An International Journal of Analytical Chemistry

Title Section, Contents List, Author
Subject Indexes to Vol. 18, Nos. 7–12
are included in this issue

ταλαντα

talanta

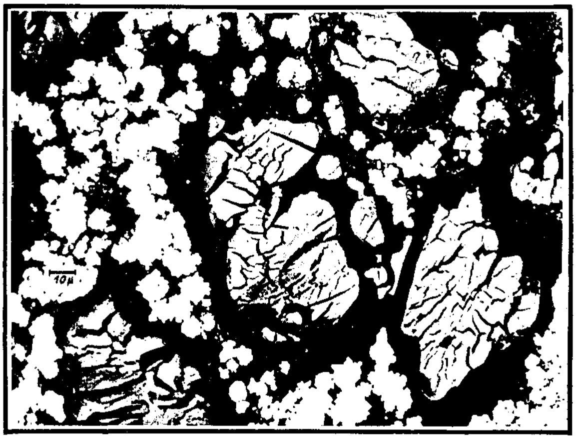
PERGAMON PRESS
OXFORD • LONDON • NEW YORK • PARIS

1971 VOLUME 18, NO. 12 DECEMBER

ELECTROCHIMICA *Acta*

Editor-in-Chief: DR T P HOAR, Cambridge

Electrochimica Acta is published by Pergamon Press Ltd under the auspices of the International Committee for Electrochemical Thermodynamics and Kinetics (CITCE).



Microphotograph of a DSK working layer.

Executive Editorial Board:
DR T P HOAR
University of Cambridge, England
PROFESSOR J O'M BOCKRIS
University of Pennsylvania, USA
PROFESSOR N IBL
Swiss Federal Institute of Technology, Zurich, Switzerland
PROFESSOR P Van RYSSELBERGHE
Stanford University, USA
PROFESSOR G VALENSI
Faculté des Sciences de Poitiers, France

This is an international journal of pure and applied electrochemistry, publishing papers on every aspect of this subject. More than two hundred papers are presented each year, either in the form of original reports or as serious, critical reviews. Electrochimica Acta thus provides a comprehensive up-to-date coverage of current activity throughout the rapidly expanding field of electrochemistry.

Some papers appearing in Vol 16 No 6:

R L KAY and T L BROADWATER:
Solvent structure in aqueous mixtures—I. Ionic mobilities in dioxane–water mixtures at 25°C.

J-C JUSTICE:
An interpretation for the distance parameter of the Fuoss–onsager conductance equation in the case of ionic association.

R WACHTER and J BARTHEL:
A method for determining the precise dependence of conductivity data on temperature.

M KESTEN und H G FELLER:
Uber die rolle der Sulfationen bei der anodischen Auflösung und bei der Passivierung von Nickel.

W SMIT and J G HOOGLAND:
The mechanism of the anodic formation of the peroxodisulphate ion on platinum-II. Time dependence of the anode potential.

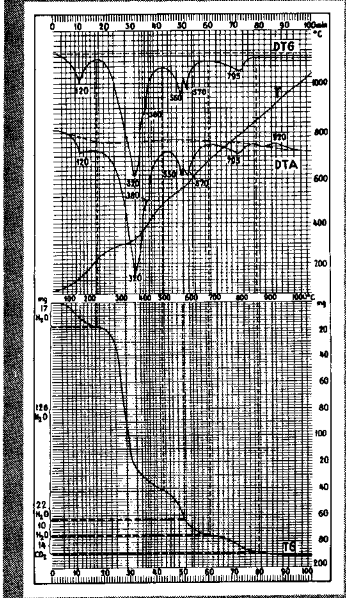
J AUGUSTYNSKI, F DALARD et J C SOHM:
Etude de la pile oxyde-d'argent–magnesium.

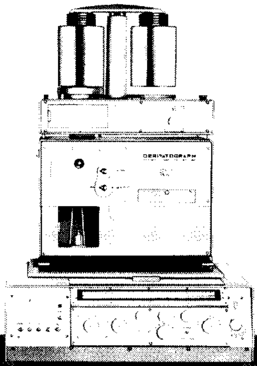
Published monthly
Subscription: £44/$110 per annum

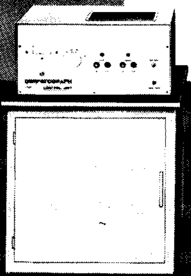
Pergamon Press

OXFORD · NEW YORK · SYDNEY · TORONTO

6/71


DTG
DTA
T
TG
120
320
360
380
550
570
795
990
H_2O
CO_2
°C
mg
min


DERIVATOGRAPH


DERIVATOGRAPH

N-benzoylphenylhydroxylamine and its Analogues

A. K. Majumdar

Contents: Introduction; The Effect of Atomic Groupings and Substituents on Reagents; Methods of Preparation and properties of N-benzoylphenylhydroxylamine and its analogues; Gravimetric Determinations using N-benzoylphenylhydroxylamine and its analogues; Sprectrophotometric Determinations using N-benzoylphenylhydroxylamine and its analogues; Separations by Solvent Extraction using N-benzoylphenylhydroxylamine; Titrimetric and Paper Chromatographic Applications of N-benzoylphenylhydroxylamine.

224 pages £7.00 hard cover

Field Ionization Mass Spectrometry

H.-D. Beckey

Contents: Preface; Introduction; Theory of Field Ionization (FI) and Field Emission (FE); Field Ionization Sources; Application of the FI Mass Spectrometer to Physico-Chemical Problems; Qualitative Analyses with the FI Mass Spectrometer.

359 pages £9.50 hard cover

Analytical Chemistry of Molybdenum and Tungsten

W. T. Elwell and D. F. Wood

Partial Contents: Physical and Chemical Properties; Gravimetric; Titrimetric; Emission Spectroscopic; Radiochemical and Mass-Spectrometric; Determination of Impurities and alloying elements.

288 pages £8.00 hard cover

Recent Advances in Liquid-Liquid Extraction

Edited by C. Hanson

Presents an authoritative review of developments in the science and practice of liquid-liquid extraction which have taken place during the last decade.

Partial Contents: The Chemistry of Solvent Extraction; Industrial Inorganic Processes; Industrial Contacting Equipment; The Study of Longitudinal Mixing in Liquid-liquid contactors.

604 £8.00 hard cover

Selected Readings in Chromatography

Edited by R. J. Magee

Contents: Types of Chromatography; A New Form of Chromatogram Employing Two Liquid Phases; Thin-layer Chromatography, Separation and Identification of Some Terpenes by a New Chromatographic Technique; Chromatography with Electrophoresis, Partition Chromatography of Amino Acids with Applied Voltage; Ion Exchange Chromatography, the Chemistry of Elements 99 and 100; Gas Chromatography, Gas-Liquid Partition Chromatography.

144 pages £1.75 hard cover £1.25 flexi cover

Pergamon

T279

Talanta

An International Journal of Analytical Chemistry

The illustration of a Greek balance from one of the Hope Vases is reproduced here by kind permission of Cambridge University Press

---

Editor-in-Chief

DR.R.A.CHALMERS, Department of Chemistry, University of Aberdeen, Old Aberdeen, Scotland

Assistant Editors

DR.D.BETTERIDGE, University College, Swansea, Wales
DR.J.R.MAJER, University of Birmingham, England
DR.I.L.MAAR, University of Aberdeen, Scotland

Regional Editors

PROFESSOR I.P.ALIMARIN, Vernadsky Institute of Geochemistry and Analytical Chemistry, U.S.S.R. Academy of Sciences, Vorobievskoe Shosse 47a, Moscow V-334, U.S.S.R.

PROFESSOR E.BLASIUS, Institut für Analytische Chemie und Radiochemie der Universität des Saarlandes, 66 Saarbrücken 15, Bundesrepublik Deutschland

MR.H.J.FRANCIS, JR., Pennwalt Corporation, 900 First Avenue, King of Prussia, Pennsylvania 19406, U.S.A.

PROFESSOR J.S.FRITZ, Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.

DR.M.PESEZ, Roussel-Uclaf, 102 et 111 route de Noisy, Romainville (Seine), France

DR.R.PŘIBIL, Laboratory of Analytical Chemistry, Polarographic Institute of J. Heyrovský, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia

Consulting Editors

DR.M.WILLIAMS, Oxford, England
PROFESSOR C.L.WILSON, Belfast, N. Ireland

Editorial Board

Chairman: PROFESSOR R.BELCHER, *representing Advisory Board*
DR.R.A.CHALMERS, *Editor-in-Chief*
DR.M.WILLIAMS, *Consulting Editor*
PROFESSOR C.L.WILSON, *Consulting Editor*
DR.D.BETTERIDGE, *Assistant Editor*
DR.J.R.MAJER, *Assistant Editor*
MR.H.J.FRANCIS, JR., *representing Regional Editors*
MR.G.F.RICHARDS, *Director, Pergamon Press Ltd.*

Annual Subscription Rates (including postage)

Published monthly—1 volume per annum

$10(£3.50)—For *bona fide* students, who place their orders with the publisher together with a note from their professor or tutor certifying their status

Private individuals whose departmental libraries subscribe, may obtain this Journal for their personal use at the reduced rate of $25(£8) per annum

$90(£36)—For libraries, government laboratories, research establishments, manufacturing houses and other multiple-reader institutions

Payments must be made in advance

Back numbers are available—write for Back Issues Price List

Publishing and Advertising Offices

American Continent: Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.
Rest of the World: Pergamon Press Ltd., Headington Hill Hall, Oxford OX3 0BW, England

Copyright © 1971 Pergamon Press Ltd.

ห้องสมุด [illegible]วิทยาศาสตร์
— [illegible]

Advisory Board

Aims and Scope

Established as a medium for the rapid publication of papers dealing with all aspects of analytical chemistry, *Talanta* is the natural vehicle for the international communication of progress in this field. As an international journal, its papers are expected to be of a very high standard and to make definite contributions to the subject: they must be new publications. Papers may be written in English, French, or German; all papers have abstracts in these three languages and also in Russian. Special importance is attached to work dealing with the principles of analytical chemistry in which experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields or of hitherto widely scattered material are considered for publication, but should be critical. Original papers, short communications and reviews are refereed in the normal manner. Preliminary communications are refereed urgently and accorded priority in publication. Correspondence of interest to analytical chemists is welcomed by the Editor-in-Chief, at whose discretion it is published. A new feature is Annotations, which are critical commentaries on some aspect of analytical chemistry and deal with topics such as sources of error, or the scope and limitations of methods and techniques; these commentaries are refereed.

Allied Journals

Other Pergamon Journals which are of interest to readers of *Talanta:*

Annals of Occupational Hygiene
Applied Radiation and Isotopes
Atmospheric Environment
Carbon
Chemical Engineering Science
Corrosion Science
Electrochimica Acta
European Polymer Journal
Food and Cosmetics Toxicology
Geochimica et Cosmochimica Acta
Inorganic and Nuclear Chemistry
Inorganic and Nuclear Chemistry Letters
Materials Research Bulletin
Petroleum Chemistry
Photochemistry and Photobiology
Physics and Chemistry of Solids
Phytochemistry
Polymer Science USSR
Spectrochimica Acta, Part A: Molecular Spectroscop
Spectrochimica Acta, Part B: Atomic Spectroscopy
Tetrahedron
Tetrahedron Letters
Water Research

Each journal has an individual Information and Index Leaflet giving full details. Write now for any o these leaflets which interest you.

