curve for anodic stripping of 0.5 µg of Pb in 20 ml of 0.1 *M* KCl–0.01 *M* HCl after 15-min pre-electrolysis.

Fig. 2. Elution curve of lead. Sample solution: 5 ml of 5 *M* HNO_3 solution containing 1 g of Bi and 100 µg of Pb. Eluent: 8 *M* HCl.

RESULTS AND DISCUSSION

Anodic stripping voltammetry of lead

Of the various mercury electrodes[16] (including hanging drop and pool) tried in this laboratory, a mercury-plated platinum electrode as described by MARPLE AND ROGERS[17] and OZAKI AND NAKAYAMA[18] was selected because of its excellent reproducibility and ease of preparation. When a saturated solution of mercury(II) nitrate was used for plating mercury onto a platinum electrode, however, a relatively thick mercury layer was formed, and, as a result, lower peak heights of lead were observed. Therefore, a 0.25 *M* solution was used in the present work. A typical current–voltage curve is shown in Fig. 1. A mercury-plated platinum electrode could be used repeatedly about 20 times and stored for over 3 days in water without change in peak height. Reproducible results were also obtained when the electrode was re-plated with mercury.

The equations of calibration curves were as follows:

$$C = 0.011\, I_p \qquad (0 < C < 1.0) \tag{1}$$

for 15-min pre-electrolysis, and

$$C = 0.0016\, I_p - 0.006 \qquad (0 < C < 0.1) \tag{2}$$

for 30-min pre-electrolysis, where C is the amount of lead (µg) in 20 ml of electrolyte, and I_p the peak height (mm). The maximum deviations were about ±5% in the range 0.1–1 μg for eqn. (1), and ±10% in the range 0.01–0.1 μg for eqn. (2). A low but distinct peak was observed in a current–voltage curve after the supporting electrolyte alone was pre-electrolyzed for 30 min. This peak did not appear when the pre-electrolysis time was shorter than 15 min. The most probable cause of this peak was lead remaining in purified potassium chloride. By extrapolating the calibration curve, lead in purified potassium chloride was roughly estimated to be 0.05 p.p.m.

The effect of foreign elements on the peak height of lead is summarized in Table I. The results indicate that it is necessary to remove bismuth almost completely before the anodic stripping square-wave voltammetric determination of lead.

TABLE I

EFFECT OF FOREIGN ELEMENTS ON PEAK HEIGHT OF LEAD

(Pb present: 0.5 μg. Pre-electrolysis time: 15 min)

Foreign element	*Added as*	*Amount added (μg)*	*Peak height (mm)*
None	—	—	45
Bi(III)	$Bi(NO_3)_3 \cdot 5H_2O$	10.0	45
		100	42
		200	—
Ag(I)	$AgNO_3$	0.5	46
		1.0	75
		5.0	93
Cu(II)	$Cu(NO_3)_2 \cdot 3H_2O$	1.0	45
		10.0	47
		50.0	13
As(III)	As_2O_3	1.0	43
		10.0	43
		50.0	35
Fe(III)	$Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	1.0	48
		10.0	43
		50.0	45
Sb(III)	$SbCl_3$	1.0	41
		5.0	54
Sn(IV)	$SnCl_4 \cdot 5H_2O$	0.5	41
		1.0	49
		5.0	60

Anion-exchange separation of lead from bismuth

In order to separate traces of lead from large amounts of bismuth, various existing methods were tried. These included volatilization of bismuth as bromide[13], anion exchange in hydrochloric acid media[14], controlled-potential electrolysis with a mercury cathode, and selective amalgamation of bismuth in hydrochloric acid solution[12]. Since none of them offered satisfactory results in our experiments, the anion exchange method with the use of nitric and hydrochloric acid media described under *Recommended procedure* was adopted. This method is based on the fact that, in 5 *M* nitric acid[19,20] or 8 *M* hydrochloric acid[20], bismuth(III) is adsorbed on anion-exchange resin, whereas lead(II) shows little adsorption. A typical elution curve of lead is shown in Fig. 2, where the lead concentration in each 3-ml fraction was measured by square-wave polarography. Bismuth accompanying lead was less than 50 μg. Other interfering trace elements such as silver were also separated from lead simultaneously. Bismuth adsorbed on the column was eluted completely with 300 ml of 0.5 *M* nitric acid.

ANALYTICAL RESULTS

Synthetic samples prepared from lead-free bismuth and standard lead solutions, and a sample of commercial high-purity bismuth metal were analyzed by the proposed method with the results shown in Tables II and III. The blank value through the entire procedure was about 0.006 μg of lead, which seemed to originate mainly from hydrochloric acid. The precision of the analytical value is about ±5% at the parts per billion level. The lower limit of determination is about 0.01 p.p.m., which can be improved by reducing the lead contamination. A time required for a determination is approximately 5 h.

TABLE II

DETERMINATION OF LEAD IN SYNTHETIC SAMPLES

(Bi present: 1.00 g)

Pb added (μg)	*Pb found (μg)*	*Pb recovered (%)*	*Pre-electrolysis time (min)*
0.020	0.018	90	30
0.050	0.049	98	30
0.050	0.051	102	30
0.50	0.51	102	15
0.50	0.51	102	15

TABLE III

DETERMINATION OF LEAD IN HIGH-PURITY BISMUTH METAL

(Pre-electrolysis time: 15 min)

Sample taken (g)	*Pb found[a] (μg)*	*Pb in Bi (p.p.m.)*
1.00	0.65	0.65
1.00	0.60	0.60
0.40	0.25	0.63
0.40[b]	0.43	0.58
		Av. 0.62

[a] A blank value (0.006 μg) was subtracted.
[b] 0.20 μg of lead was added before ion-exchange.

SUMMARY

Anodic stripping voltammetry of lead with a mercury-plated platinum electrode and the square-wave technique is described. In combination with anion-exchange separation in nitric and hydrochloric acid media, this method is applicable to the determination of down to 0.01 p.p.m. of lead in high-purity bismuth. The error is about ±5% at the 0.6 p.p.m. level.

RÉSUMÉ

On décrit une méthode voltamétrique comprenant la dissolution anodique du plomb en utilisant comme cathode une électrode de platine plaquée au mercure; la technique de l'onde carrée est également décrite. En combinant avec une séparation au moyen d'une résine échangeuse d'anions en milieu acide nitrique et acide chlorhydrique, la méthode est applicable à la détermination du plomb jusqu'à 0.01 p.p.m. dans le bismuth de haute pureté. L'erreur est environ de ±5% pour une teneur de 0.6 p.p.m.

ZUSAMMENFASSUNG

Die anodische Stripping-Voltammetrie von Blei mit einer quecksilberplatierten Platinelektrode und der "square-wave"-Technik wird beschrieben. In Verbindung mit einer Anionenaustauschertrennung in salpeter- und salzsaurem Medium ist diese Methode zur Bestimmung bis hinab zu 0.01 p.p.m. Blei in hochreinem Wismut geeignet. Der Fehler beträgt etwa 5% bei 0.6 p.p.m. Pb.

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SIMULTANEOUS DETERMINATION OF STRONTIUM AND BARIUM BY NEUTRON ACTIVATION ANALYSIS WITH A Ge(Li) DETECTOR

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In recent years, COBB[1] and GORDON *et al.*[2] have reported on the use of a high-resolution lithium-drifted germanium detector (Ge(Li) detector) in instrumental activation analysis and have described schemes for the non-destructive determination of many elements in various rock samples of geochemical interest. On the other hand, for a more effective utility of a Ge(Li) detector in applications to neutron activation analysis, our group have recommended the employment of the Ge(Li) detector in conjunction with simple chemical group-separations, in order to diminish the background and eliminate spectral interferences. The technique was successfully applied to the determinations of rare earth elements[3,4] and rubidium and cesium[5] in rock samples by neutron activation analysis.

The proposed technique has a limitation in relation to the measurement of the chemical yield, namely it is desirable that there must be no chemical fractionation within all elements of interest during group-separation. However, even if there is chemical fractionation in the group-separation procedure employed, the limitation can be overcome by introducing a re-activation technique to determine the chemical yields of individual elements. The idea seems to have general applicability.

In the present paper, a procedure is described for a rapid simultaneous determination of strontium and barium in rock samples with a Ge(Li) detector after short sample irradiation and rapid chemical group-separation by a conventional precipitation method. The chemical yields for both elements are obtained individually by a simple re-activation technique without any additional chemical treatment. The development of a simple, convenient, and sensitive analytical method for strontium and barium in rocks and minerals is of great interest in the geochemical field.

EXPERIMENTAL

Samples and irradiations

Samples of six U. S. G. S. Standard Rocks G-1 (granite), W-1 (diabase), G-2 (granite), GSP-1 (granodiorite), AGV-1 (andesite), and BCR-1 (basalt), were studied. Approximately 0.5-g samples of the powdered rocks were weighed into polyethylene ampoules which were then sealed. A 10-μl aliquot each of standard strontium and barium solutions (22.89 mg Sr/ml and 14.84 mg Ba/ml) was impregnated into a piece of filter paper placed in polyethylene ampoule which was then sealed. Samples and standards were then positioned inside a polyethylene capsule and irradiated for 1 h at a power level of 100 kW and a neutron flux of *ca.* $1.5 \cdot 10^{12}$ n/cm^2/sec, in the Triga Mark-II reactor of Rikkyo University.

Radiochemical separation of strontium and barium

After cooling for 30 min, the irradiated sample was decomposed by sodium peroxide fusion in a nickel crucible containing strontium and barium carriers (22.9 mg Sr and 14.8 mg Ba). The melt was dissolved with water and minimal amounts of concentrated hydrochloric acid. To the clear solution obtained was added concentrated ammonia solution to precipitate the hydroxides, which were spun down and discarded. Then 20 ml of 10% sodium carbonate solution was added to the supernatant solution and the strontium and barium carbonate mixture was spun down. The precipitate was dissolved in 10 ml of fuming nitric acid and cooled in ice for 10 min to precipitate strontium and barium nitrates. The nitrate mixture was dissolved in 10 ml of water and 2 ml of concentrated ammonia solution, and the strontium and barium carbonate mixture was precipitated by adding 5 ml of 10% sodium carbonate solution. The mixture was washed with two 20-ml portions of water, spun down to the bottom of 1-cm diameter polyethylene tube and transferred to a Ge(Li) detector for γ-counting. The irradiated reference standard was dissolved in a small amount of concentrated hydrochloric acid in the presence of the strontium and barium carriers, and treated by the same chemical procedure stated above (except the hydroxide scavenge and nitrate precipitation step) so as to obtain the same counting geometry as the samples. The time required for the chemical separation was 1.5 h for 5 samples.

Detector and γ-ray measurements

The Ge(Li) detector used in this study was made in this Institute and the active volume of the detector is estimated to be *ca.* 9.6 ml. The detector is operated in a vacuum at 77°K with a bias voltage of 1080 V. The output signal from the detector was fed into an Ortec Model 118A preamplifier and an Ortec Model 410 linear amplifier. The resultant pulse was then analyzed by an RCL 400-channel pulse-height analyzer. Resolution for the ^{57}Co 122-keV peak was 3 keV.

Nuclear data for the nuclides used in the determination of strontium and barium are as follows: ^{86}Sr(9.86%) (n_{th}, γ)^{87m}Sr; effective cross-section for this reaction, 1.3 barns; half-life of ^{87m}Sr, 2.83 h; energy and intensity of γ-ray emitted by ^{87m}Sr, 388 keV (100). ^{138}Ba(71.66%) (n_{th}, γ)^{139}Ba; effective cross-section for this reaction, 0.5 barns; half-life of ^{139}Ba, 82.9 min, energies and intensities of γ-ray emitted by ^{139}Ba, 166 keV (100), 1.09 MeV (0.12), 1.27 MeV (0.3), 1.43 MeV (1.8). In this study, the 388-keV photopeak of ^{87m}Sr and the 166-keV photopeak of ^{139}Ba were used for the determination of strontium and barium, respectively.

Re-activation for chemical yield determination

The chemical yields of strontium and barium for the procedure were obtained by a simple re-activation technique without any additional chemical treatment. After complete decay of both photopeaks from ^{87m}Sr and ^{139}Ba, the strontium and barium carriers recovered as a carbonate mixture were irradiated at a neutron flux of $5 \cdot 10^{11}$

n/cm^2/sec for 5 min and the same photopeaks stated above from the samples and the reference standard were compared to obtain the chemical yields for both elements independently. The chemical yields were approximately 70%.

RESULTS AND DISCUSSION

Figure 1 shows a representative γ-ray spectrum of strontium and barium mixture isolated from the standard rock BCR-1 (basalt) along with that of the reference standard. As shown in Fig. 1, the γ-ray spectrum of both strontium and barium activities from the sample was identical with that of the reference standard. No extraneous γ-activities were found in either spectra. From the decay plots of the 388-keV and 166-keV photopeaks, it was checked that the half-lives were 2.8 h for ^{87m}Sr and 83 min for ^{139}Ba respectively.

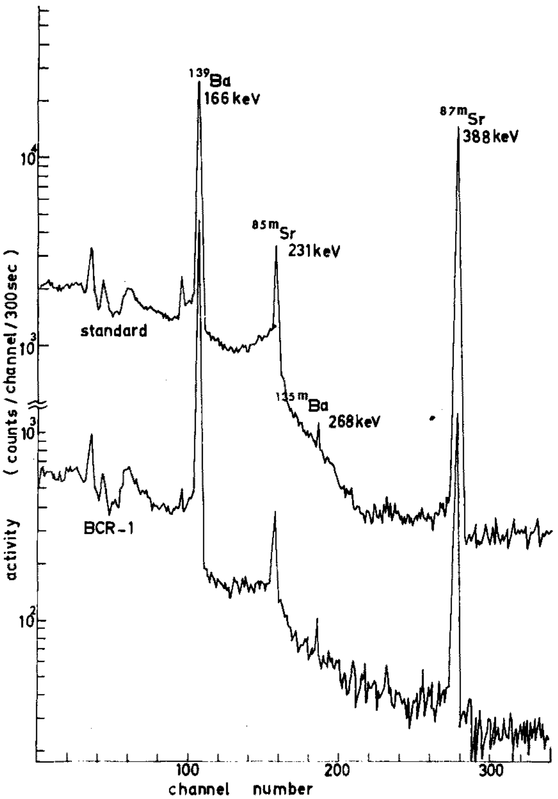

Fig. 1. γ-Ray spectra from the sample BCR-1 and the reference standard (about 2 h after the end of irradiation).

When the simple re-activation technique is applied for the independent determination of the chemical yield of strontium and barium, it is necessary to check whether there is any self-shielding effect with the milligram amounts of strontium and barium carriers or not. Milligram amounts of strontium (ranging from 1.2 mg to 24 mg) and of barium (ranging from 0.8 mg to 13 mg) were irradiated and counted under the

TABLE I

CONCENTRATIONS OF STRONTIUM AND BARIUM IN SEVERAL GEOCHEMICAL STANDARD ROCKS

Sample	*Split/position*	*Sr (p.p.m.)*[a]	*Ba (p.p.m.)*[a]
G-1		256 ± 4	1005 ± 20
(Granite)		254 ± 11	1050 ± 33
		av. 256 ± 4	av. 1015 ± 17
W-1		192 ± 3	161 ± 3
(Diabase)		195 ± 6	178 ± 4
		av. 193 ± 3	av. 167 ± 3
G-2	54/10	442 ± 14	1640 ± 40
(Granite)		446 ± 14	1610 ± 41
		av. 445 ± 10	av. 1627 ± 29
GSP-1	13/22	220 ± 7	1102 ± 22
(Granodiorite)		242 ± 14	1168 ± 20
		av, 224 ± 7	av. 1137 ± 15
AGV-1	26/3	617 ± 22	1040 ± 22
(Andesite)		597 ± 38	1128 ± 44
		av. 612 ± 19	av. 1060 ± 20
BCR-1	39/20	332 ± 15	623 ± 16
(Basalt)		325 ± 10	626 ± 13
		av. 327 ± 9	av. 625 ± 10

[a] The errors in the third and fourth columns were calculated from the counting statistics. The averages were computed by suitable weighting.

conditions described in the re-activation procedure. The results showed that the radioactivities measured *vs.* the mg amounts of both elements were linear in the ranges stated above and no self-shielding effects for either element were found.

Strontium and barium abundances found in the geochemical standard rocks used are summarized in Table I. G-1 and W-1 were received from M. FLEISCHER of U. S. Geological Survey, and G-2, GSP-1, AGV-1, and BCR-1 from F. J. FLANAGAN of U. S. Geological Survey. In Table II, the mean values for these standard rocks are compared with the recommended values given by FLEISCHER[6] in the latest summaries of data on G-1 and W-1, and with reported values of other workers[2,7–9]. It is shown in Table I that the values obtained from duplicate analysis agree well within the experimental errors. As shown in Table II, the close agreement with previous reported values for all of these geochemical standard rocks also indicates that the accuracy of the present procedure is good.

In the non-destructive neutron activation technique with a Ge(Li) detector after long irradiation and long cooling reported by GORDON *et al.* [2], it was impossible to determine the barium content in W-1 and the limit of detection was 200 p.p.m. Ba for W-1. The strontium content in various rocks could not be determined by their non-destructive technique. The non-destructive determination with ^{87m}Sr and ^{139}Ba after short irradiation and cooling is thought to be very difficult for rock samples from which large activities of ^{56}Mn and ^{24} Na are always induced. The strontium content may be

TABLE II

COMPARISON OF STRONTIUM AND BARIUM CONCENTRATIONS IN SEVERAL GEOCHEMICAL STANDARD ROCKS

Sample	*Sr (p.p.m.)*	*Ba (p.p.m.)*	*Method*	*Reference*
G-1	250	1220	Recommended value	FLEISCHER[6]
	—	1039	Isotope dilution	SCHNETZLER *et al.*[8]
	256 ± 4	1015 ± 17	Neutron activation	This work
W-1	180	180	Recommended value	FLEISCHER[6]
	—	158	Isotope dilution	SCHNETZLER *et al.*[8]
	175	145	Spark source mass spectrography	NICHOLLS *et al.*[9]
	—	< 200	Neutron activation	GORDON *et al.*[2]
	193 ± 3	167 ± 3	Neutron activation	This work
G-2	340–500	1400–2000	Emission spectrography	FLANAGAN[7]
	—	1800 ± 70	Neutron activation	GORDON *et al.*[2]
	445 ± 10	1627 ± 29	Neutron activation	This work
GSP-1	220–300	1000–1600	Emission spectrography	FLANAGAN[7]
	—	1110 ± 50	Neutron activation	GORDON *et al.*[2]
	224 ± 7	1137 ± 15	Neutron activation	This work
AGV-1	610–900	1200–1800	Emission spectrography	FLANAGAN[7]
	—	1180 ± 100	Neutron activation	GORDON *et al.*[2]
	612 ± 19	1060 ± 20	Neutron activation	This work
BCR-1	300–410	460–880	Emission spectrography	FLANAGAN[7]
	—	650 ± 30	Neutron activation	GORDON *et al.*[2]
	327 ± 9	625 ± 10	Neutron activation	This work

determined also with the NaI(Tl) detector after the decontamination procedure described in this paper. On the other hand, the accurate determination of barium by this technique seems to be difficult, especially for samples containing smaller amounts of the element compared to the strontium, because of incomplete resolution between the 166-keV ^{139}Ba and 231-keV ^{85m}Sr peaks and the interference by Compton background from the 388-keV ^{87m}Sr radiations. With the present procedure, a better sensitivity (Sr:10 p.p.m., Ba:5 p.p.m.) can be achieved and the technique is applicable to the determination of both elements in geochemically important rock samples. However, the detection of strontium and barium in ultramafic rocks was difficult by this procedure and both elements may be best determined by β- and/or γ-counting technique after mutual separation of strontium and barium.

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SUMMARY

A method is described for the simultaneous determinations of strontium and barium in rock samples by neutron activation analysis with a Ge(Li) detector after chemical group-separation. The re-activation technique was employed to obtain the chemical yields for both elements without any additional chemical treatment. The values obtained for several geochemical standard rocks (G-1, W-1, G-2, GSP-1, AGV-1 and BCR-1) are in reasonable agreement with previously published data.

RÉSUMÉ

On décrit une méthode pour déterminer simultanément le strontium et le baryum dans des échantillons de roches, selon une analyse par activation neutronique, au moyen d'un détecteur Ge(Li), après séparation du groupe chimique. La technique de la réactivation a été employée pour obtenir les rendements chimiques pour les deux éléments sans traitement chimique supplémentaire. Les valeurs obtenues pour plusieurs échantillons de roches standards géochimiques (G-1, W-1, G-2, GSP-1, AGV-1 et BCR-1) sont en bon accord avec les valeurs publiées antérieurement.

ZUSAMMENFASSUNG

Es wird eine Methode zur gleichzeitigen Bestimmung von Strontium und Barium in Gesteinsproben mit der Neutronenaktivierungsanalyse beschrieben. Nach einer chemischen Gruppentrennung wird ein Ge(Li)-Detektor verwendet. Die Reaktivierungstechnik wurde angewandt, um chemische Ausbeuten für beide Elemente zu erhalten ohne eine zusätzliche chemische Behandlung vorzunehmen. Die erhaltenen Werte für zahlreiche geochemische Standardgesteine stehen in vernünftiger Übereinstimmung mit früher veröffentlichten Date.

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SHORT COMMUNICATIONS

The determination of molybdenum by atomic absorption spectroscopy

KIRKBRIGHT, SMITH AND WEST have recently reported the determination of molybdenum in alloy steels[1] and of niobium and tantalum[2] with a nitrous oxide–acetylene flame. These authors did not find interference from foreign ions, either because of the presence of large concentrations of the matrix element iron which causes severe depression of molybdenum absorption[1], or because of a rather selective extraction of molybdenum(VI) as its oxinate from a medium containing both EDTA and fluoride. Earlier work on the determination of aluminum[3] and vanadium[4] in nitrous oxide–acetylene flames indicated that the presence of certain ions caused considerable enhancement in the absorption signal of these metals. This observation prompted us to ascertain the effect of various ions on the determination of molybdenum in aqueous samples. The results indicated that numerous ions interfere. This communication describes the details of this investigation and a simple and rapid procedure is proposed to overcome the interferences.

Apparatus

A Perkin-Elmer (Model 303) atomic absorption spectrophotometer was used for absorption measurements. The standard burner head on the Perkin-Elmer burner mount was replaced by a nitrous oxide–acetylene burner head with a slot length of 3 in and a width of 0.015 in. In addition to the two-stage regulators on the gas tanks, pressure gauges were used in the nitrous oxide lines and a flow meter was used in the acetylene line. A Perkin-Elmer hollow-cathode lamp was used as radiation source.

Reagents

A stock solution containing 1 mg/ml of molybdenum(VI) was prepared by dissolving 1.840 g of ammonium molybdate tetrahydrate in 1 l of distilled water. Standard working solutions were prepared by appropriate dilution of the stock solution. Solutions for interference studies were prepared from reagent-grade chemicals.

TABLE I

OPERATING CONDITIONS

Wavelength: 3132.6 Å	Nitrous oxide
Slit: 0.3 mm (2 Å)	Atomizer: 35 p.s.i.
Lamp current: 35 mA	Auxiliary: 15 p.s.i.
	Acetylene: 5 l/min.

Operating conditions

The optimum operating conditions listed in Table I were established with a 20-p.p.m. solution of molybdenum. Absorption measurements were made at the rose-red inner cone of the flame about 1 cm above the burner head. Water was first sprayed to set the zero of the instrument and, while the standard molybdenum solution was aspirated, the burner position was adjusted to give maximum absorption. Under these conditions the sample uptake was about 4 ml per min and the sensitivity was 1 p.p.m. of molybdenum for 1% absorption.

Interference studies

DAVID[5] has reported the suppressing effect of certain ions in the molybdenum absorption in an air–acetylene flame which were completely eliminated by the addition of aluminum chloride. MOSTYN AND CUNNINGHAM[6] later recommended the use of ammonium chloride as an interference-suppressing agent for the analysis of molybdenum in ferrous alloys. Our examination of the effect of various foreign ions in a nitrous oxide–acetylene flame showed that most ions affect molybdenum absorption. The ions examined and their effect on molybdenum absorption are shown in Table II. The cations were added as chlorides or nitrates, or, in certain instances, as sulfates, and the anions as sodium or potassium salts. In these investigations the concentration of molybdenum was 20 p.p.m. and that of interferent 200 p.p.m.

TABLE II

INTERFERENCES FROM VARIOUS SUBSTANCES ON MOLYBDENUM ABSORPTION

(Molybdenum: 20 p.p.m.)

Interferent (200 p.p.m.)	*Absorption (%)*	*Interferent (200 p.p.m.)*	*Absorption (%)*	*Interferent (200 p.p.m.)*	*Absorption (%)*
None	19.8	HCO_3^-	23.5	Cd^{2+}	13.3
Br^-	22.6	$HAsO_4^{2-}$	24.5	Hg_2^{2+}	19.7
I^-	22.4	Li^+	19.8	Hg^{2+}	19.0
F^-	16.7	Na^+	20.0	Sn^{2+}	18.4
Cl^-	19.6	K^+	19.8	Fe^{3+}	23.6
SO_4^{2-}	23.8	La^{3+}	23.3	Cr^{3+}	20.8
SO_3^{2-}	22.9	Ca^{2+}	8.7	Pb^{2+}	22.6
NO_3^-	21.5	Sr^{2+}	2.7	Sb^{5+}	22.8
HPO_4^{2-}	26.8	Ba^{2+}	13.2	Ce^{4+}	12.3
SeO_3^{2-}	21.4	Mg^{2+}	19.8	U^{6+}	23.6
TeO_3^{2-}	22.8	Mn^{2+}	19.8	Al^{3+}	27.3
WO_4^{2-}	19.8	Co^{2+}	21.4	Ti^{4+}	27.2
$B_4O_7^{2-}$	19.6	Ni^{2+}	23.5	Zr^{4+}	24.8
VO_3^-	21.6	Pd^{2+}	23.2	Be^{2+}	27.0
SiO_3^{2-}	25.0	Cu^{2+}	24.3		
CO_3^{2-}	23.5	Zn^{2+}	23.7		

The effect of acids was examined by adding 5 ml of the appropriate concentrated acid to the solution followed by dilution to 100 ml with distilled water. Both perchloric and acetic acids enhanced the absorption by about 30%, whereas sulfuric acid interfered by reducing the sensitivity by about 25%. Hydrochloric acid and nitric acid showed little affect on molybdenum absorption.

An examination of Table II indicates that most ions caused an enhancement in molybdenum absorption. The few ions that showed suppressing effect included Ca^{2+}, Ba^{2+}, Sr^{2+}, Cd^{2+} and Ce^{4+}. It is also evident from Table II that the presence of ions such as Al^{3+} and Ti^{4+} which readily form stable oxides in the flame, caused maximum enhancement of molybdenum absorption. Later experiments confirmed that the interferences from these ions were not additive, as no further enhancement was noticed when more than one refractory metal ion was present in the sample. Although, in these instances, the enhancement in sensitivity could be attributed to the competitive reaction to form stable oxides, as was noticed in the case of aluminum[3] and vanadium[4], the reason for an enhancement in the presence of most other ions was not clear.

An attempt was next made to determine the interfering effect of various ions on molybdenum absorption in the presence of a refractory metal ion. Aluminum was chosen for examination as it is readily available and has already been shown to be effective in overcoming the interferences in air–acetylene flames[5]. Although it was confirmed experimentally that 50 p.p.m. of aluminum is sufficient to produce maximum enhancement of molybdenum absorption, a higher concentration of aluminum (100 p.p.m.) was present when the effect of various ions was re-investigated. The concentration of molybdenum and interferents were, as before, 20 p.p.m. and 200 p.p.m. respectively. None of the ions listed in Table II showed any effect on molybdenum absorption when the absorption values were compared to solutions containing identical concentrations of molybdenum and aluminum in the absence of extraneous ions. The interfering effect of the few ions that were found to suppress molybdenum absorption also disappeared in the presence of aluminum.

Conclusion

The results of this investigation indicated that the determination of molybdenum in nitrous oxide–acetylene flame was subject to interference from several extraneous ions and compounds. Depending upon the ion present, the interference was either an enhancement or a depression in the molybdenum absorption. However, the method could be made more selective by the addition of aluminum to the samples. The sensitivities in the absence and presence of aluminum were respectively 1 p.p.m. and 0.8 p.p.m. of molybdenum for 1% absorption.

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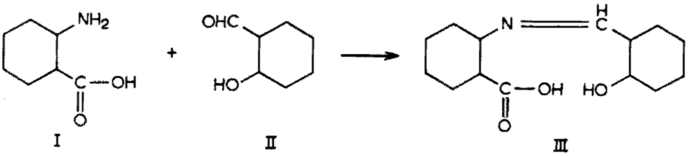
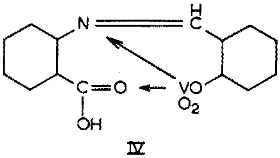
Specific microdetermination of vanadium(V) on the ring oven

Methods for the determination of vanadic acid are usually based on the oxidative power of vanadic acid by which colored substances are formed, or on the reaction of vanadate with certain organic bases to form voluminous precipitates. The main deficiency of these methods is their lack of selectivity.

In a search for a new reagent, a compound which is highly selective for the easy detection of vanadic acid was found[1]. The reagent is a Schiff base (III) formed from the condensation between anthranilic acid (I) and salicylaldehyde (II).



Compound III forms a gray-violet colored ester with vanadic acid (IV), which can serve for the selective identification and determination of vanadic acid.



Although it is easy to isolate the solid reagent (III), a suitable mixture of anthranilic acid and excess of salicylaldehyde in alcohol–benzene solution was used as the reagent solution because at least a ten-fold excess of aldehyde is usually needed to prepare and stabilize Schiff bases[2].

Reagent solution

(A) Dissolve 400 mg of anthranilic acid in 20 ml of ethanol and add 5 ml of benzene.

(B) Dissolve 12 ml (14 g) of salicylaldehyde in 4 ml of ethanol. Mix A and B and dilute to 100 ml with benzene. The reagent is ready for use after 1 h in a water bath at 40–50°. (An alcohol–benzene mixture is used as a solvent because in pure alcohol, compound III hydrolyzes rather quickly, while in benzene it is stable but its solubility is too low for analytical purposes.)

Apparatus used

A Weisz Ring-Oven (National Appliance Co., Portland, Oreg.), a Pandux Surface Temperature thermometer, range +20 to 180° (Pacific Transducer Corporation, Los Angeles 64, Calif.) and calibrated 1–20-μl capillary pipets were used.

F. H. Munktells Swedish filter paper No. IF, 55-mm diameter, was preferred.

Procedure

The central area (diameter about 8–10 mm) of the filter paper was impregnated with a small drop of the reagent solution. The dried paper was then placed on the ring-oven maintained at 45–50° and fixed in position by means of the retainer ring. The sample solution was then added to the reagent spot and dried. The resulting reaction product was washed out with chloroform to the ring zone, using care to avoid flooding the ring. The paper was then exposed to the steam for 1 min in order to wash out any color due to the reagent itself. The gray-yellow ring of a positive vanadate reaction was then matched against standard rings.

A standard scale was prepared from a standard solution containing 0.05 mg V/ml. By using 0.05, 1, 2, 5, 10, 15 and 20 μl of the standard solution, rings containing 0.05, 0.1, 0.25, 0.50, 0.75 and 1.0 μg of vanadium were obtained.

Three rings made from different numbers of microliter drops of the solution are sufficient for each unknown. The color of each of the three rings was compared visually with that of the standard scale. The sum of the numbers of microliter drops of the standard was divided by the sum of the numbers of microliter drops of the three rings made from the unknown solution referred to the standard solution. When this quotient was multiplied by the concentration of the standard solution used to prepare the standard scale, the concentration of the unknown sample was obtained.

Study of interferences

The effect of foreign ions was investigated by developing 2 rings for each species as in the above procedure. The first ring contained 10 μg of the foreign ion while in the second ring 10 μg of the foreign ion and 0.2 μg of vanadium (as vanadate) were present.

The following ions were tested: Na^+, Li^+, Tl^+, Ag^+, Rb^+, Cu^{2+}, Hg^+, Hg^{2+}, Rb^+, Cs^+, Au^{3+}, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, BO_2^-, Al^{3+}, Ga^{3+}, Ce^{3+}, CO_3^{2-}, SiO_3^{2-}, Ti^{4+}, GeO_3^{2-}, Zr^{4+}, Sn^{2+}, Sn^{4+}, Pb^{2+}, Th^{4+}, NH_4^+, NO_2^-, NO_3^-, HPO_4^{2-}, AsO_3^{3-}, Sb^{3+}, Sb^{5+}, Bi^{3+}, $S_2O_3^{2-}$, SO_4^{2-}, SeO_3^{2-}, SeO_4^{2-}, TeO_3^{2-}, TeO_4^{2-}, Cr^{3+}, CrO_4^{2-}, $Cr_2O_7^{2-}$, MoO_4^{2-}, WO_4^{2-}, ReO_4^{2-}, UO_2^{2+}, F^-, Cl^-, ClO_3^-, Mn^{2+}, MnO_4^-, Br^-, BrO_3^-, I^-, IO_3^-, CN^-, SCN^-, $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, Fe^{3+}, Co^{2+}, Ni^{2+}, Pd^{2+}, Rh^{4+}, Pt^{4+}.

None of these ions interfered in any way, so that the method can be considered to be essentially specific. It is remarkable that not even molybdate and tungstate had any effect on the reagent. On the other hand, iron(III) reacted with salicylaldehyde (one of the components of the reagent) to yield the familiar dark colored complex. This coloration, although formed on the center of the filter paper, was not washed out with chloroform to the ring zone, and so this potential interference was obviated.

Preparation of vanadium compounds for their determination

Because this reaction is characteristic for vanadium(V) only, all other vanadium compounds should be oxidized in an acidic medium with 0.1 *N* potassium permanganate until a slight excess of permanganate is visible. The violet color of this excess can be discharged with hydrogen peroxide.