TALANTA MEDAL

DR. RUDOLF PŘIBIL

The Editorial Board of *Talanta* has pleasure in announcing that, with the approval of the Advisory Board, the Sixth Award of the Talanta Medal has been made to

DR. RUDOLF PŘIBIL

of the Laboratory for Analytical Chemistry, J. Heyrovský Polarographic Institute, Czechoslovak Academy of Sciences.

Rudolf Přibil has made an outstanding contribution to analytical chemistry in his development of numerous practical applications of complexometric reagents. His methods are distinguished by their simplicity, practicality and reliability, and his development of new metallochromic indicators, especially Xylenol Orange and Methylthymol Blue, has greatly extended the scope of complexometric titrimetry. His knowledge of chemical reactions is almost unrivalled, and his practical skill has delighted many an audience. His 230 papers and his books and patents (his books have appeared in Czech, English, German, Russian, Romanian, Bulgarian and Chinese) show how efficiently and extensively he has developed this important field of chemical analysis.

Talanta, 1971, Vol. 18, pp. 1175 to 1196. Pergamon Press. Printed in Northern Ireland

TALANTA REVIEW

USE OF BASIC DYES IN THE DETERMINATION OF ANIONS, PARTICULARLY AS A MEANS OF DETERMINING ANTIMONY, THALLIUM, AND GALLIUM

A. G. FOGG, C. BURGESS and D. THORBURN BURNS
Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire

(*Received* 7 *December* 1970. *Accepted* 22 *April* 1971)

Summary—The use of xanthene, triphenylmethane and other basic dye cations as reagents for the determination of anions is reviewed. Elements and anions determined include Sb, Tl, Ga, Au, Te, In, Zn, Ta, Hg, Re, Sn, U, Os, B, Cr, Ag, ClO_4^-, PO_4^{3-}, SO_4^{2-} and NO_3^-. Difficulties encountered in developing satisfactory procedures involving basic dyes are discussed. Procedures for the purification and analysis of basic dye samples are outlined.

MANY metals can be determined spectrophotometrically as coloured complexes with unidentate or chelating ligands. *p*-Group elements, however, are often more conveniently determined by the formation of ion-association complexes than by the formation of conventional complexes. In these determinations, anions containing the metal, or other element to be determined, are extracted into an organic solvent, in the form of an ion-pair with a large cation. The two groups of reagents in general use are the "onium" compounds and the basic dyes. The use of the former compounds has been reviewed recently.[1] As onium cations are colourless it follows that, for direct colorimetry, the anion to be determined must itself be coloured: alternatively, if the anion is colourless, measurements may be made in the ultraviolet region or the anion may be reacted with a second reagent, after the extraction procedure, to produce a coloured product.

The main advantage of using basic dyes as extractants is that many of them have high molar absorptivities ($0{\cdot}6 \times 10^4$—$1{\cdot}2 \times 10^4$ $l.mole^{-1}.mm^{-1}$); the anion to be determined, therefore, need not be coloured. In the present survey the use of basic dyes as extractants is reviewed. Neither acidic dyes, which can be used to extract cations, nor dyes which form chelate complexes, have been considered here.

Most of the published papers in this field are concerned equally with the determination of antimony and thallium. About a fourth as many papers are concerned with the determination of gallium. Still fewer are concerned with the determination of tantalum, perchlorate, gold, boron, tellurium, rhenium and mercury and other occasional papers deal with the determination of several other elements and ions.

Two main groups of dyes have been used in these determinations—xanthene dyes and triphenylmethane dyes—but some use has been made of azine, oxazine, thiazine and other dyes. The oxygen bridge of the xanthene cation causes it to be more rigid than the triphenylmethane cation and absorbed light energy is less readily lost by vibration or rotation. Thus xanthene dyes find many applications in fluorimetric analysis. Many of the xanthene dyes are neutral molecules and some are chelating agents; these are not considered here.

Extraction blanks tend to be higher with the xanthene dyes than with the triphenylmethane dyes. Solvents used for extraction of the ion-association complex include benzene, toluene, pentyl acetate, ethyl acetate and mixtures of benzene with either ether or acetone. The most satisfactory solvent in many cases seems to depend mainly on the dye;[2] benzene is reported to be the best solvent for ion-association complexes of Crystal Violet and Rhodamine 6J, whereas benzene with ether or acetone is most satisfactory for Rhodamine B and Victoria Blue B.

The anion extracted may be a simple oxyanion, such as ClO_4^- or ReO_4^-, or it may be a halo- or thiocyanato-complex anion, such as $TlBr_4^-$ or $Zn(SCN)_4^{2-}$. Some selectivity can be attained by the choice of medium (*e.g.*, hydrochloric or hydrobromic acid), in addition to the choice of dye. In general an increase in molecular weight of the dye cation increases the solubility of the ion-pair in the organic solvent but decreases its selectivity.[2]

Further selectivity is obtained because many elements react in only one oxidation state. Thus antimony and thallium generally have to be oxidized to the +V and +III states respectively and tin has to be reduced to Sn(II). Kothny[3] has described a procedure for determining mercury, thallium and gold in the same sample, with Crystal Violet, which illustrates these points. Total mercury and gold are determined by extracting their complex iodo-anions without thallium interfering, whereas total thallium and gold are determined by extracting their complex bromo-anions without mercury interfering. Owing to the rarity of gold the correction for its presence is negligible in most determinations of thallium and mercury. If significant amounts are present, however, the sample may be dry-ashed to volatilize mercury prior to the determination of gold as its complex iodo-anion. An alternative procedure for estimating gold is based on the fact that the bromo-anion is reduced by sulphite at two hundred times the rate of that of gold.

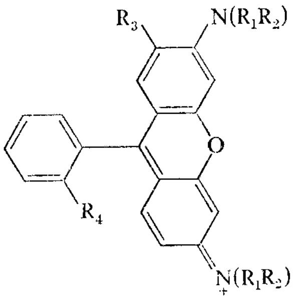
In our work we have been concerned more with the suitability of various dyes and dye types for the determination of metal-containing and other anions. Accordingly in the following review the procedures have been grouped under the type of dye used. Several papers refer to more than one type of dye. To avoid repetition the reviews of these papers have been included only in the section considered most appropriate.

EXTRACTION WITH XANTHENE DYES

Antimony

The first ion-association reaction of a basic dye with an anion was reported by Eegriwe[4] in 1927 although the mechanism of the reaction was not indicated. Eegriwe described a sensitive test for antimony in which antimony(III) was oxidized with nitrite to antimony(V) and Rhodamine B was added. A trace of antimony gave a violet or blue violet colour; 0·5 μg of antimony could be detected in the presence of 6·2 mg of tin. Tungsten(VI) at the 0·5-μg level gave a similar reaction to antimony.

Fredrick[5] developed a colorimetric procedure for the determination of antimony (0·1–300 μg), using this reaction. The antimony was oxidized with cerium(IV), excess of oxidant being removed with hydroxyammonium chloride. After the



Rhodamine B $R_1 = R_2 = C_2H_5$
$R_3 = H$
$R_4 = COOH$
Rhodamine 3B $R_1 = R_2 = C_2H_5$
$R_3 = H$
$R_4 = COOC_2H_5$
Rhodamine 6G $R_1 = H$
$R_2 = C_2H_5$
$R_3 = CH_3$
$R_4 = COOC_2H_5$

TABLE I.—XANTHENE DYES

Colour Index name and number	Common name	Names commonly used in translations of Russian papers
Basic Violet 10 (45170)	Rhodamine B	Rhodamine S Rhodamine C
Basic Violet 11 (45175)	Rhodamine 3B	Rhodamine 3B Ethyl Rhodamine S
Ethyl ester of Basic Red 8 (45150)		Rhodamine 6J
Basic Red 1 (45160)		Rhodamine 6G Rhodamine 6Zh

solution had been cooled in an ice-bath for 15 min, 1 ml of 0·2% Rhodamine B solution was added and the solution was cooled for a further 10 min to allow the precipitate of the ion-association complex to form completely. Bromine water was then added to destroy the excess of Rhodamine B but sodium thiosulphate was added immediately afterwards to prevent the precipitate also being bleached. Alcohol was then added to dissolve the precipitate, and the colour was compared with standards in a colorimeter.

Webster and Fairhall[6] collected SbH_3 in mercuric chloride solution and hydrochloric acid and cerium(IV) were then added. After chlorine had been removed by passage of clean air, hydroxyammonium chloride was added, chlorine was again removed, and Rhodamine B was added immediately. The ion-association complex was extracted with benzene and determined spectrophotometrically at 565 nm.

Maren[7] determined antimony in blood and tissue after wet oxidation of the matrix, by first reducing the solution with sodium sulphite, and then adding hydrochloric acid, cerium(IV), orthophosphoric acid and Rhodamine B. The ion-association complex was extracted with benzene. Gellhorn *et al.*[8] have applied Maren's method to tissues, plasma and urine, and determined 2–15 μg of antimony with an error of ±1 μg.

Kuznetsov[9] pointed out that the reaction probably involved the formation of a slightly soluble salt of $SbCl_6^-$ and was not due to the oxidizing effect of antimony(V). Other metal halo-anions also gave colour reactions with Rhodamine B, and $SbCl_6^-$ reacted with other basic dyes. Kuznetsov[10] determined antimony in bronze or brass by dissolving the sample in a hydrochloric acid–nitric acid mixture and adding stannous chloride after nitrogen oxides ceased to be evolved. Sodium nitrite was then added, followed by Rhodamine B.

Maren[11] gave an alternative procedure which overcomes iron interference. Antimony(V) is quantitatively extracted into isopropyl ether from 1·5*M* hydrochloric acid; at this acidity over 90 per cent of the iron remains in the aqueous phase. The antimony(V)–Rhodamine B ion-association complex is formed directly in the isopropyl ether by shaking the latter with an aqueous solution of Rhodamine B. Further, Maren studied in detail the recovery of antimony after wet oxidation. When nitric acid–sulphuric acid mixtures are used, antimony exists finally in both the +III and +V oxidation states, and also in a mixed oxidation state tentatively termed a +IV state. Cerium(IV) oxidizes Sb(III) to Sb(V), but does not oxidize Sb(IV) completely. Sb(IV) must be reduced with sulphite to Sb(III) before oxidation with cerium(IV). When sulphuric acid alone is used only Sb(III) is obtained and the sulphite step can be omitted, but this wet oxidation procedure is unsuitable for large samples.

In Maren's modification[11] to his original procedure perchloric acid was included in the wet oxidation mixture, and he obtained a quantitative yield of antimony(V). Thus both the cerium(IV) and sulphite stages could be omitted. This was confirmed by Freedman[12] who further indicated that iron interference could be eliminated by the addition of sodium pyrophosphate.

Sabinina and Zolotukhina[13] used a slight modification of Fredrick's method,[5] stabilizing the aqueous solution of the ion-association complex by the addition of gum arabic.