Range of the proposed method

The lower limit for the determination of vanadium was found to be 0.1 μg. The upper limit for accurate estimation was 3 μg of vanadium. Above the upper limit the visual comparison was difficult.

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Derivate von Salicylketonen[1] III. Mitt. Die analytische Anwendung von N,N'-Bis-(*o*-aminoacetophenon)-äthylendiimin zur Palladiumbestimmung

N,N'-Bis(*o*-aminoacetophenon)-äthylendiimin bildet mit einigen Übergangselementen intensivfarbige Metallchelate, die in organischen Lösungsmitteln teilweise recht gut löslich sind. Über die Anwendung dieser Schiffschen Base zur extraktionsphotometrischen Bestimmung von Nickel wurde bereits berichtet[1]. In Fortsetzung dieser Untersuchungen wurde das Reagens auf seine Extraktionseigenschaften für Palladium geprüft.

Reagenzien und Apparate

N,N'-Bis(*o*-aminoacetophenon)-äthylendiimin wurde durch Kondensation von *o*-Aminoacetophenon mit wasserfreiem Äthylendiamin hergestellt[1] und kam in Form einer 0.04 *M* Lösung in Toluol zum Einsatz.

Für die Extraktionsversuche wurde eine $0.4 \cdot 10^{-3}$ *M* Palladium(II)-Lösung benutzt. Zur Herstellung dieser Lösung wurde eine entsprechende Menge Palladiummetall in Königswasser gelöst, bis zur Trockne eingedampft und in Salsäure aufgenommen. Nach mehrmaligem Eindampfen mit Salzsäure wurde der Rückstand in verdünnter Salzsäure aufgenommen, zur vollständigen Reduktion des Palladium(IV) 10 Minuten mit etwas Alkohol gekocht und schliesslich nach Zusatz von Natriumacetat entsprechend mit Wasser aufgefüllt. Die Standardlösung muss in einer dunklen Flasche aufbewahrt werden.

In ähnlicher Weise wurde eine Testlösung der Platinmetalle Rhodium, Osmium und Platin durch Auflösen entsprechender Mengen der Metalle in Königswasser hergestellt. Iridium und Ruthenium wurden dieser Lösung in Form von K_2IrCl_6 bzw. K_3RuCl_3 zugesetzt. Weiterhin kamen als Testsubstanzen K_2PtCl_4, K_2PtCl_6 und K_3RhCl_6 zum Einsatz.

Zur Durchführung der photometrischen Untersuchungen diente das Spektralphotometer VSU 1 vom VEB Carl Zeiss, Jena. Die Extinktionsmessungen erfolgten bei 470 nm, die pH-Messungen wurden am Universal-pH-Meter Typ OP 204 Budapest durchgeführt.

Ergebnisse und Diskussion

N,N'-Bis(*o*-aminoacetophenon)-äthylendiimin bildet einen orangefarbenen Palladiumkomplex mit günstigen Absorptionseigenschaften. Sein Absorptionsspektrum ist in Fig. 1 wiedergegeben. Die analytische Bestimmung des Palladiums beruht auf der Extraktion dieses Komplexes mit einem geeigneten Lösungsmittel. Als Lösungsmittel wurden Chloroform, Benzol, Toluol, Xylol, Cyclohexan, Isoamylalkohol, Essigsäureäthylester, Methyläthylketon und Cyclohexanon überprüft. Von ihnen ist in Isoamylalkohol, Cyclohexan und Cyclohexanon der Ligand nur wenig löslich. Die Löslichkeit in Methyläthylketon, Essigester und Chloroform ist sehr gut, jedoch zersetzt sich der Palladiumkomplex in diesen Lösungen recht schnell. Toluol erwies sich als bestes Extraktionsmittel, da der Ligand darin gut löslich ist und die Phasentrennung günstig verläuft. Durch einen geringen Zusatz von Isoamylalkohol wird die Trennbarkeit der Phasen noch weiter verbessert.

Die Extraktion des Palladiumkomplexes ist stark pH-abhängig. Für die Palladiumbestimmung muss auf pH 7±0.2 eingestellt werden. Dies geschieht am besten unter Verwendung von Boraxpufferlösungen. Die Anwendung von Ammoniak–Ammoniumchlorid-Puffern führt zu einer empfindlichen Störung der Palladiumbestimmung, weil das Palladium durch die Bildung stabiler Amminkomplexe maskiert wird. Für die Bestimmung von Nickel mit N, N'-Bis(*o*-aminoacetophenon)-äthylendiimin neben Palladium ist diese Maskierungsreaktion von grosser Bedeutung.

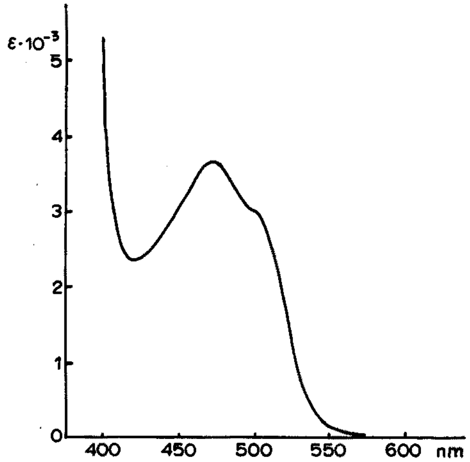

Fig. 1. Absorptionsspektrum des Palladiumchelates von N,N'-Bis(*o*-aminoacetophenon)-äthylendiimin in Toluol.

Zur Palladiumbestimmung ist eine einmalige Extraktion mit der Lösung des Reagenses in Toluol ausreichend. Oberhalb eines 90fachen Überschusses des Liganden ist die Extraktion quantitativ. Das Lambert–Beersche Gesetz ist im Bereich von 3.2–32 µg Pd/ml erfüllt (1-cm Küvette). Bei der Mikrobestimmung (3-cm-Küvette) ergibt sich ein Bereich von 1.06–10.6 µg Pd/ml. Die Extraktion ist zeitunabhängig.

Arbeitsvorschrift

Zur Durchführung der Palladiumbestimmung werden 10 ml Standardlösung (3.2–32 µg Pd/ml bzw. 1.06–10.6 µg Pd/ml) in einen 100-ml Schütteltrichter gegeben.

Man stellt mit Pufferlösung pH 7 ein, gibt 2 ml Isoamylalkohol und 10 ml 0.04 *M* Reagenslösung in Toluol hinzu und schüttelt 5 Min auf der Schüttelmaschine. Die organische Phase wird von der wässrigen abgetrennt, filtriert (Filter 388 w, VEB Spezialpapierfabrik Niederschlag) und am Spektralphotometer bei 470 nm in einer 1 cm- bzw. 3 cm-Küvette gegen Blindlösung gemessen.

Einfluss von Fremdionen

Störungen der Palladiumbestimmung mit N,N'-Bis(*o*-aminoacetophenon)-äthylendiimin sind vor allem durch Metalle zu erwarten, die mit dem Reagens ebenfalls farbige Chelate bilden. Dies trifft für Eisen, Kobalt, Nickel und Kupfer zu. Ionen dieser Metalle können jedoch durch Zusatz von EDTA leicht maskiert werden und stören dann selbst bei tausendfachem Überschuss die Palladiumbestimmung nicht mehr. Dabei ist ein einfacher Überschuss an EDTA ausreichend.

Von den Platinmetallen zeigen Osmium, Iridium, Ruthenium und Rhodium—ebenfalls bei Zusatz von EDTA—keine Störung. Lediglich wenn Rhodium in höheren Konzentrationen vorhanden ist, beobachtet man an der Phasengrenzfläche Schlierenbildung. Diese Schlieren können durch Filtrieren beseitigt werden und üben keinen Einfluss auf die Palladiumextraktion aus. Die Schüttelzeit muss aber auf 10 Minuten erhöht werden.

In Gegenwart von Platin(IV) unterbleibt die Extraktion des Palladiumkomplexes, dafür tritt an der Phasengrenzfläche Niederschlagsbildung ein. Diese Störung lässt sich durch Reduktion des Platin(IV) zu Platin(II) umgehen. Von den untersuchten Reduktionsmitteln erwiesen sich Natriumsulfit und Hydrazin als ungeeignet. Günstige Resultate wurden mit Ascorbinsäure erhalten, wobei es zweckmässig ist, das Reduktionsmittel im einfachen Überschuss zuzusetzen. Bei Anwendung eines grösseren Überschusses erfolgt langsame Reduktion zu metallischem Platin. Dabei bildet sich an der Phasengrenzfläche ein Platinniederschlag, der aber durch Filtrieren leicht zu beseitigen ist und keinen Einfluss auf die Palladiumextraktion hat.

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The analysis of inorganic siliceous materials by atomic absorption spectrophotometry and the hydrofluoric acid decomposition technique Part IV. The analysis of cements, clinkers, raw mixes and siliceous limestones

In the cement and related industries rapid and reliable methods are required for production control, particularly of the constituents silicon, aluminium, iron and calcium. Atomic absorption spectrophotometric methods have been described[1] for the determination of various components of cement. However, some of these schemes do not describe a method for silicon, and in other schemes the determination of silicon is lengthy and tedious.

In the present scheme, hydrofluoric acid is used to obtain silicon in solution. Methods are described for the determination of silicon, aluminium, iron and calcium in cements, clinkers and raw mixes, particularly of the Portland type; the scheme is also applicable to the analysis of siliceous limestones. In the sample solution it is possible to determine other constituents, *e.g.* magnesium, sodium, potassium, titanium, manganese and chromium.

Before analysis, samples of raw mix and siliceous limestone must be ignited, *e.g.* in a high-frequency induction furnace, to convert them to an acid-decomposable state.

Reagents and solutions

The reagents required for the present determinations are listed in Part I[2]; the detailed preparation of the primary standard solutions (designated below as metal standard I) is also described in Part I. The composition of the secondary standard solutions is given below. Each of these series is prepared for measurement of a definite dilution of the sample solution; this is indicated in each case.

Silicon (undiluted sample solutions). Transfer by plastic pipette 8–12 ml, in steps of 0.5 ml, of silicon standard I to plastic bottles, add 20 ml of calcium reagent solution (31.5 mg CaO/ml) and water to a final volume of 100 ml. (Range: 16–24% SiO_2, in steps of 1%.)

Aluminium (undiluted sample solutions). Transfer up to 40 ml, in steps of 2 ml, of aluminium standard I to 100-ml volumetric flasks, add 20 ml of calcium reagent solution and dilute to volume with water. (Range: up to 8% Al_2O_3, in steps of 0.4%.)

Iron (undiluted sample solutions). Transfer up to 50 ml, in steps of 1 ml, of iron standard I to 1000-ml volumetric flasks and dilute to the mark with water. (Range: up to 5% Fe_2O_3, in steps of 0.1%.)

Calcium (sample solutions diluted 100 times). Dilute calcium standard I to a concentration of 0.02 mg CaO/ml with water. Transfer 30–34 ml, in steps of 1 ml, of this solution to 100-ml volumetric flasks, add 1 ml of nitric acid and 20 ml of lanthanum reagent solution (50 mg La/ml) and dilute to volume with water. (Range: 60–68% CaO, in steps of 2%.)

Procedure

Weigh 1.0000 g of cement, clinker, ignited raw mix or limestone, and transfer to a plastic beaker. Moisten the sample with water, cover the beaker and add 40 ± 2 ml of hydrochloric acid (1 + 1). Place the beaker on the boiling water bath and heat until the sample has decomposed. Add 3.0 ± 0.2 ml of hydrofluoric acid, heat on the boiling water bath for 5–6 min, add 20 ml of saturated boric acid solution and continue the heating until a clear solution is obtained. Transfer the cooled solution to a 1000-ml volumetric flask and dilute to volume with water.

Determine silicon, aluminium and iron in the main solution. Determine calcium by pipetting 10 ml of the main solution into a 100-ml volumetric flask, dilute to volume with water. Transfer 10 ml of this solution into another 100-ml volumetric flask, add 1 ml of nitric acid, 20 ml of lanthanum reagent solution and dilute to volume with water.

Determine silicon and aluminium with the acetylene–nitrous oxide flame, and iron and calcium with the acetylene–air flames. Make the measurements and calculations as described in Part I[2].

Applications

The methods were tested by analyzing the U.S. Bureau of Standards sample No. 1014 (Portland cement) and 2 clinkers. The analytical data are given in Table I.

TABLE I

ANALYTICAL DATA FOR THE U. S. BUREAU OF STANDARDS SAMPLE NO. 1014 (PORTLAND CEMENT) AND TWO SAMPLES OF CLINKER[a]

Sample	*Si as SiO_2 (%)*	*Al as Al_2O_3 (%)*	*Fe as Fe_2O_3 (%)*	*Ca as CaO (%)*
U.S.B.S.1014	19.53; $\overline{X}$=19.51	6.43; $\overline{X}$=6.40	2.55; $\overline{X}$=2.56	63.27; $\overline{X}$=63.13
	19.48; A=19.49	6.36; A=6.38	2.57; A=2.50	62.98; A=63.10
Clinker I	19.53	5.56	2.86	64.47
	19.65; $\overline{X}$=19.52	5.55; $\overline{X}$=5.57	2.88; $\overline{X}$=2.86	64.34; $\overline{X}$=64.28
	19.39; S = 0.12	5.60; S =0.03	2.86; S =0.02	64.14; S = 0.13
	19.62; C = 0.61	5.54; C =0.54	2.86; C =0.69	64.21; C = 0.20
	19.39	5.60	2.82	64.24
Clinker II	21.43	4.50	3.24	65.58
	21.24; $\overline{X}$=20.92	4.37; $\overline{X}$=4.46	3.26; $\overline{X}$=3.25	65.64; $\overline{X}$=65.39
	20.81; S = 0.42	4.45; S =0.06	3.23; S =0.01	65.58; S = 0.28
	20.58; C = 2.0	4.45; C =1.3	3.26; C =0.31	65.14; C = 0.43
	20.56	4.53	3.26	65.05

[a] $\overline{X}$ = arithmetic mean value; S = standard deviation; C = relative deviation; A = certificate value.

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Supplementary interpretations of the NMR spectra of phosphorus pesticides

A recent publication in this journal[1] closely parallels our study of the high-resolution NMR spectra of many of these phosphorus pesticides[2]. It is pertinent to note the more precise interpretation made possible by measuring spectra obtained with a 100-MHz NMR spectrometer, which has increased resolution and homonuclear decoupling capability.

Apparatus

The 100-MHz spectra were recorded with a Varian* HA-100 nuclear magnetic resonance spectrometer; a 2–3% solution of tetramethylsilane (TMS) was used as an internal standard and deuterochloroform and carbon tetrachloride were used as solvents. Spectra were recorded using the frequency-sweep mode at a sweep time of 500 sec.

Analytical standards of commercial organophosphorus pesticides and some experimental compounds were used at a concentration of 300 mg/ml. Homonuclear decoupling was accomplished with a Hewlett Packard* Model 200 AB audio oscillator.

Discussion

It is possible with the 100-MHz spectrometer partially to resolve the multiplet composed of the signals from the three SCH_2 groups of Di-syston and meta-Systox-R[1]. In both cases, the SCH_2—CH_3 signal is a quartet[2] centered at τ 7.40 (J=7.5 Hz) and at τ 7.21 (J=7.5 Hz), respectively. Whereas an 8-line multiplet was reported for Thimet[1], we find that on a 100-MHz instrument it is composed of 18 lines[2], two pairs of quartets from the non-equivalent methylenes of the ethoxy groups (τ 5.815 and 5.83; $J_{H-H}=7$ Hz, $J_{P-H}=10$ Hz) and a doublet (τ 5.97; $J_{P-H}=13$ Hz) from the P–S–CH_2–S protons. An analogous situation is observed with the spectrum of Trithion. Two pairs of quartets (τ 5.88 and 5.91; $J_{H-H}=7$ Hz, $J_{P-H}=10$ Hz) from the non-equivalent methylene protons and a doublet (τ 5.72; J=13.5 Hz) from the P–S–CH_2–S protons are observed.

The complex signals of the non-equivalent aromatic protons of several of the phosphorus pesticides studied (methyl parathion, dicapthon, Ruelene, Zytron, and Co-Ral) are resolved sufficiently to be analyzed in terms of coupling between protons *ortho*, *meta*, and *para* to one another. In some cases (ronnel, dicapthon, Ruelene, Zytron, methyl parathion, ethyl parathion, and paraoxon), long-range (through 4 and 5 bonds) phosphorus–hydrogen coupling is observed in the aromatic hydrogen signals (J=0.8–1.8 Hz). It is also possible to measure this P–H coupling in the methyl protons of the phosphoethoxy groups (J=0.5–1.2 Hz).

Evidence was found for non-equivalence of the methylene groups of several of the compounds containing two phosphoethoxy groups, each group being in a slightly different environment owing to steric effects. This produces 16 peaks for the methylene signals (Thimet, Di-syston, Trithion, and ethion) rather than the eight peaks reported by BABAD *et al.*[1]. A similar non-equivalence of methoxyl groups is observed in malathion, malaoxon, Dibrom, and Neguvon ($\Delta\nu \leqq 1.5$ Hz), all of which contain two methoxyl groups and an asymmetric carbon.