West and Hamilton[14] introduced an unusual spot test for antimony, using Rhodamine B, which overcame previous interferences. In this test antimony(III) is extracted into benzene as its iodo-complex, and is then reacted with Rhodamine B. Apparently in this procedure antimony reacts in the tervalent state throughout.

Luke,[15] in determining antimony in lead, indicated that most of the lead had to be removed as lead sulphate. Antimony must be reduced with sulphite just before the addition of Rhodamine B, and the Rhodamine B must be added as quickly as possible as the antimony appears to be slowly converted into an unreactive form. Excess of cerium(IV) is reduced with excess Rhodamine B. The ion-association complex is extracted into benzene.

White and Rose[16] were concerned with separation of antimony from tin and arsenic before its determination. Extraction of antimony(V) from 1–2*M* hydrochloric acid with ethyl acetate is suggested, and the antimony is determined subsequently by a procedure which is essentially that of Webster and Fairhall.[6]

Luke and Campbell,[17] in a paper on determination of impurities in germanium and silicon, determine antimony by Maren's method,[11] but indicate that oxidation of antimony(III) to antimony(V) is not quite complete with perchloric acid, and that a cerium(IV) oxidation step must be included.

Ward and Lakin[18] determine antimony in soils and rocks, and separate the antimony from interfering elements, including iron, by extracting it into isopropyl ether as suggested by Maren.[11] The antimony(V)–Rhodamine B ion-association complex is formed in the organic phase by shaking the latter with a solution of the dye in $1M$ hydrochloric acid. At higher hydrochloric acid concentrations the dye itself is extracted.

Onishi and Sandell[19] determine antimony in silicate rocks, using a photometric finish which is essentially that of Webster and Fairhall.[6] The procedure includes precipitation of antimony as Sb_2S_3 to prevent interference from iron(III), gallium(III), thallium(III), tungsten(VI) and gold(III) which also give colour reactions with Rhodamine B.

Nielsch and Böltz[20] prefer to extract the ion-association complex with isopropyl ether, but its apparent molar absorptivity varies with the hydrochloric acid concentration of the aqueous phase.

MacNulty and Woollard[21] found that separation of antimony from interfering elements by co-precipitating it with manganese dioxide was more satisfactory than other procedures. The perchloric acid–sulphuric acid–nitric acid oxidation proposed by Maren[11] is preferred, but as nitric acid attacks Rhodamine B, all traces of it must be removed before continuing to the colorimetric finish.

Ramette and Sandell[22] have discussed in detail the chemistry of the antimony(V)–Rhodamine B reaction, and have suggested certain modifications to the method of Webster and Fairhall[6] to improve its precision. The acidity of the aqueous solution from which extraction of the ion-association complex takes place is critical, as it determines which of the dye forms RH^+, RH_2^{2+} or RH_2Cl^+ extracts the $SbCl_6^-$ ion, and, further, it determines the rate of hydrolysis of the $SbCl_6^-$ ion. $RHSbCl_6$ is the main species extracted from $6M$ hydrochloric acid and this is the medium recommended by Webster and Fairhall for the extraction. Small amounts of the orange salts $RH_2(SbCl_6)_2$ and $RH_2ClSbCl_6$ are also formed, especially in hydrochloric acid solutions more concentrated than $6M$. The rate of hydrolysis of $SbCl_6^-$ to $Sb(OH)Cl_5^-$ which then hydrolyses further, is about 1%/min in $6M$ hydrochloric acid. As these hydrolysed forms do not react with Rhodamine B, it is essential to add the reagent very soon after oxidizing the antimony. The rate of hydrolysis is less in $3M$ hydrochloric acid and as $SbCl_6^-$ is extracted more completely as $RHSbCl_6$ at this concentration, they recommend that the extraction be effected from $3M$ hydrochloric acid media. Interferences by other elements at $3M$ and $6M$ hydrochloric acid concentration differ. A higher concentration of Rhodamine B than that suggested by Webster and Fairhall[6] may be advantageous. Ramette and Sandell have reported a more detailed account of their studies of Rhodamine B equilibria elsewhere.[23] A study of antimony(V) species in hydrochloric acid solution has been reported by Neumann.[24]

In the procedure of Coppins and Price[25] for the determination of antimony in tin and tin-lead solder, antimony(V) is extracted first from hydrochloric acid solution with isopropyl ether, and the ion-association complex is then formed in the organic layer by shaking it with a solution of Rhodamine B in $1M$ hydrochloric acid. Luke[26] has given more detailed information on the co-precipitation of trace metals (including Sb and Tl) in lead prior to their determination with Rhodamine B.

Tanaka and Kawahara[27] state that heating of the organic extract and cooling before measuring its absorbance gives greater precision as the formation of a suspension of Rhodamine B is prevented.

Thallium

Feigl, Gentil and Goldstein[28] provided a spot test for thallium with Rhodamine B. Tl(I) is oxidized in neutral or slightly acid solution with bromine water, excess of bromine is removed with sulphosalicylic acid, Rhodamine B is added, and the thallium(III)–Rhodamine B ion-association complex is extracted into benzene. The benzene layer is coloured red-violet by the complex and fluoresces orange-red in ultraviolet light. Sb, Au and Hg, which interfere, are removed by boiling the original solution with copper wire.

Onishi[29] developed a colorimetric procedure for the determination of thallium with Rhodamine B. The sample is heated with 5 ml of 2*M* hydrochloric acid and bromine water until excess of bromine has disappeared; then Rhodamine B is added and the tetrachlorothallium(III) ion-association complex is extracted into benzene. In later papers[30,31] Onishi has described the separation of Tl from interfering elements before its absorptiometric and fluorimetric determination.

Kliffmüller[32] wet-ashes 50 ml of urine with sulphuric acid and hydrogen peroxide, fumes the sulphuric acid and then applies paper chromatography to a hydrochloric acid solution of the residue. Thallium is identified by its fluorescence after spraying the chromatogram with Rhodamine B solution.

Stolyarov[33] has developed a microfluorimetric procedure for the determination of thallium in ores; $\mathrm{Tl\,Br_4^-}$ is extracted by Rhodamine B into benzene. A modified procedure eliminates interference by Sb and Hg. Kuznetsov and Bol'shakova[34] recommend the butyl ester of Rhodamine B as a reagent. Thallium can be extracted over a wider range of acidity than when Rhodamine B is used.

Gallium

Onishi[35] was the first to use Rhodamine B to detect gallium as $\mathrm{GaCl_4^-}$. The benzene extract of the ion-association complex is red-violet with an orange-yellow fluorescence in ultraviolet light. Interference by large amounts of antimony, gold, iron, thallium and tungsten is prevented by reducing these metals with titanous chloride to lower oxidation states in which they do not react. Onishi and Sandell[36] developed this test into absorptiometric and fluorimetric procedures for the determination of gallium. Gallium can be separated from iron by extracting it from hydrochloric acid with di-isopropyl ether before reacting the $\mathrm{GaCl_4^-}$ ion with Rhodamine B. The absorptiometric method was modified by Saltykova and Fabrikova[37] who extracted the ion-association complex with ether–benzene (1:3 v/v) in determining Ga in minerals.

Culkin and Riley[38] extracted the ion-association complex with chlorobenzene–carbon tetrachloride (3:1 v/v) which gives three times the sensitivity of the benzene extraction. The presence of titanium(III) suppresses the value of the reagent blank. Mityureva and Nizhnik[39] extracted the ion-association complex with a mixture of two volumes of benzene and one volume of ether saturated with 6*M* hydrochloric acid. They were interested in determining gallium in lead and zinc matrices and showed that the presence of 10% zinc sulphate in the aqueous solution to be extracted lowers the degree of extraction of gallium by a factor of two; at zinc sulphate concentrations greater than 20% no gallium is extracted.

Shcherbov *et al.*[40] made a study of the suitability of several dyes for the fluorimetric determination of gallium. Rhodamine B is a more selective reagent for gallium than is Rhodamine 6G, but Y, Au, Tl, Sb and Te interfere. Addition of $TiCl_3$ removes most of these interferences. Benzene–diethyl ether (9:1 v/v) is used for the extraction. The application of this method to the determination of gallium in ores is described by Shcherbov and Solov'yan.[41] Vasil'ev Podval'naya and Voronkova[42] have also applied Rhodamine B to the determination of gallium in ores, but extract the ion-association complex with ether–benzene (1:6·6 v/v).

Milaev and Maksaĭ[43] determine gallium in complex ores with Rhodamine B. $GaCl_3$ is extracted with diethyl ether before addition of the reagent, in order to eliminate interfering elements. Skrebkova[44] prefers to use the butyl ester of Rhodamine B as its ion-association complex with $GaCl_4^-$ is more highly coloured than that of Rhodamine B. The ion-association complex is extracted with toluene or benzene.

Kuchmistaya[45] determines gallium in zinc by reducing the sample with titanous chloride and then extracting the gallium from hydrochloric acid (1 + 1) into butyl acetate. After back-extraction of the gallium into a more dilute hydrochloric acid solution the $GaCl_4^-$–Rhodamine B ion-association complex is extracted into benzene–butyl acetate (4:1 v/v).

Chekalin[46] describes a procedure for the determination of gallium in which the Rhodamine B ion-association complex is extracted into benzene–ether (3:1 v/v). Shcherbov and Kagarlitskaya[47,48] have studied the effect of large amounts of Al, Zn, Cu and Pb on the fluorimetric determination of gallium with Rhodamine B. Salts of these metals, even as pure reagents, contain 10^{-3}–10^{-4}% gallium, and a method of purifying them is given.

Matveets and Shcherbov[49] determine 0·05–20 μg of Ga in 6M hydrochloric acid with Rhodamine B, extracting the ion-association complex into benzene–diethyl ether (9:1 v/v). Szücs and Klug[50,51] give a procedure for determining gallium in tungsten and tungstates with Rhodamine B, extracting the ion-association complex into benzene–diethyl ether (3:1 v/v). The sensitivity is 0·05 μg of Ga per ml of final solution and the error is ±5%. Biskupsky[52] uses $NaF–H_3BO_3$ instead of $LiF–H_3BO_3$ for the decomposition of rocks, minerals and silicates. Gallium in the ppm range is determined with Rhodamine B in the presence of Fe, Nb, Ta and W.

Other ions

Gold. MacNulty and Woollard[53] determined 0–30 μg of gold as part of their study of the use of Rhodamine B in analytical chemistry. Elements likely to interfere with the determination of gold, *viz.* Sb, Tl, Pt or V, are all carried down on a manganese dioxide precipitate; the gold which is left in solution may be concentrated by co-precipitating with tellurium. They state that in the case of antimony it is difficult to ensure that all the element is present in the +V state and this has been one of the main obstacles to the development of a satisfactory method. Gold, however, reacts in its stable tervalent state and there is no difficulty of this kind. Unfortunately the procedure for gold was found to be critically dependent on the hydrochloric acid concentration. Extraction of the ion-association complex is only satisfactory with isopropyl ether; benzene gives low recoveries. Pompowski and Trokowicz[54] adapted the Rhodamine B procedure of MacNulty and Woollard[53] for the determination of 0–30 μg of gold in copper concentrates. Interference by a hundredfold excess of iron was prevented by addition of sodium fluoride. A procedure for the determination of gold in mineral raw materials with the butyl ester of Rhodamine B is described by Podberezskaya, Sushkova and Shilenko.[55] A sample weight containing 0·1–1 μg of gold is used; the ion-association complex is extracted with benzene.