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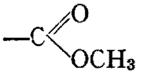
* The trade names mentioned herein do not imply endorsement by the Federal Water Pollution Control administration or the U.S. Department of the Interior.

In a few cases, there is a discrepancy in the values obtained for coupling constants and chemical shifts. The methoxyl signal of Imidan[2] in $CDCl_3$ is found to be at τ 6.23, 0.77 p.p.m. downfield from that previously reported[1]. The SCH_3 signal of Tiguvon appears at τ 7.60 in $CDCl_3$ and at τ 7.63 in CCl_4, as opposed to τ 7.17 (BABAD *et al.*[1]). A less significant difference ($\Delta\nu = 5$–15 Hz) is observed in other cases, some of which can be attributed to solvent and/or concentration shifts. A discrepancy of ± 1.5 Hz in P–H coupling constants is observed in Meta-Systox-R, Thimet, and Aspon.

In malathion, the "unsymmetrical triplet" (τ 7.15)[1] reported for the CH_2–$C=O$ protons is in fact two pairs of doublets possessing the characteristics of the AB portion of an ABX pattern, with the two methylene protons being non-equivalent[2]. The ethoxy methylene protons, reported as a septet[1], are actually two partially-overlapping quartets, as shown by decoupling experiments[2], produced by two non-equivalent methylene groups.

In Ciodrin and Bidrin, the olefinic methyl proton "singlet" exhibits fine splitting ($J = 0.8$ Hz), owing to coupling through the carbon–carbon double bond to a *trans* hydrogen.

The isopropyl methine proton of Diazinon was reported as a sextet[1] but is actually a septet[2], as would be expected.

The analysis[1] of the NMR spectrum of Phosdrin is rather disturbing, since the sample is a mixture of *cis* and *trans* isomers. By using Ciodrin, a similar compound of known *cis* geometry, as the model for the CH_3–$C=C$–H and P–OCH_3 signals of the *cis* isomer of Phosdrin, it is possible to make assignments of chemical shifts and coupling constants to the appropriate isomer. The "unsymmetrical sextet" reported[1] (τ 6.04–6.4) is, in fact, closely spaced signals of the *cis* and *trans*  $—C\begin{smallmatrix}\nearrow O \\ \searrow OCH_3\end{smallmatrix}$ (two singlets, τ 6.29 and 6.31, respectively) and the *cis* and *trans* $(CH_3O)_2\overset{|}{P}=O$ (two doublets, τ 6.14 and 6.09, respectively, $J_{P\text{-}H} = 11.5$ Hz)[2].

Since NMR spectroscopy is one of the most important tools for the structural elucidation of organic molecules, the supplementary interpretations presented here will be beneficial to analytical chemists interested in phosphorus pesticides and their metabolites or degradation products.

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Spectrophotometric determination of phenolic hydroxyl groups with titanium(IV) chloride as reagent

In recent years there has been enhanced interest in the determination of small amounts of phenols or their derivatives, and particularly phenolic end groups in polymers. Since 1935 it has been known that titanium(IV) chloride reacts with phenol to form a colored compound[1], and a spectrophotometric method has been developed for the determination of phenolic hydroxyl end groups in polymers on this basis[2]. The color reaction of phenolic hydroxyl groups with titanium(IV) chloride has been investigated with the particular aim of presenting a simple, reliable analytical procedure.

The combination of the titanium(IV) chloride dissolved in dichloromethane and acidified with acetic acid, and the sample dissolved in dichloromethane gives reproducibility with convenience. Many polymers, antioxidants and other phenolic hydroxyl-containing compounds can be determined. The complex formed from titanium(IV) chloride and the phenol exhibits different color and intensity, depending upon the electron density at the carbon atom bearing the hydroxyl group, as well as the groups adjacent to the hydroxyl group. Acetic acid is added to suppress hydrolysis of titanium(IV) chloride. Color development is usually completed after about 3 min. Steric hindrance can make the method invalid, as in the case of Ionol.

Reagent solution

It is necessary to use dry reagents. Titanium(IV) chloride is distilled over charcoal. Dichloromethane is boiled under reflux for 2 h over potassium carbonate. A *ca.* 0.2 M solution of titanium(IV) chloride is prepared by dissolving 4 g (2.32 ml) in 100 ml of dichloromethane, 60 μl of glacial acetic acid being added (the solution is 10^{-5} M in acetic acid) to suppress hydrolysis. The resulting solution is stable if kept dry.

Procedure

To 5 ml of a sample solution in dichloromethane acidified with *ca.* 25 μl of glacial acetic acid, add 1 ml of reagent solution. After about 3 min, measure the absorbance of the titanium-chloro-phenoxy complex at room temperature at the proper wavelength against a blank solution.

Discussion

It was found that a 100-fold molar excess of titanium(IV) chloride over phenolic hydroxyl groups leads to satisfactory linearity; 65–135-fold excesses were checked. The color of the complex remains stable so long as no water causes hydrolysis. Less reagent leads, as expected, to non-linearity, while greater amounts cause a steady decrease in the intensity of the color with time.

Acetic acid is added to retard hydrolysis, and to neutralize phenol salts which otherwise could hydrolyze the reagent; acetic acid also improves the solubility of several phenol compounds in dichloromethane. Ratios of acetic acid to phenolic hydroxyl group of 0–150 moles were studied. If the acetic acid concentration is too high, the time for stable color development is very long; high acid concentrations also cause non-linearity in the absorbance observed, because the reaction equilibrium is not reached. Acetic acid reacts with the titanium(IV) chloride to form aceto-chloro-titanium complexes, with different amounts of acetate per mole $TiCl_4$, depending upon the acetic acid concentration. It is advisable to use between 50 and 150 moles of acetic acid per mole of phenolic hydroxyl group.

In a few compounds investigated, particularly Ionol (2,6-di-*tert*-butyl-4-methylphenol), equilibrium is not reached in a reasonable time, because of the steric hindrance of the two tertiary butyl groups in Ionol both in *ortho* position to the hydroxyl group; reproducible results could not be achieved even after reaction times of 15, 30 or 45 min. Interestingly, this instability of the Ionol–$TiCl_4$ complex can be used to distinguish between Ionol and other phenolic antioxidants with no steric hindrance effect.

Thiophenols interfere, as they react in the same way as phenolic hydroxyl groups. Titanium(IV) chloride may cleave, especially at elevated temperature, ether bonds and produce new hydroxyl end groups in polymers. However, it was proved that polymers with known amounts of hydroxyl groups did not show any increase in their hydroxyl content if treated for 1 h or longer with the reagent under similar conditions as applied for the determination of hydroxyl groups; even at 60° no cleavage could be observed. In several samples, the phenolic hydroxyl group was converted to the methyl ether. Phenolic hydroxyl group analyses before and after conversion, showed the expected decrease in the hydroxyl content. Parallel analyses made by NMR confirmed these results. The decrease of hydroxyl groups is connected with an increase of the aliphatic moiety of the polymer investigated.

Results

Table I shows that the analysis for bisphenol A is more than 3.5 times more sensitive than that for phenol. The difference between the antioxidants Santonox R and T.B.S. is even greater. This is explained for Santonox R by the S-atom which has a strong electron-donating effect. In bisphenol A, the hyperconjugation effect of the two methyl groups influences positively the density of the electrons in the benzene ring.

TABLE I

PHENOLIC HYDROXYL GROUP DETERMINATION IN VARIOUS COMPOUNDS

Compound	*Color with $TiCl_4$*	*Wavelength (nm)*	*Limit of detection*[a] *(μg/ml)*
Phenol	Yellow	546	20
Santonox R[b]	Brown-violet	515	2.4
T.B.S.[c]	Gold-orange	480	14
Bisphenol A	Yellow	546	6.6
2,4-Di-*tert*-butylphenol	Yellow	546	4.5

[a] Measured in 1-cm cells and based on a reading for the absorbance of 0.100 units. With 10-cm cells a tenfold increase in sensitivity could be obtained.

[b] Bis-(2-methyl-4-hydroxyl-5-*tert*-butylphenyl)sulfide.

[c] *p*-*tert*-Butylphenylsalicylate.

The simultaneous determination of two phenols

Phenols with different absorption maxima may be determined simultaneously. This was done for Santonox R and T.B.S. The colored solution of the two components with titanium(IV) chloride is scanned from x nm to y nm, absorbances of A_x and A_y being obtained. It was shown that for the two components alone, X and Y, the colored complex of each obeyed Lambert–Beer's law at both wavelengths, x nm and y nm. The absorbance for component X was measured at x nm and y nm, and the same was done for component Y. The data obtained were used to calculate that factor for each component, which allowed the conversion of the absorbance at one wavelength to that of the other wavelength. Thus:

$$A_y^X = A_x^X \cdot K_1 \text{ and } A_x^Y = A_y^Y \cdot K_2,$$

where A_x^X, A_y^X = calculated absorbance for component X at x nm and y nm, respectively, and A_x^Y, A_y^Y = calculated absorbance for component Y at x nm and y nm, respectively. The two factors, K_1 and K_2, are the ratios of the averaged values for component X and Y, respectively, at both wavelengths.

In the mixture of component X and Y, the absorbances measured at x nm and y nm are each the sums of the individual absorbance of both components. Thus:

$$A_x = A_x^X + A_x^Y \text{ and } A_y = A_y^X + A_y^Y,$$

where A_x = absorbance measured at x nm, and A_y = absorbance measured at y nm.

$$A_x^X = A_x - A_x^Y$$

By suitable substitution, the percentages of each phenol can be found:

$$\% \text{ X by weight} = \frac{A_x^X \cdot \text{m.w. of X} \cdot 100}{\text{g sample/ml} \cdot E_x^X \cdot 10^3}$$

where E_x^X = molar absorptivity of X at x nm; the analogous equation is valid for component Y.

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Analysis of micron-sized particles: detection of iron

The technique for detecting and estimating calcium in individual particles collected on membrane filters, reported by LODGE[1], uses ammonium hexacyanoferrate-(II) as reagent. In addition to the typical calcium precipitate, particles collected from the ambient atmosphere frequently contain enough iron(III) to give areas of blue color. In view of the increasing interest in metals in the atmosphere, an exploration of the quantitative aspects of the test seemed worthwhile.

Initial experiments were made with iron(III) ammonium sulfate which gave well-defined blue circular areas, or halos on the filter, with the calcium reagent as an aqueous 30% (w/v) solution. Attempts to use the usual methods[2] to compare particle size and halo size were thwarted by the highly hygroscopic nature of the test salt. Therefore, an accurately weighed 10% (w/v) solution of iron(III) ammonium sulfate dodecahydrate was nebulized simultaneously at close range onto a membrane filter and onto a microscope slide coated with a layer of Shillaber's immersion oil[3]. Assuming that no moisture evaporated from or condensed onto the droplets—*i.e.* that they were still 10% solutions of the iron salt—it was possible to compute from their size distribution an equivalent mass distribution of iron. Comparison of the iron distribution of halo sizes gave the empirical equation relating the sizes as

$$M_{\mathrm{Fe}} = 1.7 \cdot 10^{-4} D_{\mathrm{h}}^3$$

where M_{Fe} is mass of iron in the particle, pg, and D_{h} is diameter of halo, μm.

Examination of several atmospheric samples, however, revealed few halos. Many particles were stained blue by the reagent, showing that their iron was largely immobilized and suggesting the presence of still less reactive iron compounds. To test this theory, the filters were placed in a closed petri dish with 2 ml of concentrated hydrochloric acid for 20 min. Then 2 drops of concentrated nitric acid were added, and exposure was continued for 10 min more. After this vapor treatment in which some iron was dissolved and converted to the trivalent form, atmospheric samples invariably yielded halos. However, there was evidence that only a small fraction of the iron present had been dissolved. Treatment long enough for total dissolution to occur was accompanied by attack on the filter of the acid. It was concluded, therefore, that no greater inaccuracy would result from simply assigning a particle mass computed as iron(III) oxide based on the microscopic size of the particle residue in the center of each halo. The figure so obtained would generally be an upper limit.

Despite these limitations, the method permits unequivocal identification of iron in particles yielding as little as 0.1 pg of soluble iron.

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Effect of TRIS buffer on the biuret reaction

The biuret reaction was found to be satisfactory for determining protein concentration except for those solutions in which tris(hydroxymethyl)aminomethane (TRIS) was present as the buffer. In these solutions, the sensitivity of the method was reduced and the results were generally poor. Others have used the biuret method to determine protein in solutions buffered with TRIS[1-3], but they did not indicate if TRIS was removed before the determination of the amount of copper(II) in the reagent given, both of which would have been necessary for comparison with the results in this paper.

Earlier workers recognized that there was slight interference by ammonium ion when the biuret method was used for determining proteins in serum samples, yet they considered the results to be reliable[4,5]. LAYNE found, however, that protein could not accurately be determined in the presence of ammonium ion with a reagent containing 0.006 *M* copper(II)[6].

The TRIS–copper(II) complex has been well studied, but no information regarding its interference specifically with the biuret reaction seemed to be available, although GELLERT *et al.*[7] suggested that TRIS or ammonium ion at concentrations greater than 0.1 *M* be removed by dialysis before protein determination by the Lowry modification of the biuret reaction. It was impossible, however, to make any valid inferences about the effect of TRIS on the biuret reaction from the results with the Lowry method since the latter has two color reagents, *i.e.*, copper(II) and Folin phenol reagent, and thus had different conditions[8].

There are many published modifications of procedure for the biuret determination of proteins, including variations of reagent concentration[4]. Consequently, we have studied the levels of interfering agents in relation to reagent concentration in order to develop a satisfactory procedure for using the biuret method in the presence of these interfering agents.

Methods

Alkaline copper(II) tartrate solutions were prepared as described by WEICHSELBAUM[9]. TRIS (General Biochemical and Sigma) was shown by its infrared spectrum to be free of amide linkages. Electrophoretically pure bovine plasma and serum albumins (BSA) (Sigma and Calbiochem) were used interchangeably throughout the experiments.

Titrations were carried out by the method of continuous variations. Equal volumes of alkaline copper(II) tartrate and protein solutions were used and the resulting solutions were read with a Beckman DU spectrophotometer in 1-cm cells at 555 nm. Copper(II) reagent concentrations of 0.012 *M*, 0.024 *M*, and 0.048 *M* (1, 2, and 3 times the 0.3% $CuSO_4 \cdot 5H_2O$ suggested by WEICHSELBAUM) were used for the titrations. Protein concentration was the variable in each titration.

Results and discussion

Since TRIS is a primary amine, it would be expected to react similarly to the ammonium ion. TRIS was found to complex the copper(II) to a much greater extent than the ammonium ion. The absorbance maximum for the TRIS-copper(II) complex was practically the same as for the protein–copper(II) complex (see spectra in Fig. 1).

When a 0.009 *M* copper(II) solution was titrated with TRIS or ammonium chloride, with absorbance readings at 555 nm, there was essentially no color formation in the latter case, whereas there was obvious color formation with TRIS, the absorbance maximum occurring at a 2:1 molar ratio of TRIS to copper(II). These data for TRIS confirm earlier findings[10].

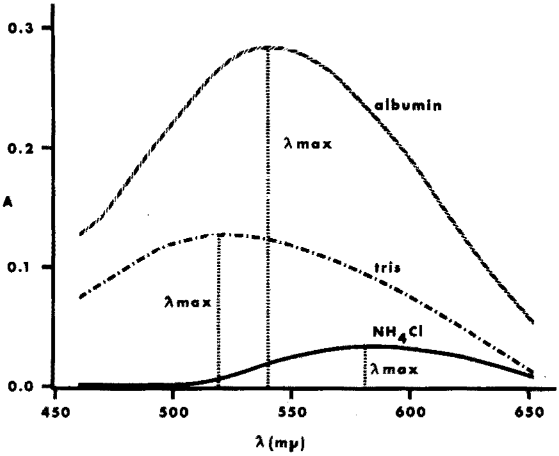

Fig. 1. Absorption spectra of 0.004 *M* copper(II) with (1) 0.067 *M* NH_4Cl, (2) 0.067 *M* TRIS, and (3) 1.0 mg/ml bovine serum albumin (BSA). Concentrations are those of final solutions.

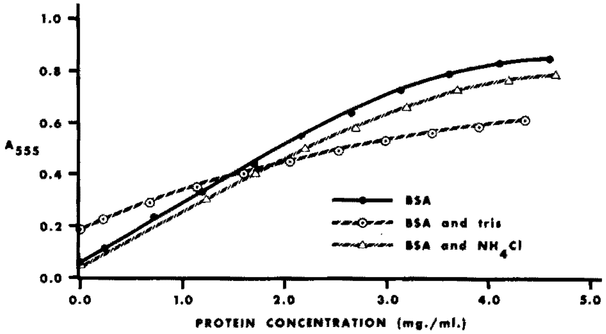

Fig. 2. Titration of 0.006 *M* copper(II) with bovine serum albumin (BSA), BSA and 0.0125 *M* TRIS, and BSA and 0.0125 *M* NH_4Cl. Absorbance at 555 nm was read against a water blank. Concentrations are those of final solutions.