Tellurium. Shcherbov and Ivankova[56] determined tellurium fluorimetrically with Rhodamine B, which is more suitable for the determination than Rhodamine 6G. The tellurium–Rhodamine B ion-association complex is extracted from 5–7% hydrochloric acid with benzene–ether (2:1 v/v). Ivankova and Blyum[57] separate tellurium from selenium, and then determine tellurium with the butyl ester of Rhodamine B by extraction from $3{\cdot}5M$ hydrobromic acid. Vladimirova, Davidovich, Kuchmistaya and Razumova[58] use a similar procedure to determine tellurium in arsenic; the tellurium is first extracted as its diethyldithiocarbamate complex.

Indium. Blyum and Dushina[59] determine indium with Rhodamine 3B, extracting the $InBr_4^-$ ion into benzene.

Tantalum. Tantalum is determined by Blyum and Shebalkova[60] and by Pavlova and Blyum[61] as its fluoro-complex anion with either the butyl ester of Rhodamine B or with Rhodamine 6G, by extracting the ion-association complex with benzene from 5–$6M$ sulphuric acid solution. Dorosh[62] has determined small amounts (about 0·015%) of tantalum in ores with Rhodamine 6G and with the butyl ester of Rhodamine B. Acetone is added to stabilize the ion-association complex, which is extracted into benzene. The relative error of a single determination at the 0·015% level of tantalum is ±6%.

Zinc. Babko and Chalaya[63,64] determine zinc by extracting the $Zn(SCN)_4^{2-}$ ion-association complex with Rhodamine B into diethyl ether, and measuring its yellow fluorescence. Selezneva and Bragina[65] have provided procedures for the determination of zinc in pure cadmium, lead and copper with Rhodamine B. Slovák and Přibyl[66] extract the Rhodamine B–$Zn(SCN)_4^{2-}$ ion association complex into diethyl ether to determine $1{\cdot}5 \times 10^{-5}$–$9{\cdot}2 \times 10^{-5}M$ zinc. The optimum pH of extraction is 5·5–6·5. The procedure is rapid, but conditions must be carefully standardized and reagents must be purified for reproducible results to be obtained.

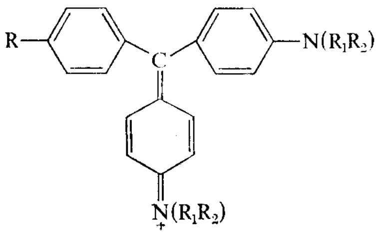
Mercury. Mercury has been determined with Rhodamine B by Imai.[67]

Rhenium. Rhenium in ores is determined by Blyum and Dushina[68] by benzene extraction of the ReO_4^- ion-association complex with the butyl ester of Rhodamine B from $3M$ phosphoric or $2{\cdot}5M$ sulphuric acid solution.

Tin. Arnesen and Selmer-Olsen[69] have shown that although the chlorostannate(IV) ion-association complex with Rhodamine B is not extractable into benzene or isopropyl ether and therefore does not interfere with the determination of Sb, Ga or Au, tin can be determined by extracting the complex into ethyl acetate.

Uranium. Andersen and Hercules[70] determined uranium fluorimetrically with Rhodamine B. The uranyl–benzoic acid complex anion is extracted into benzene containing Rhodamine B. The fluorescence intensity is a function of benzoic acid concentration, Rhodamine B concentration, pH, volume of the aqueous phase and time of ultraviolet irradiation. The lower limit of detection is $5 \times 10^{-8}M$ uranium. Moeken and Van Neste[71] extracted 0·02–3 μg/ml of uranium(VI) in nitrate samples dissolved in a benzoate buffer into a benzene–ether–hexane mixture with Rhodamine B. The molar absorptivity was $1{\cdot}03 \times 10^4$ l.mole^{-1}.mm^{-1} at 555 nm and the relative standard deviation varied from 20 to 0·6%.

EXTRACTION WITH TRIPHENYLMETHANE DYES



Brilliant Green (C.I. 42040: Basic green 1)	$R = H$ $R_1 = R_2 = C_2H_5$
Malachite Green (C.I. 42000: Basic green 4)	$R = H$ $R_1 = R_2 = CH_3$
Methyl Violet (C.I. 42535: Basic Violet 1)	$R = N(R_1R_2)$ $R_1 = R_2 = CH_3$ and H (but highly methylated)
Crystal Violet (C.I. 42555: Basic Violet 3)	$R = N(R_1R_2)$ $R_1 = R_2 = CH_3$
Ethyl Violet (C.I. 42600: Basic Violet 4)	$R = N(R_1R_2)$ $R_1 = R_2 = C_2H_5$

Antimony

Kuznetsov[72] considers Methyl Violet to be a valuable substitute for Rhodamine B in the detection of antimony. Antimony(III) is oxidized to antimony(V) with sodium nitrite, excess of nitrite being removed with urea. On the addition of a 0·2% solution of Methyl Violet greenish-gold crystals are precipitated; in the absence of antimony a yellow-green solution is obtained. By a similar reaction Jean determines antimony in copper alloys[73] and in zinc, aluminium and tin alloys[74] with Methyl Violet; the ion-association complex is extracted into benzene.

Gotô and Kakita[75–77] extract the $SbCl_6^-$–Methyl Violet ion-association complex into pentyl acetate. Addition of sodium chloride and sodium citrate increases the intensity of the colour. The reaction is reputed to be specific for antimony and 0·1 μg/ml can be determined. Antimony is oxidized with cerium(IV), excess being removed with hydrazinium sulphate. Jean[78] has indicated that the oxidation technique with cerium(IV) is suitable for the determination of antimony with Methyl Violet. Benzene must be used for the extraction as pentyl acetate tends to extract the dye itself.

Crystal Violet was used as a reagent for antimony by Ginzburg and Shkrobot,[79] who determined antimony in non-ferrous ores and metals. Oxidation was effected with nitrite (excess being removed with urea), and the ion-association complex was extracted into toluene. The determination of thallium by a similar procedure is described by these authors.

Lapin and Geĭn[80] obtained more reliable results when diaminotriphenylmethane dyes, such as Brilliant Green or Malachite Green, were used for the detection of Sb. Nitrite was used as oxidant, and the extraction was made with toluene. Gold and thallium reacted similarly with Brilliant Green. Blyum, Vasil'eva and Skrinskaya[81] have compared the analytical characteristics of Crystal Violet and Methyl Violet with respect to their reactions with the complex chlorides of Sb, Tl, Au, and Hg. Procedures for avoiding interference when determining a particular metal are discussed.

Blyum, Solov'yan and Shebalkova[82] have discussed the use of arylmethane dyes in inorganic analysis. Procedures are given for the determination of antimony and thallium with Crystal Violet, and for indium with the xanthene dye, Rhodamine 6G.

In the determination of antimony described by Stanton and McDonald,[83] antimony(III) in 6M hydrochloric acid solution is oxidized to the hexachloroantimonate (V) ion with nitrite, and any iron(III) present is complexed with hexametaphosphate to avoid interference. After addition of a freshly-prepared aqueous solution of Brilliant Green, the ion-association complex is extracted into 5 ml of toluene, the two phases being shaken together for 30 sec. The aqueous layer is discarded and the toluene is dried by passing it through a filter paper. The absorbance of the clear toluene solution is measured at 640 nm. For complete extraction of the complex the aqueous solution must be between 1 and 1·8M with respect to hydrochloric acid. Galliford and Yardley[84] applied this method to the determination of antimony in titanium dioxide. They state that the oxidation of antimony should take place below 25°. Ratcliffe and Stevens[85] have extended these methods further and have determined antimony in titanium dioxide and in pharmaceutical materials containing titanium dioxide. They obtained low results by Galliford and Yardley's method, and this they attributed to a variable shift in the peak of maximum absorbance of the complex. The development of a stable peak at 638 nm was only possible when excess of nitrite was removed with urea. They also found that the presence of nitrate caused low results to be obtained.

Soldatova, Kilina and Kataev[86] give optimum conditions for the extraction and subsequent determination of as little as 0·5 ppm of antimony in alloys containing indium and gallium or indium and zinc, with Brilliant Green. Results are accurate to within ±10%, and means of preventing interferences are discussed, including the deposition of Sb onto a tin electrode.

Burke and Menis[87] have made a critical examination of the many parameters associated with the determination of antimony with Brilliant Green. A strong spectral dependence of the extracted ion-association complex on the oxidant used to oxidize antimony(III) to antimony(V) was noted. Both cerium(IV) and hydrogen peroxide gave an extract with an absorbance maximum at 640 nm ($\varepsilon = 1{\cdot}05 \times 10^4$ l.mole^{-1}.mm^{-1}); nitrite gave an extract with an absorbance maximum at 625 nm ($\varepsilon = 6{\cdot}70 \times 10^3$ l.mole^{-1}.mm^{-1}). Excess of impure commercial dye was shown to give lower absorbance values, and this was considered to be caused by reducible impurities in the dye samples.

Fogg, Jillings, Marriott and Burns[88] re-examined the procedure for determining antimony with Brilliant Green in an investigation of suspected variability of samples of the dye. The reaction times were shown to be critical, and a modified procedure giving higher sensitivity and precision compared with previous procedures was given. The various reactions and extractions are carried out at 0°, and urea is added to remove excess of nitrite. A smaller amount of Brilliant Green is used, and the dye is added last after addition of the toluene to facilitate the rapid extraction of the ion-association complex. The Brilliant Green solution deteriorates rapidly under the conditions necessary for the extraction.

Matsuo, Kuroyanagi and Meguro[89] have studied the use of Malachite Green, Methyl Violet and Ethyl Violet for the determination of antimony. Ethyl Violet, which gives the highest molar absorptivity ($8{\cdot}30 \times 10^3$ l.mole^{-1}.mm^{-1}), is preferred. Oxidation is effected with cerium(IV), excess being removed with hydroxyammonium chloride. After adjustment of the pH of the solution to 10 with sodium citrate the reagent is added and the ion-association complex is extracted into isopentyl acetate.

Thallium

Using Methyl Violet, Gur'ev[90] determined as little as 0·0001 % of thallium in solid samples weighing 0·2–0·5 g. The ion-association complex ($\varepsilon = 6{\cdot}40 \times 10^3$ l.mole^{-1}.mm^{-1} at 620 nm) was extracted into toluene. A procedure involving the quantitative extraction of the tetrachlorothallium(III)–Methyl Violet ion-association complex from 0·14*M* hydrochloric acid into toluene is given by Shemeleva and Petrashen'.[91] Gur'ev and Shkrobot[92] have discussed the separation of thallium from antimony prior to the determination of the former with Crystal Violet. The sensitivity of the reaction of thallium with Methyl Violet and Brilliant Green is reported by Voskresenskaya[93] to be 0·05 and 0·03 μg/ml respectively when the tetrabromothallium ion-association complexes are extracted into pentyl acetate. The reaction with Brilliant Green is more sensitive to acid concentration.