A comparison was made of the amount of interference with the biuret reaction produced by identical concentrations of ammonium ion and of TRIS. The effect of the ammonium ion was negligible (Fig. 2), but TRIS interfered, reducing the sensitivity of the protein determination markedly.

The experiment with 0.025 *M* TRIS shown in Fig. 3 was at about a 4:1 TRIS–copper(II) ratio, which was double the amount of TRIS necessary to complex all the copper(II) present. Nevertheless, the absorbance of the protein complex increased as a function of increased protein concentration, thus demonstrating that the TRIS complex was more labile than the protein complex. The sensitivity of the determination decreased as the amount of TRIS was increased over the range 0.005–0.025 *M*. The TRIS concentration used by some workers was lower than the 0.025 *M* TRIS used most often in the present work and was probably not competing with protein for nearly so much copper(II)[1-3].

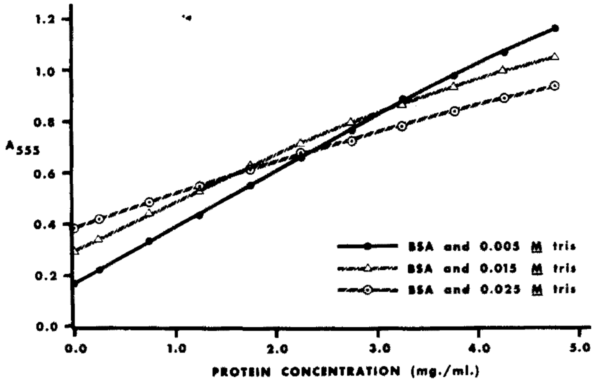

Fig. 3. Titration of 0.012 *M* copper(II) with bovine serum albumin (BSA) and 0.005 *M* TRIS, BSA and 0.015 *M* TRIS, and BSA and 0.025 *M* TRIS. Absorbance at 555 nm was read against a water blank. Concentrations are those of final solutions.

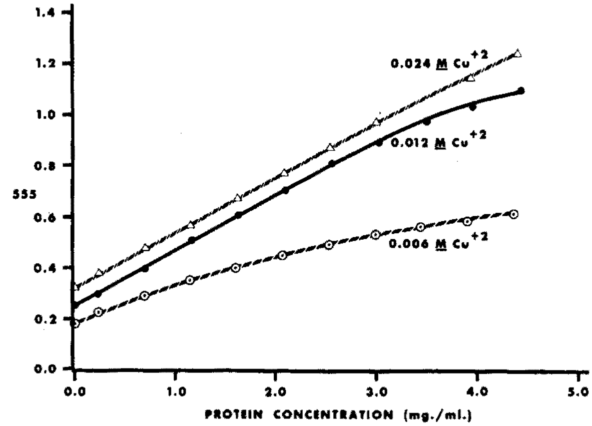

Fig. 4. Titration of 0.006 *M* copper(II), 0.012 *M* copper(II), and 0.024 *M* copper(II) with bovine serum albumin (BSA) and 0.012 *M* TRIS. Absorbance at 555 nm was read against a water blank. Concentrations are those of final solutions.

To obtain satisfactory results under the conditions shown in Fig. 4, the copper(II) concentration had to be twice the 0.012 *M* (0.3% $CuSO_4 \cdot 5H_2O$) reagent concentration suggested by WEICHSELBAUM[9]. The difference between the curves obtained for 0.024 *M* and 0.048 *M* copper(II) reagent for up to 3 mg/ml final protein concentration was due only to the absorbance of the copper(II) reagent. The concentration range over which the curve was linear was practically the same for 0.048 *M* copper(II) as for 0.024 *M* copper(II) in the reagent and was within the capacity of most spectrophotometers.

It was concluded that the conditions best suited for protein determination in the presence of TRIS were (*1*) a molar ratio of TRIS: copper(II) of 1:1 or lower, and (*2*) a protein range of 0–6 mg/ml before addition of the reagent [0.024 *M* copper(II)]. Reproducible results were obtained only when the absorbance of the 0 concentration for each determination agreed with the standard curve. If the TRIS concentration varied from that used in preparing the standard curve, the protein could not be accurately determined. A simple correction for the difference in absorbance did not suffice because curves for different TRIS concentrations did not have the same slope (Fig. 3).

Following submission of this paper, we saw the publication of ROBSON, GALL AND TEMPLE (*Anal. Biochem.*, 24 (1968) 339), whose conclusions were similar to ours.

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The preparation of electrodeless discharge tubes for some alkali and alkaline earth elements

Previously published methods from our laboratories [1-4] for the preparation of microwave-excited electrodeless discharge tubes have not been found to be satisfactory for some of the alkali and alkaline earth elements because of rapid and irreversible attack by these elements on the quartz or pyrex glass walls. These sources normally exhibit a quite rapidly decreasing spectral output which makes them unsuitable for atomic spectroscopic purposes. In some instances, for example magnesium, the attack was so severe that a discharge could be maintained for only a few minutes.

WINEFORDNER *et al.*[5], however, described the preparation of a number of electrodeless discharge tubes including magnesium, but appears to have experienced no special difficulties. On the other hand, other reported methods of preparation for alkali discharge tubes[6] and spectral discharge lamps[7] discuss in some detail the attack by such elements on glass, quartz and specially protected glass and quartz surfaces.

These effects prompted a thorough investigation of lithium, potassium, sodium and magnesium sources in particular because these showed a greater degree of attack than most other elements.

Results and discussion

Lithium, potassium, sodium and magnesium sources were prepared from the elements alone, in a manner similar to that described previously, from both pyrex and silica tubing at high and low argon filler gas pressures[1]. The metal–iodine method of preparation was also used for magnesium.

The sources gave an intense and moderately stable discharge for only quite short periods. In the case of magnesium the discharge lasted for only *ca.* 5 min; this tube could not be initiated subsequently. Sodium sources maintained a discharge, but only at the expense of a rapidly darkening glass surface. This produced a gradually decreasing intensity, especially at the sodium 3302 Å doublet. HAM AND WALSH[6] report that pyrex glass can be used for about 10 h for sodium before darkening becomes too serious, but this is not our experience if such sources are to be used in atomic spectroscopy. However, pyrex glass could be used for potassium without showing too much attack, although care must be taken not to let the sources become too hot during operation otherwise they will implode. The attack on silica was very much more rapid and lithium attacked both pyrex and silica more rapidly than the other alkali elements.

In consequence, two preventive methods were examined. The first involved boration of the inner surface of the silica tubing[8]. This was achieved by wetting the inner walls of the source bulb with a saturated solution of boric acid followed by heating to white heat to form a protective layer of borate glass. The second, which is effective only with pyrex (borosilicate) glass, involved washing the inner surfaces with a 40% solution of hydrofluoric acid[7]. This removed a layer of silicon thereby leaving a boron-rich glass. The recommended wash is 10% hydrofluoric acid, but this was found to be particularly ineffective for our purposes. Both methods rely on the fact that sodium, etc., will not attack borate glass and displace elemental boron because of the stability of the B–O bond in comparison to the much weaker Si–O bond.

These methods were particularly effective in slowing down the attack by sodium vapour, but neither was effective for more than a few hours of operation. Eventual attack in the former method was caused when the borate glass protective surface cracked, probably because of differences in the expansion properties of borate and silica glasses. The borated silica was, however, found to be adequate for potassium and only slight discolouration was noted after more than 25 h of operation. On the other hand, lithium and magnesium behaved very much as previously described, regardless of the preventive method employed.

Quite obviously, a different approach is necessary. One such method, which appears not to have been described previously for the preparation of microwave-excited electrodeless discharge tubes, is based on the use of a two-ply glass; the inner ply consists of a sodium vapour-resistant silica-free glass and an outer ply of normal soda glass. Such a glass is commercially available in various sizes, although only the narrowest diameter (nominal external diameter 13 mm and 0.8 mm wall thickness) is suitable for use in conjunction with most commercial resonant cavities. Sources were prepared from this glass in the usual manner and it was found that even after 50 h of operation there was no attack whatsoever from potassium, sodium or magnesium. The two-ply glass must not be drawn out to a smaller diameter tubing otherwise the inner-ply sodium-resistant glass may be broken and surface attack then readily occurs. In addition, prolonged heat causes devitrification. The sealing procedure is more difficult than when silica glass is used, because of the very low melting point of the two-ply glass, hence only a micro-burner was used during preparation. The Broida-type cavity (Electro-Medical Supplies, cavity no. 210L) which does not cause "hot-spots" at low powers, is recommended for operation of these sources. Lithium still showed very severe attack after only a few minutes and in this instance it is considered advisable to prepare the sources in silica glass from lithium chloride and not the metal. These sources show no surface attack at all because of the

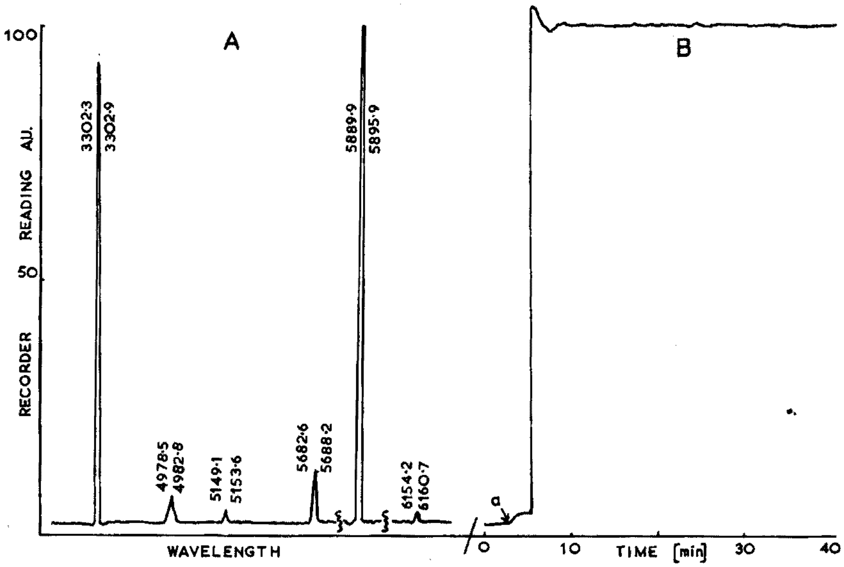

Fig. 1. Spectral intensity and stability curves for a sodium discharge tube. (A) slit width 0.01 mm, gain 2,0, electrical bandwidth 1. Intensity of 5890, 5896 Å doublet has been divided by 10. (B) (a) denotes microwave power on.

inability of lithium chloride to remain dissociated under these conditions (3 torr argon carrier gas). The only disadvantage is that the sources must be operated at relatively high temperatures because of the comparative involatility of lithium chloride. We have found the Evenson-type cavity to be the most suitable (Electro-Medical Supplies, cavity no. 214L) with operating powers of 75–100 W (reflected power < 2 W).

The spectral transmission of the X93 two-ply glass is limited in the ultraviolet region; little transmission occurs below *ca.* 3000 Å, but it is linear between 3500 and 8000 Å. Figure 1 shows the spectral and stability curves for the sodium discharge tube prepared from a few mg of sodium metal and sealed under *ca.* 3 torr of argon. The Broida-type cavity was used and the tube was operated at *ca.* 25 W. The stability was better than ±2% at the 5890, 5896 Å sodium doublet. Under these conditions this source was 10 times more intense at the 5890, 5896 Å doublet than a Woltan spectral discharge lamp operated at 0.85 A. The spectral evaluation was carried out using a Unicam SP 900A flame spectrometer which was not capable of resolving any of the doublets observed. Potassium and magnesium sources behaved similarly. The magnesium discharge tube gave sufficient intensity at the 2852 Å resonance line to be suitable for atomic absorption purposes, but the transmission characteristics of the glass would limit its use in atomic fluorescence spectroscopy. In this latter instance it would be advisable first to seal a quartz window onto the open end of the two-ply glass (with *e.g.* Araldite) and then proceed with the usual method of preparation. The tube would subsequently be operated in a horizontal position with the end of the tube containing the quartz window out of the cavity area. It is our experience that only hot magnesium vapour attacks silica glass and tubes prepared in this way are long-lived and sufficiently intense for atomic fluorescence spectroscopic purposes.

General method of preparation for potassium, sodium and magnesium discharge tubes

A length (*ca.* 10 cm) of two-ply sodium vapour-resistant glass (Glass Tubing and Components Ltd., Chesterfield, England; type X93) was sealed at one end and a narrow constriction was made *ca.* 4 cm from this end using a micro-burner. The tube was then connected to a simple vacuum line[1] and pumped down to a pressure of *ca.* 0.1 torr. Argon was introduced, the system was again evacuated and the tube was heated with a micro-burner to just below its melting point for 5 min. After cooling, the tube was removed from the line and a small piece of the metal (*ca.* 5 mg) was introduced (potassium and sodium metals were well dried with filter paper before being cut to the correct weight). The tube was again evacuated, flushed with argon and re-evacuated to *ca.* 0.1 torr. Gentle heat was then applied to the tube to degas the metal. This procedure was repeated twice more before the tube was eventually sealed under an argon pressure of *ca.* 3 torr. The 4-cm long tube was completely removed from its glass stub end and then sealed into a glass holder with an air-drying silicone rubber. If the magnesium source is to be used for atomic fluorescence purposes, then it is necessary first to seal a quartz window onto the open end.

The sources were operated with a Microtron 200 generator (Electro-Medical Supplies) in conjunction with a Broida-type cavity (Electro-Medical Supplies, cavity no. 210L). Operating powers of *ca.* 25 W were usually sufficient with this cavity. If the Evenson-type cavity is used, then the power should not exceed 25 W, otherwise hot-spots may occur. Cooling was unnecessary. Initiation was achieved with a "tesla" vacuum tester.

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The separation of iron from ruthenium by isopropyl ether extraction

The dissolution of gram quantities of ruthenium metal is done most conveniently by an alkaline-peroxide or alkaline-nitrate fusion in an iron, nickel, or silver crucible[1]. These fluxes attack the walls of the crucible at least as rapidly as they attack finely divided ruthenium metal, so that a considerable amount of the crucible is dissolved; for some applications the dissolved crucible material must be removed. Isopropyl ether is known to be an efficient and selective solvent for the extraction of iron(III)[2]; it is shown in this communication that iron may be completely removed with no loss of ruthenium by extraction of the iron into isopropyl ether. Since the separation of iron from ruthenium appears to be more straightforward than possible schemes for the separation of nickel or silver, the use of iron crucibles is preferred.

Experimental

The ruthenium stock solution was prepared by the fusion of approximately one gram of finely divided ruthenium metal with 15 g of sodium hydroxide and about 5 g of sodium peroxide (added in several portions) in an iron crucible. The cooled melt was cautiously dissolved in 100 ml of water and cautiously acidified with hydrochloric acid and 30% hydrogen peroxide. The excess peroxide was decomposed by boiling, and chlorine was bubbled through for a few minutes after cooling to insure that the iron was in the +3 state. The treatment with chlorine oxidizes any lower oxidation states of ruthenium to ruthenium(IV)[3]. After adjusting the hydrochloric acid concentration to 8 *F*, the iron was removed by two extractions with equal volumes of Mallinckrodt AR isopropyl ether which had been pre-equilibrated with 8*F* hydrochloric acid.

A solution of ruthenium(III) was prepared by passing a portion of the ruthenium(IV) solution in 8 *F* hydrochloric acid through a silver reductor. Since a considerable portion of the ruthenium is reduced to the divalent state in this reductor, the effluent solution was boiled for a few minutes to hasten the air oxidation of the ruthenium. The UV–visible spectrum of the final solution indicated the absence of appreciable quantities of ruthenium(II) or -(IV).

The quantity of ruthenium extracted was determined by analyzing the isopropyl ether layer by the spectrophotometric method of AYRES AND YOUNG[4]. Isopropyl ether hinders the formation of the blue tris(dithiooxamide)ruthenium(III) complex and so must be completely removed before color development. This may be accomplished by acidifying with hydrochloric acid, after the isopropyl ether layer has been reduced to a small volume, and continuing to boil the solution for a few minutes.

Results and discussion

The following data demonstrate that neither ruthenium(III) nor ruthenium(IV) is appreciably extracted by isopropyl ether under these conditions.

Ru in 8 F hydrochloric acid layer	*Ru in isopropyl ether layer (μg)*
0.44 g Ru(III)/250 ml	1.4
0.56 g Ru(III)/500 ml	0.4
0.44 g Ru(IV)/250 ml	7.6
0.56 g Ru(IV)/500 ml	2.3
Blank	2.3

If the ruthenium solution is required for use as a spectrophotometric standard, it may not be necessary to remove the iron. For example, iron(III) does not interfere with the dithiooxamide determination of ruthenium at a final iron concentration of $2.9 \cdot 10^{-4}$ *F*. This corresponds to a molar ratio of iron to ruthenium of about 5.6 which is somewhat above the upper limit of 2.3 set by AYRES AND YOUNG[4]. The dissolution of 65 mg of ruthenium metal by an alkaline peroxide fusion for 10 min in an iron crucible is accompanied by the dissolution of about 130 mg of iron, an amount which does not interfere in a subsequent dithiooxamide determination.