Blyum and Ul'yanova[94] give a procedure for the determination of low contents of thallium in ores. Thallium(I) is oxidized to thallium(III) with hydrogen peroxide and the tetrachlorothallium(III)–Methyl Violet ion-association complex is extracted into toluene. Kovařík and Moučka[95] have discussed the detection of thallium with Methyl Violet. The use of several dyes of the Fuchsine and Malachite Green groups for the determination of thallium has been studied by Efremov and Galibin.[96] Malachite Green, Brilliant Green and Turquoise Blue give higher sensitivities (0·3 μg/ml) than Methyl Violet. Reǐs[97] has determined thallium in urine, blood and faeces with Brilliant Green. Thallium is oxidized with nitrite and the tetrachlorothallium(III)–Brilliant Green ion-association complex is extracted into benzene or toluene.

Voskresenskaya[98] describes the determination of thallium in rocks and ores with Brilliant Green. After separation of interfering elements the ion-association complex is extracted into ethyl acetate from approximately 0·1*M* hydrochloric acid; thallium(I) is oxidized to thallium(III) with bromine water. Potential sources of loss of thallium in the preliminary extraction and separation before application of the Methyl Violet method is discussed by Efremov and Suyǐ.[99] In order to determine large amounts of thallium, Milaev[100] extracts the ion-association complex into benzene, in which it is more soluble, rather than into toluene. This widens the concentration range over which Beer's law is obeyed.

Gorzelewska[101] has used the method of Reǐs[97] in the diagnosis of thallium poisoning, but Ariel and Bach[102] have criticised Reǐs's method. They studied the $TlBr_4^-$–Brilliant Green method in some detail. Nitrite did not completely oxidize thallium(I) and bromine was preferred. Urea was added to remove excess of bromine, but, in most urine samples, sufficient urea is usually present already. A thousandfold excess of Brilliant Green over thallium is recommended. The ion-association complex was extracted with four 2·5-ml portions of toluene from an aqueous solution of acidity between 1·6 and 3·5*N*. At acid concentrations less than 1·6*N* the free dye was extracted; above 3·5*N* the efficiency of extraction was less. Interference in the determination of thallium in urine was observed only for antimony in excess of 1 ppm and for iron in excess of 50 ppm. Attention is drawn to the high blanks which can arise from the use of glassware washed with synthetic anionic detergents.

Ethyl Violet, Crystal Violet and Malachite Green have been shown by Matsuo and Funada[103] to be useful reagents for the determination of thallium: Ethyl Violet is preferred. Thallium(I) is oxidized in $6M$ hydrochloric acid with cerium(IV), excess being reduced with hydroxyammonium chloride. The ion-association complex is extracted with benzene. Lomonosov and Mil'shteĭn[104] give procedures for the determination of thallium in cadmium and antimony alloys with Crystal Violet. In the case of antimony alloys the thallium is initially extracted with Brilliant Green, which is destroyed by oxidation with 30% hydrogen peroxide before addition of the Crystal Violet. The method is sensitive to 0·1 ppm of thallium in cadmium and 1 ppm of thallium in antimony. Popa *et al.*[105] give a procedure for determining 10–40 μg of Tl(III) in the presence of up to 5 mg of Sb(III) or Bi(III), 20 mg of Cd or Cu(II) and 30 mg of Pb, Zn, Fe(II) or Al. Thallium is oxidized with permanganate, and the tetrabromothallate(III)–Methyl Violet ion-association complex is extracted into toluene.

Gallium

Colorimetric methods of determining gallium are reviewed briefly by Jankovský,[106] who suggests Malachite Green as a reagent. As little as 10^{-3}% of gallium could be determined in bauxites, zinc ores and ashes without a preliminary separation. The chlorogallium(III)–Malachite Green ion-association complex was extracted into benzene in the presence of titanium(III) as the coloured oxidized form of the dye would also be extracted. Maximum recovery of gallium occurs when the extraction is made from 6–$6{\cdot}5M$ hydrochloric acid.

Armeanu and Costinescu[107] determined 2–5 μg of Ga in by-products of the zinc industry, with Brilliant Green.

Gallium in the presence of either Cl^- or SCN^- was shown by Kuznetsova and Tananaev[108] to form an ion-association complex with Methyl Violet. The ion-association complex in each case is extractable into chloroform or benzene when some acetone is also added. With chloroform as extractant gallium can be determined in the presence of a large excess of aluminium.

Hagiwara *et al.*[109] also determine gallium with Brilliant Green, extracting the chlorogallate ion from $6M$ hydrochloric acid with Brilliant Green. Interference from Tl(III) and Fe(III) is prevented by the addition of titanium(III).

Armeanu and Costinescu[110] have made a general survey of the tetrachlorogallate (III) ion-association complexes with basic triphenylmethane and diphenylnaphthylmethane dyes. Extraction is best effected from 5·5–$6M$ hydrochloric acid irrespective of the dyestuff used, with benzene, or better, with mixtures of benzene and chlorobenzene (4:1 or 1:1 v/v) or chlorobenzene and carbon tetrachloride (4:1 v/v). Low absorbance readings were obtained with toluene. Some of the molar absorptivities obtained in this work are higher than values reported previously.

Other ions

Tantalum. Poluéktov *et al.*[111] determined tantalum by extracting Methyl Violet hexafluorotantalate from solutions of pH 2·3 into benzene. Alimarin and Makarova[112–114] have made several studies of the extraction of fluorotantalate with basic dyes. No relationship was observed between the dielectric constant of the 11 solvents tried and the extractability of the Crystal Violet ion-association complex; the best extractants were halocarbons, in particular chlorobenzene.[112] The extraction of the ion-association complexes with Methyl Violet, Crystal Violet, Malachite Green, Brilliant Green, Rhodamine 6G and Rhodamine B and its ethyl and butyl esters into benzene were compared.[113] For the triphenylmethane dyes up to a 400-fold excess of niobium does not interfere. The extent of extraction of the ion-association complexes of Crystal Violet, the butyl ester of Rhodamine B, Rhodamine 3B and Rhodamine 6G was found to be 87, 97, 98 and 79% respectively.[114] Rhodamine 6G has been applied by Alimarin *et al.*[115] to the fluorimetric determination of tantalum in silica and high-purity trichlorosilane, and by Kiparisova[116] to Ta determinations in tin-containing products.

Pilipenko and Obolonchik[117] have indicated that tantalum can be determined in the presence of niobium, with Methyl Violet. Tantalum as an impurity in zirconium, hafnium, and niobium is determined by Lauér and Poluéktov[118] by extraction of the fluorotantalate ion into benzene with Methyl Violet.

Kakita and Gotô[119] determine 0·005–0·5% of tantalum in iron, steel and niobium metal with Malachite Green, which they claim is easier to use as it gives a somewhat larger molar absorptivity than Methyl Violet. The molar absorptivity given for extraction with benzene is $7{\cdot}6 \times 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$, and with xylene as $2{\cdot}9 \times 10^3$. Ethyl acetate, pentanol, chloroform, isobutyl methyl ketone and diethyl ether extracted the free dye.

Eberle and Lerner[120] adapted the method of Kakita and Gotô[119] to the determination of tantalum in boron, uranium, zirconium and uranium-zircaloy-2 alloy, using Malachite Green. They showed that the minimum aqueous to organic solvent volume ratio for complete extraction was 1:2; when this ratio was used the true molar absorbance value of $1{\cdot}04 \times 10^4$ $\text{l.mole}^{-1}.\text{mm}^{-1}$ was obtained.

Tsukahara[121] applied the method of Lauér and Poluéktov[118] to the determination of tantalum in ferronickel and metallic niobium by extracting the fluorocomplex of tantalum into benzene with Brilliant Green.

Kirkbright *et al.*[122] have used the naphthyldiphenylmethane dye, Victoria Blue B, to determine tantalum. The sensitivity of the method using benzene as solvent is slightly better than the corresponding procedure using Methyl Violet.[111]

Rhenium. Pilipenko and Obolonchik[117,123–5] have made a detailed study of the reaction of perrhenate with Methyl Violet. The optimum pH for extracting the ion-association complex is 3·5–5; at $\text{pH} < 3{\cdot}5$ the complex is incompletely formed and at $\text{pH} > 7{\cdot}3$ Methyl Violet is decomposed. A 45–50-fold excess of Methyl Violet over rhenium should be used. Toluene is the preferred solvent. The reactions of 43 other metals with Methyl Violet have been studied and methods of overcoming most interferences are given. Poluéktov *et al.*[111] preferred to use ethyl acetate for this extraction.

The application of Brilliant Green, Malachite Green and Crystal Violet to the extraction of perrhenate with benzene was studied by Okubo and Kojima.[126] The Brilliant Green ion-association complex showed the highest molar absorptivity ($9{\cdot}8 \times 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$) and extractability (90%) in the pH range 2·5–4·2.

Okubo[127] determined 1–20 μg of rhenium by extracting the perrhenate–Methyl

Violet ion-association complex, with benzene. The molar absorptivity was 9·4 × 10^3 $l.mole^{-1}.mm^{-1}$, and the extent of extraction was about 74%.

Perchlorate. Galosnitskaya and Petrashen'[128] determine perchlorate in the presence of up to a hundredfold excess of chlorate by extracting the Brilliant Green–perchlorate ion-association complex with benzene, toluene or *m*-xylene.

Reusmann[129] determined trace amounts of perchloric acid in sulphuric acid by extracting the Brilliant Green–perchlorate ion-association complex into benzene and measuring the absorbance at 638 nm. Reproducible results could not be obtained with the procedure of Golosnitzkaya and Petrashen'[128] because of adsorption of perchlorate onto the walls of the glass vessel; quartz vessels were used exclusively in the recommended procedure and then no adsorption occurred. Brilliant Green reacted with dissolved oxygen, and this was removed with ascorbic acid.

Uchikawa[130] determined perchlorate with Crystal Violet by extracting the ion-association complex from pH 5·8 phosphate buffer into chlorobenzene. Effects of buffer concentration and shaking time on the absorbance values obtained were studied.

Boron. Poluéktov *et al.*[111] in determining boron, extracted Methyl Violet tetrafluoroborate from solutions of pH 3·4 into benzene.

Babko and Marchenko[131] determine boron with Brilliant Green, the BF_4^-–dye ion-association complex being extracted into 5 ml of benzene. As only about 60% of the boron is extracted, standardization under identical conditions is essential. Blyum *et al.*[132] have used Crystal Violet for this determination; the distribution coefficient of the ion-association complex varies with temperature, which was standardized at 20°. Marchenko[133] determined 5 × 10^{-4}–3 × 10^{-3}% boron in metallic zirconium and titanium with Brilliant Green.

Gold. Ducret and Maurel[134] determined gold in the presence of platinum, using Methyl Violet. Stanton and McDonald[135] determined up to 2 μg of gold in soil, using Brilliant Green. After concentration of the gold by co-precipitation with tellurium in the presence of iron(III) and copper(II), the chloroaurate–Brilliant Green ion-association complex was extracted from 0·5*M* hydrochloric acid into toluene, previously treated with potassium dichromate solution to oxidize impurities.