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Photometric determination of traces of pyridine by reaction with cyanogen bromide and 4,4'-diaminostilbene-2,2'-disulphonic acid

Most colorimetric determinations of traces of pyridine are based on the KÖNIG reaction[1] of this compound and structurally related pyridine bases with cyanogen bromide (or chloride) and a suitable aromatic amine[2]; the reaction mechanism[3,4] appears to involve splitting of the pyridine ring by cyanogen bromide at the proper pH and coupling of the product with the amine reagent to form a polymethine dye, which is usually yellow in colour. Such procedures have been used for the determination of pyridine and its derivatives, especially nicotinic acid. Different aromatic amines that have been proposed include: aniline[3,5,6], 2-naphthylamine[7,8], 4-aminoacetophenone[9-11], sulphanilic acid[12-14], *p*-phenylenediamine[15], 4-methylaminophenol[16], benzidine[17], and barbituric acid[18,19].

These procedures have disadvantages in that the colours produced are often unstable, the reaction is very sensitive to pH, and the procedures are often tedious.

The most sensitive available procedure (limit of detection 0.005 μg pyridine/ml) requires benzidine as the coupling component[20], the optimum pH being 7–8; however, the colour formed is light-sensitive and slow to develop, hence extraction into *n*-butanol is necessary.

In the present paper, 4,4'-diaminostilbene-2,2'-disulphonic acid is proposed as a new coupling component for the KÖNIG reaction. Several of the above-mentioned disadvantages can then be avoided: the colour development is much faster, the colour formed is much deeper in hue, and is not light-sensitive, and no prior extraction is necessary. The colour intensity still depends on pH, but pH control is less critical than in earlier methods with other coupling reagents.

Apparatus

Beckman DB Spectrophotometer, with automatic recording, equipped with 1.00-cm cells. Beckman GS pH-meter.

All the experiments and measurements were made at room temperature, that is, at 24 ± 1°.

Reagents

Cyanogen bromide (aqueous 1.5% solution). Prepare from bromine and potassium cyanide as described previously[19,21].

4,4'-Diaminostilbene-2,2'-disulphonic acid solution. Dissolve 16.6 g of sodium acetate trihydrate in 50 ml of distilled water, add 50 ml of ethanol, and dissolve 1.00 g of 4,4'-diaminostilbene-2,2'-disulphonic acid (Sandoz, chem. pure) in the mixture. Filter, if needed. The solution, kept in a dark bottle, is indefinitely stable.

Buffer solution, pH 7.8. Prepare, according to SÖRENSEN, from 0.05 *M* borax and 0.10 *M* hydrochloric acid.

Pyridine standard solution. Dissolve 1.040 g of pyridine (B.D.H., Analar) in 1.00 l of distilled water. Prepare other standards from this stock solution by suitable dilution.

Recommended procedure

To a 50.0-ml volumetric flask add successively 30 ml of buffer solution, a measured sample of the unknown solution containing 5–20 μg of pyridine, 3.0 ml of the 4,4′-diaminostilbene-2,2′-disulphonic acid solution and, from a microburet, 3.0 ml of cyanogen bromide solution. Dilute to the mark with buffer solution, mix well and let stand for 1 h. Read the absorbance at 490 nm, against a reagent blank diluted with buffer to the mark.

Prepare a calibration curve from standards treated in the same way and containing from 0.01 to 0.60 μg pyridine/ml.

The preparation of samples of pyridine-base compounds from the unknown material submitted to analysis offers no difficulty, because of the volatility of these compounds from alkaline solutions. The unknown material can be distilled in a Kjeldahl apparatus in the presence of excess of sodium hydroxide as described by KRONER *et al.*[20].

Influence of pH

The reaction is strongly influenced by pH. When the pH was adjusted with hydrochloric acid or sodium hydroxide, maximum colour intensity was found at pH 7–9; below pH 7 the colour did not form and above pH 9 it faded rapidly. Within the pH range 7–9 phosphate, boric acid–sodium hydroxide, and borax–hydrochloric acid buffers were examined; the reaction ran smoothly and the colour was most intense with the borax–hydrochloric acid buffer. Figure 1 shows the change in absorbance with pH; it can be seen that the absorbance was practically constant at pH 7.5–8.3.

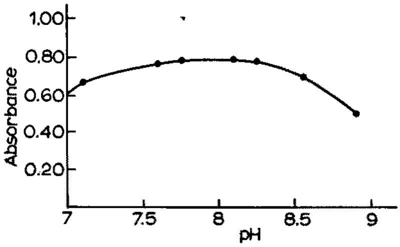

Fig. 1. Absorbance *vs.* pH for a solution containing 0.40 μg pyridine/ml, at 490 nm.

Absorption spectra and effects of light and time

The absorption spectra of the reaction product and of the reagent solutions are shown in Fig. 2. Under the conditions used, there was very little absorption by the reagents at 490 nm, the wavelength of maximum absorption of the reaction product. It is clear from spectra 1 and 2 in Fig. 2, that light has practically no effect on colour development with the 4,4′-diaminostilbene-2,2′-disulphonic acid reagent.

Colour development is substantially faster with the proposed reagent than with other coupling amines[20]. The colour reaches its maximum intensity 1 h after the reagents have been mixed, remains stable for 30 min and then decreases gradually.

Effect of the amounts of reagents

When solutions containing 0.40 μg pyridine/ml were treated by the recommended procedure, except that the volume of 4,4′-diaminostilbene-2,2′-disulphonic acid reagent was altered between 1 and 9 ml, essentially constant absorbance

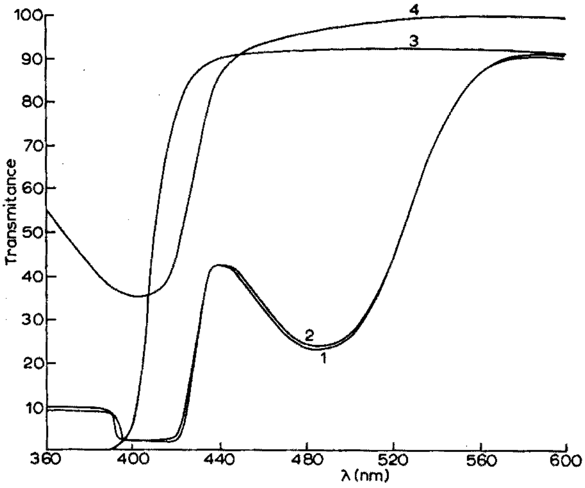

Fig. 2. Absorption spectra: (1) 0.40 μg pyridine/ml treated by the recommended procedure, colour developed in daylight; (2) as 1 but colour developed in the dark; (3) 0.40 μg pyridine/ml, treated only with CNBr; (4) 4,4′-diaminostilbene-2,2′-disulphonic acid alone. All solutions at pH 7.8.

measurements were obtained over the range 3–6 ml; a volume of 3.0 ml was chosen. The volume of cyanogen bromide used was more critical, maximal absorbance being obtained with 3.0 ml of this reagent under the conditions described. Larger volumes of reagents (especially of cyanogen bromide) did not improve the colour development, as they tended to cause pH changes that rapidly destroyed the coloured product.

Beer's law, sensitivity and reproducibility

Under the recommended conditions, Beer's law was strictly obeyed for solutions containing 0.01–0.60 μg of pyridine per ml at the final dilution. The absorptivity of the reaction product (referred to one mole of pyridine) at 490 nm was $13.4 \cdot 10^4$, corresponding to a spectrophotometric sensitivity of 0.0006 μg pyridine$\cdot$cm^{-2} on the Sandell scale[22].

Three series of seven samples each, containing 0.20, 0.10 and 0.05 μg pyridine/ml respectively, were treated by the recommended procedure. The relative standard deviation of the readings in the three series was about ±1.0%.

Selectivity of the reaction

Under the conditions recommended, the reaction is highly selective for pyridine and pyridine-base compounds. No interference was found from phenol, *p*-cresol, thymol, aniline, 1-naphthylamine, tyrosine, formaldehyde, acetophenone, acetone, acetonitrile, 2-naphthol or acridine. When the possible interfering compounds were insoluble or slightly soluble in water, they were used in ethanolic solution. Precipitates were formed with more than 400 μg/ml of phenol, 2-naphthol or 1-naphthylamine, and with more than 200 μg/ml of 1-naphthol or *p*-cresol. Table I shows the sensitivity limits for the colour reactions found with a few compounds, but the colours developed did not interfere in the photometric determination of pyridine. This was proved in all the cases by the analysis of synthetic mixtures. Furfuraldehyde and benzaldehyde did not interfere in the determination of 0.20 μg pyridine/ml even when 300–400 μg/ml of the aldehyde was present.

TABLE I

SPECIFICITY OF REACTION

Compound	*Approximate sensitivity (μg/ml)*	*Colour*
m-Cresol	100–250	Pale yellow
1-Naphthol	10–100	Pink
Benzaldehyde	10–200	Pale yellow
Furfuraldehyde	>100	Greenish yellow

The suitability of the method for the determination of traces of pyridine in complex mixtures was tested as follows: several mixtures were prepared containing 10 μg pyridine/ml and 400–500 μg/ml of each of several of the compounds mentioned above (*e.g.* a typical mixture contained 1- and 2-naphthol, 1-naphthylamine and *p*-cresol). Sodium hydroxide solution was slowly added in order to bring the pH slightly over 10, and the mixture was distilled until 100 ml of distillate was collected; 1.00 ml of the distillate was then treated by the recommended procedure. Readings showed no discrepancy, within the standard deviation of the procedure, from those obtained for a standard pyridine solution containing 0.20 μg/ml (in the example mentioned, the absorbance was 0.339 for the mixture against 0.338 for the standard).

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A highly sensitive microchemical reaction for iron particles

During research into the distribution of various trace contaminants, it became necessary to analyze for iron in particles of micron size included in natural ice of variable structure. Slices of ice, 1–3 mm thick, were sublimed at low pressure so that particles of unknown size and composition trapped in the ice were deposited locally on the microscope slide supporting the slices. A comparison of the ice sample crystal structure, as revealed in photographs taken with crossed polars, with the distribution pattern of iron particles in the residues, was required, It was, therefore, necessary to detect iron as an insoluble precipitate of characteristic color.

The literature offers some proven methods of detecting iron particles as colored precipitates. The simple and sensitive hexacyanoferrate(II) test for iron(III)[1] gave barely satisfactory results, as only the largest particles could be detected as blue-green spots in gelatin impregnated with hexacyanoferrate(II). The test was more successful on membrane filters, but gelatin-coated glass plates were a better substrate for the particular purpose.

Organic reagents for iron (*e.g.* α,α'-dipyridyl) of greater sensitivity yield only soluble compounds. However, a study of the properties of the $[Fe(dipy)_3]^{2+}$ complex cation showed the possibility, limited to this specific case, of using α,α'-dipyridyl reagent to obtain an insoluble reaction product with iron(II).

A saturated solution of $[Fe(dipy)_3]I_2$ containing an excess of iodide can be used as a highly sensitive reagent for cadmium[2]. The reaction product is a red-violet precipitate $[Fe(dipy)_3]\cdot(CdI_4)$ in which both cationic and anionic constituents are complexes. This accounts for the high sensitivity of the test.

In the present case, where iron particles are to be detected, a saturated solution of α,α'-dipyridyl reacts with the iron particles in the presence of a high concentration of iodide to produce locally a saturated solution of $[Fe(dipy)_3]I_2$ which, in its turn, can be locally precipitated by complex anions present in the solution.

Tests with cadmium in solution confirmed that the particles of the residues previously attacked with hydrochloric acid vapor became centers of accumulation of a red-violet, insoluble precipitate. However, as cadmium reacts with α,α'-dipyridyl to give a white precipitate, the use of this test is a little troublesome.

The $[Fe(dipy)_3]^{2+}$ complex can combine also with other complex anions of large atomic volume to yield analogous insoluble precipitates. A test using (HgI_4^-) as precipitant yielded a method of good reproducibility and high sensitivity for detecting iron particles as insoluble compounds in the residues.

The reagent is prepared by adding an alcoholic solution of α,α'-dipyridyl (about 30% in ethanol) to a saturated solution of potassium iodide (in proportion 1 to 50; the relative mixing ratio is not critical) containing a small amount of mercury(II) iodide.

Particles deposited on membrane filters or glass slides are left for 15–30 min in a large petri dish containing a source of hydrogen chloride vapor (this attack is necessary for those particles containing iron in insoluble form: Millipore filters should be exposed for a time sufficiently short to avoid deterioration). The sample is then dried and brought into contact with the reagent. The prodedure for the filters has been described previously[3].

The sample deposited on glass is brought in contact with a gelatin film impregnated with the reagent. A photographic plate, previously fixed, washed an dried, is placed in the reagent solution for 15–20 min. After the excess of liquid has drained off, the gelatin plate is left for several hours in a box containing water in the bottom. The gelatin reaches an equilibrium in which it remains just wet, with no excess of water visible on its surface. A precision press is then used to place the sample slide and gelatin tightly together without causing displacement of the particles. The bright red-violet precipitates formed in the gelatin are visible as circular spots each of them surrounding an iron-containing particle.

The sensitivity of the reaction, in terms of the smallest particle which can be detected, depends on the original iron content and composition of the particle. Insoluble particles contribute to the reaction product with only the small surface layer affected by the acid vapor. The reaction product is, however, of a specific volume so large that even a brief exposure to the acid is sufficient for iron oxide particles in the micron range to be recognized under the microscope. It is interesting to note that iron(III) is precipitated by the reagent. Because of the iodide present, the solution acts as a strong reductant.

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Separation of rhenium from molybdenum, tungsten, chromium, vanadium, selenium, tellurium and osmium by extraction with acetylacetone from alkaline solution

The extraction of rhenium from alkaline solution offers the following advantages: (*a*) elements such as copper, chromium, nickel, cobalt, bismuth, etc., which interfere[1] in the determination of rhenium are separated along with others that form insoluble hydroxides, without loss of rhenium[2]; and (*b*) silica and other acidic oxides remain in solution. Few methods are available for the extraction of rhenium from alkaline solution and its separation from molybdenum and other elements. Extractions with tetraphenylarsonium chloride in chloroform above pH 8[3], methyl ethyl ketone from 5 *N* sodium hydroxide[4], pyridine from 4–6 *N* sodium hydroxide[5] and quinoline from 4 *N* sodium hydroxide[6] have been suggested. Rhenium(VII) extracted by acetylacetone from acid solutions[7] cannot be back extracted by water from neutral or alkaline medium. Accordingly, the possibility of extracting rhenium from neutral or alkaline solution was studied.

Reagents

Standard stock solutions at the mg/ml level were prepared by dissolving exactly weighed amounts of potassium perrhenate (Specpure, Johnson-Matthey, Ltd, London) in water; test solutions were prepared by suitable dilution. Solutions of the other elements were prepared from sodium or potassium salts (C.P. or A.R. quality) and standardised by conventional methods.

Acetylacetone (L.R., B.D.H.) was purified[8], but benzene and chloroform (L.R., B.D.H.) were used directly.

Sample solutions

Synthetic flue dust. A solution in the minimum quantity of sulfuric acid was prepared from µg amounts of rhenium and other elements in the following proportions: Zn 80, As 30, Fe 60, Cu 10, Bi 7, Mo 100, V 20, Mg 1, Ca 4, Al 0.6, Cd 3. The solution was made just alkaline, the hydroxide precipitate was filtered and washed, and the filtrate was analysed.

Natural samples. A flue dust (500 mg) from copper manufacture, containing no rhenium, was mixed with a solution of known rhenium content and dried in an oven. After fusion of the dust in a nickel crucible with a 3:2 sodium peroxide–sodium carbonate mixture, the leach was neutralised with concentrated sulfuric acid and again made slightly alkaline. After boiling, the hydroxide precipitate was filtered and washed, the filtrate was adjusted to contain 0.5 *N* sodium hydroxide, and rhenium was separated as described below.

A Mexican molybdenite (200 mg) was treated with concentrated nitric acid and then the solution was made slightly alkaline with 5 *N* sodium hydroxide and boiled. The hydroxide precipitate was filtered and washed, the filtrate was adjusted to contain 0.5 *N* sodium hydroxide and the rhenium was extracted.

Extraction with acetylacetone

Solutions containing varying µg-amounts of rhenium and mg-amounts of other elements, or the solutions from synthetic flue dust or natural samples, were adjusted to contain 0.5 N sodium hydroxide in 20 ml of solution. The solutions were extracted with four 25-ml portions of acetylacetone, being shaken for 3 min with each portion. The solvent was then distilled off completely from the combined organic phases.

The residue was warmed with 20 ml of 1:1 benzene–water and shaken. The aqueous layer was drawn off and shaken again with 10 ml of benzene to remove organic matter. Any reduced valency states in the aqueous phase were oxidised with bromine, excess of bromine was boiled off, and the elements were determined.

The aqueous layer obtained from the residue may contain traces of molybdenum (about 100 μg from 100 mg Mo in the original sample). Rhenium was determined after the removal of this residual molybdenum by the xanthate method[9].

Determination of the elements

Rhenium was determined colorimetrically by the α-furildioxime method[9]; the volume recommended was decreased to 25 ml with proportional decreases in the amounts of reagents added. Beer's law was obeyed from 10 to 150 μg of rhenium. Other elements were determined or shown to be absent by standard colorimetric methods[1]. Measurements were made with a Spekker Absorptiometer in 1-cm cells.