Silver. Markham[136] has determined 10^{-6}–$10^{-4}M$ silver by extracting its cyanide complex into benzene with Crystal Violet. Because of the reaction of cyanide with Crystal Violet, the procedure must be followed strictly.

Chromium. Dichromate is determined by Savichev *et al.*[137] with Methyl Violet by extracting the ion-association complex from 0·016*M* hydrochloric acid with two 10-ml portions of benzene.

Nitrate. Yamamoto *et al.*[138] determined nitrate with Crystal Violet, but blank absorbance readings approaching 0·1 are quoted.

Zinc, cadmium and mercury. Colour tests for these elements with dyes of this type have been given by Kuznetsov[139–140] and by Kuznetsov and Kozyreva.[141]

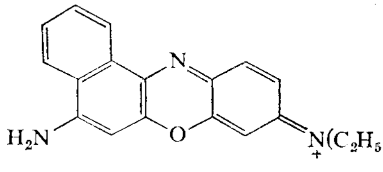
Osmium. Pilipenko and Obolonchik[117] have indicated that osmium may be determined in the presence of other platinum metals with Methyl Violet.

Tin. Ducret and Maurel[142] have determined tin with Crystal Violet.

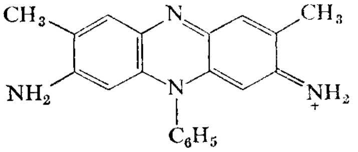
OTHER BASIC DYES

Basic dyes other than xanthene and triphenylmethane dyes have occasionally been applied to the determination of anions. Ducret[143] has determined boron in silicon and

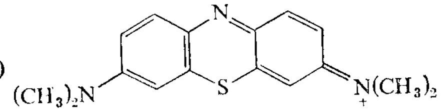
Nile Blue
(C.I. 51180: Basic Blue 12)



Safranine T
(C.I. 50240: Basic Red 2)



Methylene Blue
(C.I. 52015: Basic Blue 9)



silica by extracting the Methylene Blue tetrafluoroborate ion-association complex into dichloroethane, and Pásztor and Bode have studied thionin and nine commercially available thionin derivatives, including Methylene Blue, as reagents for boron.[144] 1,2-Dichloroethane, 1,2-dichloropropane, dichloromethane, 1,1,2-trichloroethane, *cis*-dichloroethylene, *o*-dichlorobenzene, 1,4-dichlorobutane and mixtures of these solvents proved to be suitable solvents. Many suitable dye–solvent combinations were found, and only thionin itself proved unsatisfactory. Skaar[145] has examined various oxazine dyes as reagents for boron. Brilliant Cresyl Blue, Nile Blue and Capri Blue are suitable, and the last is often more sensitive than Methylene Blue as a reagent. 1,2-Dichloroethane was used as solvent. Ducret and Drouillas[146] have determined phosphate by extracting the Safranine–phosphomolybdate ion-association complex into acetophenone at pH 1·5. The calibration graph is non-linear. Ducret and Ratouis[147] have analysed $10^{-6}M$ sulphate solutions by ion-exchanging the sulphate for thiocyanate, and extracting the Methylene Blue–thiocyanate ion-association complex into 1,2-dichloroethane.

Iwasaki *et al.*[148] have determined microamounts of perchlorate in sea-water by extracting the Methylene Blue–perchlorate ion-association complex into 1,2-dichloroethane. Serious interference was caused by ClO_3^-, IO_4^-, NO_3^-, NO_2^-, $S_2O_3^{2-}$, CrO_4^{2-}, WO_4^{2-} and Mg^{2+}.

Pilipenko and Shinh[149] have determined rhenium in molybdenite with Safranine T, extracting the ion-association complex into dichloroethane. Br^-, I^-, NO_3^-, SCN^-, ClO_3^-, BrO_3^-, and IO_3^- interfere. The mean relative error is ±10%. The same authors[150] have also determined antimony in ferrous metals with Safranine T. The dye–chloroantimonate(V) ion-association complex is extracted from 3·5*M* hydrochloric acid into benzene. Pokorny and Likussar[151] have determined nitrate with the oxazine dyestuff Nile Blue A. The ion-association complex is extracted into 1,2-dichlorobenzene. Halide interference is prevented by the addition of mercury(II) sulphate.

PURIFICATION AND ANALYSIS OF BASIC DYES

Commercial dyes, which are readily available and relatively inexpensive, are convenient for use as analytical reagents. Unfortunately many of these dye samples contain coloured as well as colourless impurities, including inorganic diluents. The use of impure dyes may lead to incorrect stoichiometries being assigned to complexes and it has been shown that errors can arise in analytical results owing to the presence of certain impurities.[152] For these reasons methods of purifying basic dyes, and of determining their purity, will be outlined.

Giles and Greczek[153] reviewed methods of purifying and analysing water-soluble dyes in general, but have given little specific information with regard to basic dyes. Recrystallization of basic dyes from ethanol–water or from dilute hydrochloric acid was recommended, and they report increased purity by repeated recrystallizations of a Malachite Green sample from 10% hydrochloric acid, as indicated by its apparent molar absorptivity.

Burke and Menis[87] recommended that Brilliant Green be purified chromatographically on silica gel followed by a double recrystallization from acetone. Kerr and Gregory,[154] on the other hand, purified the dye by precipitating Brilliant Green perchlorate, which they then used as the reagent. The purity of the dye perchlorate samples was assessed by their behaviour in determining antimony by the Stanton and McDonald method,[83] and it is clear that only a 70% recovery of antimony was made.[88] Nevertheless the samples melted sharply at 172–175° and were apparently pure. Kerr and Gregory recommended that samples of dye perchlorate be used for not more than 3–4 weeks after preparation, as they deteriorate after this period. Jablonski and Watson[155] recrystallized Rhodamine S from 20% hydrochloric acid.

The present authors have investigated the purity of several basic dyes. Owing to the high solubility of the dyes, normal recrystallization procedures proved wasteful and filtrations were difficult. Continuous Soxhlet extraction with a solvent in which the dye has a low solubility (about 1% w/v), however, has proved very satisfactory. Pure dye crystallizes in the boiling solvent over a period of several days. Fairly pure samples of Brilliant Green (>96% pure) have been prepared in this way by extraction with anhydrous acetone.[152] In this case the residue in the Sochlet thimble also proved to be purer than the original sample, indicating that a major part of the impurity was very soluble in acetone, and remained in the solvent when the Brilliant Green crystallized. This procedure has been applied successfully to other basic dyes, including Safranine O, and Rhodamine B.[156]

Vickerstaffe[157] and Giles and Greczek[153] have indicated that water-free dye samples are difficult to obtain. The present authors noted that when a pure sample (100%) of Brilliant Green was recrystallized in a Soxhlet apparatus from non-anhydrous acetone, its purity fell to 93% even after drying at 110°.[156] Methods of determining the purity of water-soluble dyes have also been reviewed by Giles and Greczek,[153] who indicate that titanium(III) and dichromate titrations give the most reliable results. Ideally the method used should be chosen with regard to the nature of the impurities present, but these are usually unknown. Ash or sulphated ash determinations give a clear indication of any inorganic diluent present. In studies of Brilliant Green the present authors analysed samples of dye by determining the nitrogen content (Kjeldahl) and by titanium(III) reduction. These results were not in good agreement, but the results by the more specific titanium(III) reduction method[158] correlated well with the behaviour of particular samples in the determination of gold.[152] Higher recoveries of gold were made with the purer samples of dye indicated by the titanium(III) determination.

Other methods have been used to determine the purity of basic dyes. Picric acid has been used as a precipitant in the photometric titration of Crystal Violet[159,160] and of Methylene Blue.[161] 12-Tungstosilicic acid has been used as a precipitant in the amperometric and gravimetric determination of several basic dyes.[162–165]

The original work on the determination of dyes with titanium(III) was done by Knecht and Hibbert,[166] and this work was extended by Calcott and English[167] to the determination of over a hundred triphenylmethane and azo dyes. Coulometric titrimetry involving externally generated Ti(III),[168] V(II),[169] Cr(II)[170–171] and dithionite[172] has been used, and reduction with thiosulphate[173] has also been used.

Matrka[174] studied the bromometric determination of triphenylmethane dyes, but obtained poor results owing to interfering impurities or bromination of the dye molecule. Vaisman and Filenko[175] have precipitated Brilliant Green as $C_{29}H_{34}O_4N_2.HI.4I_2$ and have determined the excess of iodine.

DISCUSSION

The procedures outlined above each consist of a series of unit processes the number of which depends on the nature of the sample and on the element to be determined. Organic matter, if present, is usually wet-oxidized, avoiding volatilization of the required element. Interfering elements are removed, where necessary, by the classical chemical separation techniques. If the element to be determined is present in very low concentrations it may be necessary to concentrate it by a co-precipitation procedure. Then the element must be converted into the required oxidation state; an oxidation step is necessary in the case of antimony and thallium, whereas a reduction process is necessary when tin is determined as tin(II). Then the element is converted into an anionic complex or oxy-anion suitable for extraction into an organic solvent as a salt with a basic dye cation.

All these unit processes must be carried out quantitatively if all of the element to be determined is to be measured. From a consideration of many of the papers reviewed above it is apparent that quantitative recovery of the element to be determined is not made in several procedures. The main evidence for this is the variation in the apparent molar absorptivities quoted by several authors for a particular ion-association complex measured in the same solvent.

One important reason for incomplete recovery is the difficulty of obtaining complete oxidation of the elements which require this step, and further of maintaining the element in this higher oxidation state throughout the subsequent extraction stages. Difficulties have been experienced in effecting quantitative oxidations of antimony and thallium, and a range of oxidizing reagents and procedures have been suggested. In the case of antimony a compound with a +IV oxidation state (or with mixed +III and +V oxidation states), which is not readily oxidized to Sb(V), has been postulated.[11] The prior reduction of antimony to the +III state with sulphite eliminates this difficulty.[11,15] The use of different oxidizing agents can cause the extract of the ion-association complex to have a slightly different absorption spectrum.[87] The antimony (V) ion is reported to hydrolyse quite rapidly to a non-extractable form.[15,22]

The present authors have made an experimental study of the determination of antimony with Brilliant Green,[88] and have recommended a modified procedure which gives an apparent molar absorptivity for the hexachloroantimonate(V)–Brilliant Green ion-association complex nearly double that given by previous procedures. A re-investigation of the determination of gold with Brilliant Green[152] shows again that previous procedures give low recoveries. The molar absorptivity of the Brilliant Green perrhenate complex in benzene, and those of the gold(III) and antimony(V) complexes in toluene are very similar, $1{\cdot}00 \times 10^4$, $1{\cdot}01 \times 10^4$ and $1{\cdot}03 \times 10^4$ $\text{l.mole}^{-1}.\text{mm}^{-1}$ respectively.

Similarly, Eberle and Lerner[120] showed that the molar absorptivity ($\text{l.mole}^{-1}.\text{mm}^{-1}$) of the tantalum–Malachite Green ion-association complex in both benzene and xylene is $1{\cdot}04 \times 10^4$; Kakita and Gotô[119] in their procedure obtained an apparent molar absorptivity of $0{\cdot}76 \times 10^4$ in benzene and $0{\cdot}29 \times 10^4$ in xylene owing to incomplete recoveries of tantalum. Many more such cases of incomplete recovery of the element to be determined probably exist unnoticed in the literature.

Owing to use of several unit processes in a particular procedure it is often difficult to ascertain the reason why low recoveries are made. In the determination of gold with Brilliant Green and tantalum with Malachite Green cited above, incomplete extraction of the ion-association complex is the major reason for the low recoveries that are obtained. Nevertheless in the determination of gold the present authors found that impure samples of Brilliant Green give distinctly lower apparent molar absorptivities;[152] the impurity in the Brilliant Green interferes quite distinctly in a manner not yet elucidated. Several papers indicate clearly that there is an optimum concentration of basic dye reagent and that the use of too high an excess of reagent leads to a lower recovery of the element to be determined. This effect is almost certainly due to impurities in the dye samples.

Very little attention has been paid in the literature to the acid-base equilibria existing in solutions of basic dyes. Frequently extractions have been made with triphenylmethane dyes from acid solutions in which the form of the dye extracted by the anionic species is present only in minimal concentrations at equilibrium. It is not surprising, therefore, that the speed of extraction in such procedures is an important factor. This is particularly true of the determination of antimony with Brilliant Green where antimony(V) is extracted from $2M$ hydrochloric acid.

The present authors consider that in using triphenylmethane dyes it is essential that a pure sample of the dye is used. If the extraction is to be made from acid solutions, then the extraction should be effected as rapidly as possible after addition of the reagent. If more than one extraction is to be made then additional aliquots of reagent should be added immediately before each of the subsequent extractions. A similar study of other basic dye procedures, including those using dyes other than triphenylmethane dyes, is being made; preliminary results for antimony and Safranine O indicate that here again it is advantageous to use pure samples of the dyes.

Zusammenfassung—Es wird eine Übersicht über die Verwendung von Xanthen-, Triphenylmethan- und anderen Kationen basischer Farbstoffe als Reagentieh zur Bestimmung von Anionen gegeben. Die bestimmten Elemente und Anionen sind Sb, Tl, Ga, Au, Te, In, Zn, Ta, Hg, Re, Sn, U, Os, B, Cr, Ag, ClO_4^-, PO_4^{3-}, SO_4^{2-} und NO_3^-. Schwierigkeiten beim Entwickeln zufriedenstellender Arbeitsvorschriften mit basischen Farbstoffen werden diskutiert. Vorschriften für die Reinigung und Analyse von Proben basischer Farbstoffe werden skizziert.

Résumé—On passe en revue l'emploi de cations colorants lasiques des types xanthène, triphénylméthane et autres comme réactifs pour le dosage d'anions. Les éléments et anions déterminés comprennent Sb, Tl, Ga, Au, Te, In, Zn, Ta, Hg, Re, Sn, U, Os, B, Cr, Ag, ClO_4^-, PO_4^{3-}, SO_4^{2-} et NO_3^-. On discute des difficultés rencontrées dans le développement de techniques satisfaisantes mettant en jeu des colorants basiques. On indique des techniques pour la purification et l'analyse d'échantillons de colorants basiques.

REFERENCES

1. A. J. Bowd, D. T. Burns and A. G. Fogg, *Talanta*, 1969, **16**, 719.
2. I. A. Blyum and N. N. Pavlova, *Zavodsk. Lab.*, 1963, **29**, 1407.
3. E. L. Kothny, *Analyst*, 1969, **94**, 198.
4. E. Eegriwe, *Z. Anal. Chem.*, 1927, **70**, 400; *Chem. Abstr.*, 1927, **21**, 1779.
5. W. G. Fredrick, *Ind. Eng. Chem., Anal. Ed.*, 1941, **13**, 922.
6. S. H. Webster and L. T. Fairhall, *J. Ind. Hyg. Toxicol.*, 1945, **27**, 183.
7. T. H. Maren, *Bull. Johns Hopkins Hosp.*, 1945, **77**, 338; *Chem. Abstr.*, 1946, **40**, 4973.
8. A. Gellhorn, M. E. Krahl and J. W. Fertig, *J. Pharmacol.*, 1946, **87**, 159.
9. V. I. Kuznetsov, *Compt. Rend. Acad. Sci. U.S.S.R.*, 1946, **52**, 231; *Chem. Abstr.*, 1947, **41**, 1947.
10. *Idem*, *Tsevetnye Metal*, 1947, **20**, 59; *Chem. Abstr.*, 1948, **42**, 4486.
11. T. H. Maren, *Anal. Chem.*, 1947, **19**, 487.
12. L. D. Freedman, *ibid.*, 1947, **19**, 502.
13. L. E. Sabinina and A. P. Zolotukhina, *Zavodsk. Lab.*, 1949, **15**, 398; *Chem. Abstr.*, 1949, **43**, 6937.
14. P. W. West and W. C. Hamilton, *Anal. Chem.*, 1952, **24**, 1025.
15. C. L. Luke, *ibid.*, 1953, **25**, 674.
16. C. E. White and H. J. Rose, *ibid.*, 1953, **25**, 351.
17. C. L. Luke and M. E. Campbell, *ibid.*, 1953, **25**, 1588.
18. F. N. Ward and H. W. Lakin, *ibid.*, 1954, **26**, 1168.
19. H. Onishi and E. B. Sandell, *Anal. Chim. Acta*, 1954, **11**, 444.
20. W. Nielsch and G. Böltz, *Z. Anal. Chem.*, 1954, **143**, 264.
21. B. J. MacNulty and L. D. Woollard, *Anal. Chim. Acta*, 1955, **13**, 64.
22. R. W. Ramette and E. B. Sandell, *ibid.*, 1955, **13**, 455.
23. *Idem*, *J. Am. Chem. Soc.*, 1956, **78**, 4872.
24. H. M. Neumann, *ibid.*, 1954, **76**, 2611.
25. W. C. Coppins and J. W. Price, *Metallurgia*, 1956, **53**, 183.
26. C. L. Luke, *Anal. Chem.*, 1959, **31**, 1680.
27. M. Tanaka and M. Kawahara, *Bunseki Kagaku*, 1961, **10**, 185; *Anal. Abstr.*, 1963, **10**, 2228.
28. F. Feigl, V. Gentil and D. Goldstein, *Anal. Chim. Acta*, 1953, **9**, 393.
29. H. Onishi, *Bull. Soc. Chem. Japan*, 1956, **29**, 945; *Anal. Abstr.*, 1957, **4**, 3883.
30. *Idem*, *ibid.*, 1957, **30** 567; *Anal. Abstr.*, 1958, **5**, 2141.
31. *Idem*, *ibid.*, 1957, **30**, 827; *Anal. Abstr.*, 1958, **5**, 2918.
32. R. Kliffmüller, *Z. Anal. Chem.*, 1957, **157**, 81.
33. K. P. Stolyarov, *Vest Leningr. Univ., Ser. Fiz. i Khim.*, 1959, 149; *Chem. Abstr.*, 1959, **53**, 16823.
34. V. I. Kuznetsov and L. I. Bol'shakova, *Zh. Analit. Khim.*, 1960, **15**, 523; *Anal. Abstr.*, 1961, **8**, 1823.
35. H. Onishi, *Anal. Chem.*, 1955, **27**, 832.
36. H. Onishi and E. B. Sandell, *Anal. Chim. Acta*, 1955, **13**, 159.
37. V. S. Saltykova and E. A. Fabrikova, *Zh. Analit. Khim.*, 1958, **13**, 63; *Chem. Abstr.*, 1958, **52**, 9857.
38. F. Culkin and J. P Riley, *Analyst*, 1958, **83**, 208.
39. T. T. Mityureva and A. T. Nizhnik, *Ukr. Khim. Zh.*, 1958, **24**, 790; *Chem. Abstr.*, 1959, **53**, 15861.
40. D. P. Shcherbov, I. T. Solov'yan, A. I. Ivankova and A.V. Drobachenko, *Tr. Kazakhst. Nauchn.-Issled. Inst. Mineral. Syr'ya*, 1959, 188; *Anal. Abstr.*, 1961, **8**, 3627.
41. D. P. Scherbov and I T. Solov'yan, *ibid.*, 1959, 196; *Anal. Abstr.*, 1961, **8**, 3627.
42. P. I. Vasil'ev, R. L. Podval'naya and M. A. Voronkova, *Mineral. Syr'ye, Vses. Nauchn.-Issled. Inst. Mineral'n. Syr'ya*, 1960, 302; *Chem. Abstr.*, 1961, **55**, 26841.
43. S. M. Milaev and L. I. Maksaĭ, *Sb. Nauchn.Tr. Vses, Nauchn.-Issled. Gornometallurg. Inst. Tsvet. Met.*, 1960, 459; *Anal. Abstr.*, 1962, **9**, 584.
44. L. M. Skrebkova, *Zh. Analit. Khim.*, 1961, **16**, 422; *Anal. Abstr.*, 1962, **9**, 989.
45. G. I. Kuchmistaya, *Zavodsk. Lab.*, 1961, **27**, 377; *Anal. Abstr.*, 1961, **8**, 4958.
46. V. V. Chekalin, *Nauchn. Tr., Irkutskii Nauchn.-Issled. Inst. Redkikh Metal*, 1961, 93; *Chem. Abstr.*, 1963, **58**, 11947.