Results and discussion

The percentage extraction of rhenium(VII) at different alkalinities in the aqueous solution is shown in Table I; alkalinities above 1.5 N sodium hydroxide lead to higher miscibility of acetylacetone with the aqueous phase, longer times for phase separation, and turbidity, without any increase in the percentage extraction.

TABLE I

ACETYLACETONE EXTRACTION OF RHENIUM(VII) FROM ALKALINE SOLUTION

(Solution/solvent = 4/5; shaking time = 30 min; temp. = 19 ± 1°)

N NaOH	0.0	0.3	0.5	1.0	1.5
% extn.	68.1	69.5	72.4	74.5	76.6

The extraction is only slightly affected by the time of shaking and the temperature; shaking for 1–3 min at 20° extracts 70.3% of rhenium(VII) from 0.5 N sodium hydroxide whereas shaking for 30 min extracts 72.4%. The extraction increases to 75.2% at 10° and decreases to 62.5% at 40°, *i.e.* a 0.3–0.5% decrease for each degree rise. The extraction of molybdenum(VI) is 0.33% from neutral solution, and 0.02% and 0.01% from 0.5 N and 1.0 N sodium hydroxide, respectively.

Consideration of the above data led to a choice of 0.5 N sodium hydroxide medium and a 3-min contact time for the extraction of rhenium(VII) with acetylacetone. Under the conditions given in the extraction procedure, there was no extraction of chromium(VI), selenium(VI), tellurium(VI) or osmium(VIII); the percentage extractions of silicon(IV), vanadium(V), tungsten(VI) and molybdenum(VI) were found to be 0.05, 0.018, 0.004 and 0.023%, respectively. In practical cases, only molybdenum needs to be removed before rhenium can be determined by existing colorimetric methods[10]; it is best removed by the thiocyanate method[11] when rhenium(VII) is determined by the thiocyanate–tin(II) method or by the xanthate method[9], as in the present work.

The results of analyses (Table II) of several synthetic samples and a molybdenite by the present method show that the accuracy is limited only by the method of determination. However, the estimated loss of rhenium(VII) in the extraction is about 1%. The solvent which is distilled off to recover the rhenium, can be reused directly. The time taken for a single separation is about 30 min excluding the time for distillation of the solvent.

TABLE II

ANALYSIS OF DIFFERENT SAMPLES

Composition of sample					*Re found (µg)*
Mo (mg)	*V (mg)*	*W (mg)*	*Si (mg)*	*Re (µg)*	
1000	—	—		35	34·5
100	—	—		14	13·5
—	480	—		28	27·5
—	100	—		14	13·5
—	—	500		35	34
—	—	100		14	13·5
500	200	100	2	35	33·5
200	100	50	1	14	13
75[a]	—	—		35	34·5
Synthetic flue dust				42,21	40.5,20
Reverberatory flue dust				28	27
Molybdenite				0.012%[b]	0.011%

[a] Plus 15 mg Os, 4.5 mg Cr, 2 mg Se, 3.5 mg Te.
[b] Reported value.

Thus, the difficult separation of rhenium from molybdenum, which interferes in almost all methods for its determination, can be achieved by simple extraction with acetylacetone from slightly alkaline solution, followed by removal of the co-extracted molybdenum traces by the xanthate method. The present method also separates rhenium from V(V), Cr(VI), W(VI), Se(VI), Te(VI), Os(VIII), which interfere in many methods for its determination[1].

Other β-diketones, benzoylacetone, dibenzoylmethane (10% solution in benzene from 0.5 *N* sodium hydroxide) and thenoyltrifluoroacetone (1% in chloroform from 2 *N* sodium hydroxide) do not extract rhenium.

The authors wish to thank the Council of Scientific and Industrial Research, New Delhi, for financial support, Dr. S. M. MUKHERJI for laboratory facilities, Prof. Dr. R. NEEB, Gutenberg University, Mainz, for the molybdenite sample, and the Indian Copper Corporation for the reverberatory flue dust.

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V. YATIRAJAM
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The extraction of gallium with cupferron

The ammonium salt of N-nitrosophenylhydroxylamine (cupferron) is one of the most widely used extraction agents. Such extractions have been reviewed by STARY[1], and by STARY AND SMIZANSKA[2]. Among other problems, these authors studied the pH function of the extraction of gallium(III)–cupferrate with cloroform in the presence of 0.005 *M* cupferron[2], and stated that 10^{-4} *M* gallium can be quantitatively extracted by chloroform from an aqueous phase containing 0.1 *M* sodium perchlorate in the pH range 1.5–12.

During a study of the separation of gallium from tungsten, we tried unsuccessfully to extract gallium(III) from solutions at pH 10 and 11, and therefore, the experiments of STARY AND SMIZANSKA[2] were repeated.

Apparatus and reagents

Cupferron(p.a., Riedel). An aqueous 6% (w/v) solution of the reagent was prepared immediately before use.

Sodium perchlorate was prepared from sodium carbonate and perchloric acid and was twice recrystallized from deionized water; it was tested for chloride ions.

Chloroform(p.a., Reanal) was treated with concentrated sulphuric acid, washed and distilled from sodium hydroxide immediately before use; it was finally preequilibrated with 0.1 *M* sodium perchlorate.

Gallium perchlorate was prepared from gallium oxide (pss., Ga_2O_3 content min. 99%, Reanal) by dissolution in 2 *M* perchloric acid. After filtration, the stock solution was standardized compleximetrically.

After the extraction equilibrium had been reached the hydrogen ion concentrations of the solutions were determined by means of an OP-205 pH meter (Radelkisz) and an OP 711-1-A glass electrode and saturated calomel electrode; pH standards were 0.05 *M* potassium hydrogen phthalate and 0.05 *M* sodium tetraborate.

Absorbance measurements were made with a Beckman DU spectrophotometer.

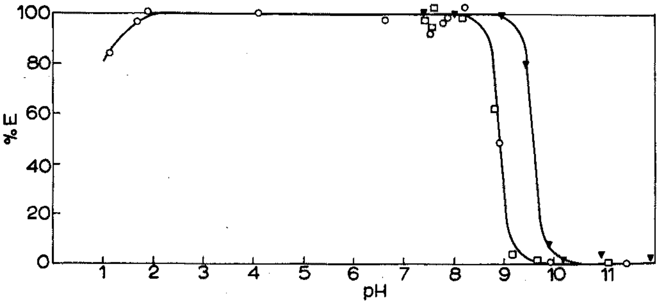

Fig. 1. Effect of pH on the extraction of gallium(III)–cupferrate into chloroform. 0.1 M $NaClO_4$.
○ $4.0 \cdot 10^{-5}$ M $GaCl_3$, $5.0 \cdot 10^{-3}$ M cupferron, $2.0 \cdot 10^{-2}$ M NaCl;
□ $3.5 \cdot 10^{-5}$ M $Ga(ClO_4)_3$, $5.0 \cdot 10^{-3}$ M cupferron;
▼ $3.5 \cdot 10^{-5}$ M $Ga(ClO_4)_3$, $5.0 \cdot 10^{-2}$ M cupferron.

Method

Equal volumes (10 ml) of the aqueous and organic phases were used. The aqueous phase contained 0.1 M sodium perchlorate, and perchloric acid and sodium hydroxide were used to adjust the pH of the solutions after the addition of the reagent. The extractions were made at 28 ± 1° for 5 min. Chloroform was then evaporated on a water bath and the organic residue was destroyed by digestion with sulphuric acid and hydrogen peroxide. The gallium content of the organic phases was determined by means of 4-(2-pyridylazo)-2-resorcinol at pH 6.5 in the presence of cyanide. Absorbances were measured[3,4] at 510 nm.

Results

The results of these measurements are shown in Fig. 1. It can be seen that gallium(III) cannot be extracted into chloroform above pH 9 in the presence of 0.005 M cupferron and above pH 10 in the presence of 0.05 M cupferron. This behaviour is similar to that of aluminium and indium which form very stable hydroxo complexes. Good agreement with the results of STARY AND SMIZANSKA[2] was obtained in the extraction of iron(III) and indium(III).

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(Received October 13th, 1968)

BOOK REVIEWS

Laboratory Handbook of Chromatographic Methods, Edited by O. MIKEŠ, Translation Editor R. A. CHALMERS, D. Van Nostrand Company, Ltd., London, 1966, 434 pp., price 75 s.

It is an unfortunate consequence of what people are content to call, nowadays, the "escalation" of science, that publication rarely keeps pace with invention. Thus this book, originally published in Czechoslovakia in 1961, translated in 1964, and published in Britain in 1966, can put on record (*in 1966*) the statement that "the importance of paper chromatography was felt to warrant fuller treatment, and Chapter 2 gives a wider survey than the others"; Thus *Partition Chromatography* is given about 140 pages. But *Thin-Layer Chromatography* is accorded 14 pages, most of these poorly related to the present state. And can so-called *Gas Chromatography*, in a work of this general title, be dealt with adequately in 20 pages; or *Gel-Filtration* in 15?

These are no complaints against the authors (it is a multi-author book) or the editors, Czech or British. It is "*anni labuntur*" — and more rapidly than ever before. If this book had appeared in 1961, it would have been stimulating, rewarding and, indeed, of first importance. Now it is simply a reminder of the (very proper) impermanence of scientific techniques.

For the young worker, about to use separation methods, this book can be a useful introduction to the subject — as long as he remembers to extrapolate. Indeed, the worker who has been using these separation methods for years could be stimulated even more by a study of this book. The book claims to be, and it is, a practical rather than a theoretical text, and should provide ideas for the worker with the flair for constructive development. Indeed, the greatest dividend from this book might be the realisation that if such radical changes could be made in the past six years, equally radical changes *can* be made *in the next year*.

CECIL L. WILSON (Belfast)

Anal. Chim. Acta, 44 (1969) 473

F. BASOLO AND R. G. PEARSON, *Mechanisms of Inorganic Reactions: A Study of Metal Complexes in Solution*, 2nd Edn., J. Wiley and Sons, Inc., New York, 1967, xi+701 pp., price 144 s.

During the nine years that have elapsed since the first edition of this book, both the quality and quantity of the information available on kinetics and mechanisms of inorganic reactions has increased enormously. Accordingly, a great deal of new information has been introduced into the present text, although the general pattern of the first edition is retained. The principal topics discussed are the theory of the coordinate bond, substitution reactions and stereochemical changes in octahedral complexes, substitution reactions of square planar complexes, oxidation–reduction reactions, reactions of transition metal organometallics, and metal ion catalysis. In this quite extensively revised edition, the authors seem to have preserved an excellent balance between rejection of earlier theories and introduction of new ideas.

This is an excellent book which can be very well recommended. It should be of great value to research workers in coordination chemistry whether from the inorganic or analytical viewpoint; it should be required reading for all postgraduate students concerned with such topics and for advanced level undergraduates.

W. I. STEPHEN (Birmingham)

W. P. GRIFFITH, *The Chemistry of the Rarer Platinum Metals*, Interscience Monographs on Chemistry, Inorganic Chemistry Section, edited by F. A. COTTON AND G. WILKINSON, Interscience Publishers–J. Wiley and Sons, Inc., New York, 1967, ix + 491 pp., price 120 s.

The rare platinum metals considered in this book are osmium, ruthenium, iridium and rhodium. In the first two chapters, the history and general properties of the metals themselves, and their general chemistry are considered briefly. However, by far the greatest part of the text deals with the coordination chemistry of the specified four metals. The material presented is classified according to the oxidation state of the metal and the nature of the ligand donor atom. The coverage is comprehensive and critical; literature references to the end of 1966 are given.

The book contains little of immediate concern to analytical chemists, for the section dealing with the analytical chemistry of the metals is cursory. Nevertheless, this is a very useful book in that a wide range of chemical reactions of these metals is presented. It should be of considerable interest to anyone involved with research on the chemistry of the platinum metals, and more importantly from an analytical aspect, it could well provide a fruitful source of reagents and reactions of value in the development of new analytical procedures.

W. I. STEPHEN (Birmingham)

A. V. NOVOSELOVA AND L. R. BATSANOVA, *The Analytical Chemistry of Beryllium*, Israel program for Scientific Translations, Jerusalem, 1968, vi + 220 pp., price $ 12.75.

V. M. PESHKOVA AND V. M. SAVOSTINA, *The Analytical Chemistry of Nickel*, Israel Program for Scientific Translations, Jerusalem, 1967, xi + 178 pp., price $ 11.50.

These two books are further volumes in the series *Analytical Chemistry of the Elements* sponsored by the USSR Academy of Sciences and translated into English by I.P.S.T. Both were originally published in Moscow in 1966, so little or no delay has occurred in the publication of these translated versions.

The pattern of both these books follows closely that of the earlier volumes in this series. Thus, the introductory chapter gives details of the physical, chemical and analytical characteristics of the element and its compounds (including compounds of purely analytical significance, principally chelate types). This is followed by an account of the main chemical processes for the detection of the elements. Each volume devotes a chapter to methods for the separation and concentration of the elements from other elements, and to the determination of the elements in natural and industrial materials. However, the major portion of each text is devoted to methods for the determination of each element, and these are dealt with under conventional headings, gravimetric, titrimetric, photometric, polarographic, spectroscopic, radiometric and fluorimetric methods being prominent.

There can be no doubt about the value of these books as general works of reference. The authors have diligently combed the literature for relevant information and although one might be justified in expressing the view that little *new* information is contained in these texts, their comprehensiveness is their main asset. The beryllium text cites 821 references, the nickel one, 1303. The appearance of further volumes in this useful series of I.P.S.T. publications is awaited with interest; if the present standards are maintained, this series will be valuable not only for purposes of reference but also to highlight hitherto difficultly accessible Russian work on the analytical chemistry of the elements.

W. I. STEPHEN (Birmingham)

GEORGE W. WEINGART, *Pyrotechnics*, 2nd Edn., Chemical Publishing Company, New York, 1968, xii + 244 pp., price $ 8.50.

This book is a general manual on the art of making fire-works. Separate chapters deal with Ingredients, Manipulation, Products of Manufacture and Formulae, Exhibition Fire-works and Miscellaneous Fire-works.

Full specifications of components and practical details for small-scale manufacture are given, with pertinent comments on the necessary precautions.

Mass Spectrometry in Inorganic Chemistry, Edited by ROBERT F. GOULD, American Chemical Society, Advances in Chemistry Series No. 72, 329 pp., price $12.00.

This book is a collection of twenty-one papers which made up a symposium on the use of mass spectrometry in inorganic chemistry. Each paper describes a different research project in inorganic chemistry such as *Ion–Molecule Reactions Involved in Pentabesane, Shock Tube Study of* D_2*–Ne Mixture from 900°–2300°K*, etc. The common theme of these articles is that mass spectrometry was used in the course of the research. The papers in general are more concerned with the solution of the inorganic chemistry problem than with the problems involved in applying the mass spectrometer.

However, there are several useful descriptions of novel mass spectrometry equipment developed. Several new inlet systems are described which were particularly suitable for the samples involved. In general, the descriptions are brief, but there is often enough information for the expert mass spectrometrist to use to advantage in designing his own equipment. Several of the articles deal with the measurement of appearance potentials, while others are concerned with the interpretation of standard mass spectra encountered in inorganic chemistry. All are concerned to a greater or lesser degree with the introduction of the sample into the instrument.

The book is most useful in pointing out how the mass spectrometer has been used to solve a variety of problems in inorganic chemistry. This should be useful in guiding the research worker in similar areas to the solution of some of his problems through the use of mass spectrometry.

J. W. ROBINSON, (Baton Rouge, La).

J. N. BUTLER, B. A. DUNELL AND L. G. HARRISON, *Problems for Introductory University Chemistry (with Complete Solutions)*, Addison–Wesley Publishing Company, Reading, Mass., 1967, ix + 213 pp., price 22 s.

This book contains some introductory information and large numbers of problems on the following topics: Composition of compounds, Avogadro's number, Isotopes and nuclear chemistry, Properties of gases, Stoichiometry, Oxidation–reduction, Volumetric measurements, Electrochemistry, Phase equilibria, Thermochemistry, Equilibria and thermodynamics, Ionic equilibria, and Descriptive chemistry and chemical bonding.

The greater part of the book consists of hints on how to solve the problems set.

T. BRAUN AND J. TÖLGYESSY, *Radiometric Titrations*, Translated by I. FINÁLY, Translation edited by A. TOWNSHEND, International Series of Monographs in Analytical Chemistry, Vol. 29, Pergamon Press, Oxford, 1967, x + 168 pp., price 55 s.

The book is entitled *Radiometric Titrations*. In effect, it presents one aspect of the use of radioactive indicators. And in the section entitled *Historical Background* it tells us that "the invention of radiometric end-point detection is ascribed to LANGER; it is first referred to in the patent granted to him in 1940". No mention of PANETH, whose book, *Radio-elements as Indicators*, appeared in 1928: no mention of VON HEVESY, who, in 1944, was awarded a Nobel Prize "for his work on the use of isotopes as tracer elements in researches in chemical processes". Alas poor PANETH! Alas poor VON HEVESY! No mention, either, of these originators in the review by the same authors (*Talanta*, 11 (1964) 1277).

The book is an amplification of the review article. For those vitally concerned with the use of radioactive indicators the book will clearly be a useful, if expensive, "buy". For the general analytical chemist, the extra 40,000 words seem scarcely justified by a mere 16 references to 1964 or later, which justifies the feeling that this does not appear to be a rapidly developing area of analytical chemistry.

For the specialist I would recommend the book — I can find no fault with the editing of the translation, and a considerable amount of detail, especially in the form of diagrams of apparatus, is added to the original review article. For the "general", I would doubt if the book could have much appeal.

CECIL L. WILSON (Belfast)

J. B. DAWSON AND F. W. HEATON, *Spectrochemical Analysis of Clinical Material*, C. C. Thomas, Springfield, Ill., 1967, xvi+118 pp., price $ 7.50.

This book deals with emission and atomic absorption spectrophotometry in the analysis of clinical material. It is divided into four parts. The first deals with physical principles and defines the detection limit. Sections on emission and absorption methods follow; these describe in general terms the design of instruments using these phenomena as analytical tools. The final chapters give good brief descriptions of techniques used to overcome the problems of interference, sensitivity and instrument instability. The authors have not written a detailed working manual. Instead they have listed the most sensitive method of detection together with recommended methods of analysis for twelve common metals. The authors set out to introduce spectrochemical analysis to the biologist and clinician. They have succeeded admirably.

K. DIXON (Birmingham)

J. RUZICKA AND J. STARY, *Substoichiometry in Radiochemical Analysis*, International Series of Monographs in Analytical Chemistry, Vol. 30, Pergamon Press, Oxford, ix + 150 pp., price 55s.

The authors of this book have been the principal developers of substoichiometric analysis, a technique that has been used to speed and simplify separations used in activation analysis and to increase the sensitivity of isotope-dilution analysis.

The theory of the application of this method in neutron-activation analysis and isotope-dilution analysis is dealt with in great detail. An outline of the general experimental techniques involved in the use and development of substoichiometric methods is followed by experimental procedures for the determination of 23 elements by neutron activation, isotope dilution or both. Short chapters on the use of substoichiometry in the analysis of radioactive materials, the automation of substoichiometric analysis, a critical comparison of substoichiometric isotope-dilution analysis with similar radiometric methods of trace analysis, and current trends and developments, complete the coverage of all aspects of this subject.

This volume will be invaluable to those who contemplate using substoichiometric analysis.

J. W. MCMILLAN (Harwell)

Anal. Chim. Acta, 44 (1969) 478

R. A. CHALMERS, *Aspects of Analytical Chemistry*, Contemporary Science Paperbacks — 19, Oliver and Boyd Ltd., Edinburgh, 1968, vii + 144 pp., price 7s.6d.

This small volume presents a descriptive account of the underlying principles of methods of analytical chemistry. The author attempts to place analytical chemistry in its proper perspective in relation to chemistry as a whole. The longest chapter, chapter 2, is concerned with classical methods and is probably the most useful and instructive to the general reader. The remaining short chapters deal with spectroscopic, electrical and radiochemical techniques and methods of separation and automation. These chapters do little more than briefly mention the techniques involved and their underlying physico-chemical principles.

This text might be recommended to students in order to stimulate their interest in analytical chemistry, as it presents a picture of the extensive scope and diverse aims of modern analytical chemistry.

G. F. KIRKBRIGHT (London)

Anal. Chim. Acta, 44 (1969) 478

Porous Carbon Solids, Edited by R. L. BOND, Academic Press, London and New York, 1967, xi + 311 pp., price 80 s.

The ever-increasing industrial use of various sorts of carbon has made it essential to develop methods of characterizing the physical structure of porous carbonaceous materials. In the present book several such methods are considered, the information that they can provide is indicated, and the theory involved described. Descriptions of special apparatus are also included. Eight chapters written by top authorities deal with (*1*) physical adsorption of gases, (*2*) adsorption from solution, (*3*) use of molecular probes, (*4*) permeability and flow studies, (*5*) further techniques for the study of pore structure by liquid metal penetration, (*6*) mercury porosimetry, (*7*) studies of macroporosity by silver impregnation and by soft X-rays, and (*8*) radiographic techniques. (Chapter 6 would more logically precede 5.) The techniques of photomicrography, electron microscopy, optical and X-ray stereophotomicrography are not described fully in any of the chapters. The merit of the book is that it describes extensively some more modern methods (Chapters 5, 7 and 8), which are less widely used than mercury porosimetry. The book is suitable both for research workers acquainted with some of the problems of porous structure and for those who need basic information about characterizing the structure of a carbon for a particular application.

KAREL MICKA (Prague)

Analysis of High-purity Materials, Edited by I. P. ALIMARIN, Translated by J. SCHMORAK, Israel Program for Scientific Translations, Jerusalem, 1968, xviii + 584 pp., price $ 20.25.

Modern technology has created a rapidly increasing demand for materials of guaranteed high purity. It is necessary, therefore, for the analyst to analyse such materials for their trace constituents with reasonable accuracy. This book is a compendium of the methods used by Russian chemists for the analysis of highly pure Si, Ge, Ga, In, Tl, As, Sb, P, Al, Pb, Bi, Sn, Zn, Cd, S, Se, Te, I, B, C and some of their compounds; analysis of water and various acids is also discussed. Most modern instrumental techniques, with the surprising exception of flame methods, are used.

This is a translation of the Russian version that was published in 1965. The presentation is generally good, despite some printing errors and poorly reproduced photographs. The very detailed procedures given for each trace element in each matrix make the book excellent value for anyone concerned with the analysis of high-purity materials.

A. TOWNSHEND (Birmingham)

WALTER SLAVIN, *Atomic Absorption Spectroscopy*, Interscience Publishers–J. Wiley and Sons, New York, 1968, xvii+307 pp., price 125 s.

This is the fourth English text on atomic absorption spectroscopy to appear in the last two years, whereas only one had existed previously; this reflects the rapid development of this analytical technique. The present book is authoritative and comprehensive. The simplicity of the theory is underlined by its brief treatment in the opening chapter, but instrumentation and technique are discussed at length. This is followed by a detailed discussion of the atomic absorption properties of 69 elements (67 can be analysed by atomic absorption) with full information about optimal flame conditions, spectral lines, lamps, interferences, sensitivity, etc. The author has gone to some trouble to ensure that the sensitivities quoted are all based on the same definition of sensitivity, often a source of some confusion (and optimism?) in the original literature.

The situations in which the nitrous oxide–acetylene flame is advantageous are emphasized. The final chapters are devoted to applications to the analysis of biological and industrial materials and to geochemistry. The bibliography lists 669 references.

The text covers few theoretical concepts, and is essentially practical in nature. It provides a wealth of information about all aspects of atomic absorption spectroscopy in a readable manner and should enable the analyst to apply atomic absorption to his particular problems with maximal efficiency. The book is well produced and free from typographical errors, and should be a worthy addition to any chemical library.

A. TOWNSHEND (Birmingham)

Anal. Chim. Acta, 44 (1969) 480

Organometallic Compounds. Methods of Synthesis, Physical Constants and Chemical Reactions. Vol. III. Compounds of Arsenic, Antimony and Bismuth, 2nd Edn., Edited by M. DUB, Springer Verlag, Berlin, 1968, xx + 925 pp., price DM 98,—, $ 24.50.

The second edition of this volume contains a comprehensive survey of the literature on arsenic, antimony and bismuth compounds over the period 1937 to the end of 1964. The information given covers methods of synthesis, physical properties and chemical reactions; reference is also made to biological activities and uses.

As with previous volumes, the survey is uncritical, but its comprehensiveness will make it an invaluable work of reference. The book is well-produced and the extensive use of tables renders the gleaning of information relatively simple. This is not a book to be bought by the individual, but, along with the previous volumes, it deserves a place in every library.

E. J. FORBES (Birmingham)

Anal. Chim. Acta, 44 (1969) 480

R. L. PECSOK AND L. D. SHIELDS, *Modern Methods of Chemical Analysis*, J. Wiley and Sons, New York, 1968, xvi+480 pp., price 88 s.
Experiments in Modern Methods of Chemical Analysis, edited by R. L. PECSOK, J. Wiley and Sons, New York, 1968, v+135 pp., price 38 s.

These two books, each complementing the other, are the basis of a course in organic analytical chemistry at the University of California. The image of analytical chemistry is changing fast and for the majority of students, who will not be analytical chemists but will only want to use the results of analytical chemistry, a knowledge of the scope of analytical chemistry may be of greater importance than the ability to do accurate and precise classical analysis. Some textbooks in practical organic chemistry attempt to introduce the new techniques with an inadequate coverage of the theory and the result is merely an extension of "black box chemistry". From these books it is possible to teach and learn chemistry.

The practical course extends over 27–30 four-hour periods and is supplemented by 50 hours' lecturing time. Whilst the book of experiments deals with organic and biochemical examples, the corresponding chapters of the companion book give relevant examples from all branches of chemistry. The practical work begins with basic manipulative experiments such as the determination of melting points, solvent extraction, recrystallization and distillation; the necessary accompanying study of phase transitions is covered in the other book. From distillation the course proceeds via G. L. C. to all types of chromatography and ion exchange.

A second section deals with modern spectroscopy including N.M.R. and mass spectrometry; for the practical work in the latter techniques the students are provided with worked examples and interpreted spectra as well as exercises on unknown samples. A further series of well designed experiments gives the student the opportunity of applying these and other techniques to the study of kinetics, illustrated by experiments in reaction rates, enzyme catalysis and some radiochemical methods.

There are many points to commend in the two books; although one is a "recipe book", when it is used in conjunction with its companion volume it becomes a very useful book. The examples are well chosen and cover a wide field. The coverage is ideal for students who do chemistry as a subsidiary part of their course, *e.g.* students of life sciences, but it is unfortunately not deep enough for the specialist chemistry courses in many universities. However, within this limitation, the books are a worthwhile addition to the textbooks in modern analytical chemistry.

L. S. BARK (Salford)

Encyclopedia of Industrial Chemical Analysis. Vol. 5. Alkanolamines to Antibiotics, Edited by F. D. SNELL AND C. L. HINTON, Interscience Publishers–J. Wiley and Sons, Inc., New York, 1968, xi+677 pp., price 425 s (subscription price 310 s).

The fifth volume of this Encyclopedia has appeared with commendable speed after the fourth volume. The topics covered are alkanolamines, alkyl resins, alloys, allyl compounds, aluminum, amines, amino resins, ammonia, ammonium compounds, anesthetics, aniline and its derivatives, and antibiotics. The longest sections are those devoted to antibiotics, and to aluminum and its alloys and compounds. In the latter section (148 pp.), apart from the normal type of information, methods for the determination of 40 impurities in aluminum alloys are mentioned and, in many cases, full experimental detail is given.

The section on antibiotics is more a monograph than an encyclopedia entry and runs to 233 pp. A good deal of information on antibiotic structure is given before the assay methods, which are predominantly microbiological, are discussed. Various direct spectrophotometric and spectrofluorimetric assays are mentioned, but there are very few chemical methods for the assay of these compounds. The information in this section is apparently comprehensive and even includes an hitherto unpublished "kinetic" method for antimycin assay. This requires 24 goldfish (or 48 albino goldfish for high precision) and the plotting of average survival time against antibiotic concentration; full instructions on the importance of constant alcohol concentrations and on how to establish death are given but no mention is made of interfering species (cats?). Patently, here is a vast area open to the endeavours of more conventionally minded analysts.

However, in general, this volume maintains the high standard of its predecessor and should prove very valuable for reference.

A. M. G. MACDONALD (Birmingham)

PUBLICATIONS RECEIVED

R. P. EARDLEY AND A. H. MOUNTFORD, *Atomic Absorption Spectrophotometry in Ceramic Analysis: Evaluation of Some Commercial Spectrophotometers*, British Ceramic Research Association, Special Publication 59, B.C.R.A., Stoke-on-Trent, England, 60 pp., price 20 s.

Most Significant New Books on Chemistry, 1966, Edited by D. E. SEABROOK, R. Maxwell & Co., Ltd., Oxford, 1968, 47 pp., price 20 s.

ANNOUNCEMENT

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION ANNUAL REPORT

The Analytical Chemistry Division is administered by the Division Committee, the present members being:

Professor P. W. West, U.S.A. (President); Professor W. Kemula, Poland (Vice-President); Professor I. P. Alimarin, U.S.S.R.; Professor R. Belcher, U.K.; Professor C. Duval, France; Professor L. Erdey, Hungary; Professor T. Fujinaga, Japan; Professor D. N. Hume, U.S.A.; Professor H. Kaiser, Germany; and Mr. R. W. Fennell (Secretary), Materials Department, Royal Aircraft Establishment, Farnborough, Hants., U.K.

The bulk of the scientific work of the Division is done by the seven Commissions, whose terms of reference are the study of topics of international scientific or technical significance requiring agreement, regularisation, standardisation or codification within the sphere of their respective expertise.

Brief summaries of the work currently being done by these Commissions follow. Requests for further information or suggestions for future projects should be addressed to the appropriate Commission Secretary or, in case of doubt, to the Division Secretary.

Commission 1. Analytical Reactions and Reagents

Chairman: Professor H. Malissa, Institut für Analytische Chemie und Mikrochemie, Technische Hochschule, Getreidemarkt 9, A-1060 Wien, Austria.

At the present time, this Commission is concerned entirely with standardisation of analytical methods required by the European Economic Community with whom IUPAC has a working agreement.

Commission 2. Microchemical Techniques and Trace Analysis

Chairman: Dr. W. Schöniger (Switzerland), Secretary: Dr. R. Lévy, Service central de Microanalyse du CNRS, 2, Rue H.-Dunant, 94 Thiais, France.

Studies are being carried out, on an international basis, on the elemental analysis of organic materials, in particular:

1. carbon and hydrogen, especially in compounds containing heteroelements,
2. fluorine,
3. nitrogen, based on the Dumas method,
4. metals, excluding simple residue procedures.

In addition, known sources of errors in microanalysis are being collated and studies being made on the purification of chemicals used for micro and trace analysis and on mass absorption coefficients used in electron beam microanalysis.

Commission 3. Analytical Nomenclature

Chairman: Professor R. BELCHER (U.K.). Secretary: Professor T. S. WEST, Department of Chemistry, Imperial College, London, S. W. 7, U.K.

Internationally acceptable nomenclature, definitions and symbols are being sought in the following areas of analytical interest:

1. liquid–liquid distribution (solvent extraction),
2. automatic analysis,
3. ion exchange,
4. chromatography,
5. scales of working,
6. mass spectrometry,
7. contamination phenomena in analytical precipitation.

The Commission is also compiling a list of trivial names of analytical reagents and examining the need for primary standards other then acid–base standards. Other projects under consideration are the concept of a selectivity index and the presentation of analytical methods for publication.

Commission 4. Spectrochemical and Other Optical Procedures

Chairman: Professor H. KAISER (Germany). Secretary: Professor V. A. FASSEL, Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.

The Commission is concentrating its efforts on nomenclature, symbols and usage in atomic spectrochemical analysis. The first part of its report, dealing with atomic emission spectroscopy, is being finalised and work is proceeding to cover:

1. flame atomic absorption and atomic fluorescence spectroscopy,
2. X-ray fluorescence spectroscopy (including X-ray microprobe techniques),
3. excitation source descriptions and parameters,
4. terms and concepts related to rigorous determination of detection limits.

Pending the standardisation of concepts and procedures for establishing detection limits, a project on the compilation of lists of minimal detectable concentrations is in abeyance.

Commission 5. Electroanalytical Chemistry

Chairman: Professor I. M. KOLTHOFF (U.S.A.). Secretary: Dr. P. ZUMAN, Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham 15, U.K.

The purification and purity of solvents and reagents of interest in electroanalytical chemistry is a continuing project of the Commission. Other projects include:

1. the compilation of physico-chemical data in non-aqueous media,
2. the production of polarographic data cards and critical evaluation of polarographic procedures,
3. studies on solid electrodes,
4. the revision of tables of oxidation–reduction potentials.

Commission 6. Equilibrium Data

Chairman: Professor Y. MARCUS (Israel). Secretary: Dr. F. J. C. ROSSOTTI, Inorganic Chemistry Laboratory, South Parks Road, Oxford, U.K.

The Commission is actively engaged on the compilation and revision of data under the following headings:

1. stability constants,
2. distribution and solubility constants,
3. ion-exchange equilibrium constants,
4. stability constants of complexes.

Commission 7. Analytical Radiochemistry and Nuclear Materials

Chairman: Dr. G. B. Cook (U.K.). Secretary: Dr. W. W. Meinke, National Bureau of Standards, Chemistry Division, Washington, D.C. 20234, U.S.A.

Studies are being made on:

1. the purity of commercial radioactively labelled preparations,
2. the use of radioactive methods in analytical chemistry,
3. national regulations for the use of small quantities of radioisotopes,
4. reference materials for activation analysis.

The limits of reliability in the analysis of nuclear materials and the results of an intercomparison of laboratory methods for the determination of uranium are being studied. Multi-lingual nomenclature and basic reference reports are also being studied.

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