47. D. P. Shcherbov and N. V. Kagarlitskaya, *Tr. Kazakhsk. Nauchn.-Issled. Inst. Mineral'n, Syr'ya*, 1961, 255; *Chem. Abstr.*, 1963, **58**, 11946.
48. *Idem, Zavodsk. Lab.*, 1962, **28**, 30; *Chem. Abstr.*, 1962, **57**, 30.
49. M. A. Matveets and D. P. Shcherbov, *Zh. Prikl. Spektroskopii, Akad. Nauk Belorussk. SSR*, 1965, **2**, 111; *Anal. Abstr.*, 1966, **13**, 3443.
50. A. Szücs and O. M. Klug, *Magy. Kem. Lap.* 1966, **21**, 328; *Anal. Abstr.*, 1967, **14**, 5390.
51. *Idem, Chem. Analit. Warsaw*, 1966, **11**, 665, *Anal. Abstr.*, 1967, **14**, 6805.
52. V. S. Biskupsky, *Chemist-Analyst*, 1967, **56**, 49; *Anal. Abstr.*, 1968, **15**, 5893.
53. B. J. MacNulty and L. D. Woollard, *Anal. Chim. Acta*, 1955, **13**, 154.
54. T. Pompowski and J. Trokowicz, *Chim. Analit. Warsaw*, 1965, **10**, 1211; *Anal. Abstr.*, 1967, **14**, 1303.
55. N. K. Podberezskaya, V. A. Sushkova and E. A. Shilenko, *Zavodsk. Lab.*, 1967, **33**, 152; *Anal. Abstr.*, 1968, **15**, 2504.
56. D. P. Shcherbov and A. I. Ivankova, *ibid.*, 1958, **24**, 1346; *Anal. Abstr.*, 1959, **6**, 2942.
57. A. I. Ivankova and I. A. Blyum, *ibid.*, 1961, **27**, 371; *Anal. Abstr.*, 1961, **8**, 4998.
58. V. M. Vladimirova, N. K. Davidovich, G. I. Kuchmistaya and L. S. Razumova, *ibid.*, 1963, **29**, 1419.
59. I. A. Blyum and T. K. Dushina, *ibid.*, 1959, **25**, 137; *Chem. Abstr.*, 1960, **54**, 18186.
60. I. A. Blyum and G. N. Shebalkova, *Tr. Kazakhst., Nauchn.-Issled. Inst. Mineral. Syr'ya*, 1961, 265; *Anal. Abstr.*, 1963, **10**, 993.
61. N. N. Pavlova and I. A. Blyum, *Zavodsk. Lab.*, 1962, **28**, 1305; *Anal. Abstr.*, 1963, **10**, 3665.
62. V. M. Dorosh, *Zh Analit. Khim.*, 1963, **18**, 961; *Anal. Abstr.*, 1964, **11**, 4242.
63. A. K. Babko and Z. I. Chalaya, *ibid.*, 1961, **16**, 268; *Anal. Abstr.*, 1962, **9**, 568.
64. *Idem, ibid.*, 1962, **17**, 286; *Anal. Abstr.*, 1963, **10**, 554.
65. E. A. Selezneva and Z. I. Bragina, *Uchen. Zap. Permsk. Gos. Univ.*, 1966, 226; *Anal. Abstr.*, 1968, **15**, 1892.
66. Z. Slovák and M. Přibyl, *Collection Czech. Chem. Commun* , 1966, **31**, 1742; *Anal. Abstr.*, 1967, **14**, 4571.
67. H. Imai, *Nippon Kagaku Zasshi*, 1969, **90**, 275.
68. I. A. Blyum and T. K. Dushina, *Zavodsk. Lab.*, 1962, **28**, 903; *Anal. Abstr.*, 1963, **10**, 1427.
69. R. T. Arnesen and A. R. Selmer-Olsen, *Anal. Chim. Acta*, 1965, **33**, 335.
70. N. R. Andersen and D. M. Hercules, *Anal. Chem.*, 1964, **36**, 2138.
71. H. H. Ph. Moeken and W. A. H. Van Neste, *Anal. Chim. Acta*, 1967, **37**, 480.
72. V. I. Kuznetsov, *Zh. Analit. Khim.*, 1947, **2**, 179; *Chem. Abstr.*, 1949, **43**, 6937.
73. M. Jean, *Chim. Anal.*, 1949, **31**, 271; *Chem. Abstr.*, 1950, **44**, 2890.
74. *Idem, Anal. Chim. Acta*, 1952, **7**, 462.
75. H. Gotô and Y. Kakita, *Nippon Kagaku Zasshi*, 1952, **73**, 339; *Chem. Abstr.*, 1953, **47**, 2629.
76. *Idem, Sci. Rep. Res. Inst. Tohoku Univ. Ser. A*, 1952, **4**, 582, 589; *Chem. Abstr.*, 1953, **47**, 9850, 10400.
77. *Idem, Nippon Kinzoku Gakkaishi*, 1952, **16**, 560; *Chem. Abstr.*, 1954, **48**, 5715.
78. M. Jean, *Anal. Chim. Acta*, 1954, **11**, 82.
79. L. B. Ginzburg and E. P. Shkrobot, *Zavodsk. Lab.*, 1955, **21**, 1289; *Anal. Abstr.*, 1956, **3**, 1283.
80. L. N. Lapin and V. O. Geǐn, *Tr. Komiss. Anal. Khim. Akad. Nauk SSSR*, 1956, **7**, 217; *Anal. Abstr.*, 1957, **4**, 3630.
81. I. A. Blyum, A. P. Vasil'eva and R. P. Skrinskaya, *Tr. Kazimsa*, 1961, 260; *Anal. Abstr.*, 1963, **10**, 908.
82. I. A. Blyum, I. T. Solov'yan and G. N. Shebalkova, *Zavodsk. Lab.*, 1961, **27**, 950; *Anal. Abstr.*, 1962, **9**, 1021.
83. R. E. Stanton and A. J. McDonald, *Analyst*, 1962, **87**, 299.
84. D. J. B. Galliford and J. T. Yardley, *ibid.*, 1963, **88**, 653.
85. R. J. M. Ratcliffe and S. G. E. Stevens, *Mf. Chemist and Aerosol News*, 1964, 83.
86. L. A. Soldatova, Z. G. Kilina and G. A. Kataev, *Zh. Analit. Khim.*, 1964, **19**, 1267; *Anal. Abstr.*, 1966, **13**, 1236.
87. R. W. Burke and O. Menis, *Anal. Chem.*, 1966, **38**, 1719.
88. A. G. Fogg, J. Jillings, D. R. Marriott and D. T. Burns, *Analyst*, 1969, **94**, 768.
89. T. Matsuo, Y. Kuroyanagi and S. Meguro, *Bunseki Kagaku*, 1963, **12**, 515; *Anal. Abstr.*, 1964, **11**, 4814.
90. S. D. Gur'ev, *Sb. Nauchn Tr. Gos. Nauchn.-Issled. Inst. Tsvetn Metal.*, 1955, 371; *Chem. Abstr.*, 1958, **52**, 970.
91. G. G. Shemeleva and V. I. Petrashen', *Tr. Novocherk. Polit. Inst.*, 1956, **41**, 35; *Anal. Abstr.*, 1957, **4**, 3600.
92. S. D. Gur'ev end E. P. Shkrobot, *Sb. Nauchn. Tr. Gos. Nauchn. Inst. Tsvetn. Met.*, 1956, 79; *Anal. Abstr.*, 1958, **5**, 418.

93. N. T. Voskresenskaya, *Zh. Analit. Khim.*, 1956, **11**, 585; *Chem. Abstr.*, 1957, **51**, 7230.
94. I. A. Blyum and I. A. Ul'yanova, *Zavodsk. Lab.*, 1957, **23**, 283; *Chem. Abstr.*, 1958, **52**, 970.
95. M. Kovařík and M. Moučka, *Anal. Chim. Acta*, 1957, **16**, 249.
96. G. V. Efremov and V. A. Galibin, *Uch. Zap. Leningr. Gos. Univ. Ser. Khim Nauk*, 1957, **4**, 83; *Anal. Abstr.*, 1958, **5**, 2558.
97. N. V. Reĭs, *Lab. Delo*, 1957, **3**, 12; *Chem. Abstr.*, 1959, **53**, 6336.
98. N. T. Voskresenskaya, *Zavodsk. Lab.*, 1958, **24**, 395; *Chem. Abstr.*, 1960, **54**, 13980.
99. G. V. Efremov and Chzhi-Gu Syuĭ, *Vestn Leningr. Univ., Ser. Fiz. i Khim.*, 1958, **13**, 156; *Chem. Abstr.*, 1959, **53**, 4004.
100. S. M. Milaev, *Sb. Nauchn. Tr. Vses. Nauchn.-Issled, Gorno-Met. Inst. Tsvetn. Metal.*, 1958, 258; *Chem. Abstr.*, 1959, **53**, 19700.
101. K. Gorzelewska, *Med. Weterynar (Poland)*, 1958, **14**, 553; *Chem. Abstr.*, 1959, **53**, 15189.
102. M. Ariel and D. Bach, *Analyst*, 1963, **88**, 30.
103. T. Matsuo and S. Funada, *Bunseki Kagaku*, 1963, **12**, 521; *Anal. Abstr.*, 1964, **11**, 4769.
104. S. A. Lomonosov and F. Ya. Mil'shteĭn, *Zavodsk. Lab.*, 1967, **33**, 14; *Anal. Abstr.*, 1968, **15**, 1893.
105. G. Popa, Ri Zin Su and C. Pătroescu, *Rev. Roumaine Chim.*, 1967, **12**, 969; *Anal. Abstr.*, 1968, **15**, 6545.
106. J. Jankovský, *Talanta*, 1959, **2**, 29.
107. V. Armeanu and P. Costinescu, *An. Stiint. Univ. "Al. I. Cuza", Iasi, Sect.* 1, 1960, **6**, 943, *Anal. Abstr.*, 1963, **10**, 555.
108. V. K. Kuznetsova and N. A. Tananaev, *Zh. Neorgan. Khim.*, 1961, **6**, 476; *Anal. Abstr.*, 1962, **9**, 2679.
109. K. Hagiwara, M. Nakane, Y. Osumi, E. Ishii and Y. Miyake, *Bunseki Kagaku*, 1961, **10**, 1374; *Anal. Abstr.*, 1963, **10**, 4090.
110. V. Armeanu and P. Costinescu, *Talanta*, 1967, **14**, 699.
111. N. S. Poluéktov, L. I. Kononenko and R. S. Lauér, *Zh. Analit. Khim.*, 1958, **13**, 396; *Chem. Abstr.*, 1959, **53**, 4004.
112. I. P. Alimarin and S. V. Makarova, *ibid.*, 1964, **19**, 90; *Anal. Abstr.*, 1965, **12**, 2204.
113. S. V. Makarova and I. P. Alimarin, *ibid.*, 1964, **19**, 564; *Anal. Abstr.*, 1965, **12**, 4503.
114. *Idem, ibid.*, 1964, **19**, 847; *Anal. Abstr.*, 1965, **12**, 5749.
115. I. P. Alimarin, A. P. Golovina, I. M. Gibalo and Yu. A. Mittsel', *ibid.*, 1965, **20**, 339; *Anal. Abstr.*, 1966, **13**, 5470.
116. L. S. Kiparisova, *Uch. Zap. Tsent. Nauchn.-Issled. Inst. Olovyan. Prom.*, 1965, 26; *Anal. Abstr.*, 1967, **14**, 1365.
117. A. T. Pilipenko and V. A. Obolonchik, *Ukr. Khim. Zh.*, 1959, **25**, 359; *Chem. Abstr.*, 1959, **53**, 21418.
118. R. S. Lauér and N. S. Poluéktov, *Zavodsk. Lab.*, 1959, **25**, 903; *Anal. Abstr.*, 1960, **7**, 2180.
119. Y. Kakita and H. Gotô, *Anal. Chem.*, 1962, **34**, 618.
120. A. R. Eberle and M. W. Lerner, *ibid.*, 1967, **39**, 662.
121. I. Tsukahara, *Bunseki Kagaku*, 1967, **16**, 583; *Anal. Abstr.*, 1968, **15**, 6617.
122. G. F. Kirkbright, M. D. Mayhew and T. S. West, *Anal. Chem.*, 1968, **40**, 2210.
123. A. T. Pilipenko and V. A. Obolonchik, *Dopovidi Akad. Nauk Ukr. RSR*, 1958, 648; *Chem. Abstr.*, 1958, **52**, 16971.
124. *Idem, Ukr. Khim. Zh.*, 1958, **24**, 506; *Anal. Abstr.*, 1960, **7**, 518.
125. *Idem, ibid.*, 1960, **26**, 99; *Chem. Abstr.*, 1960, **54**, 17154.
126. T. Okubo and M. Kojima, *Bunseki Kagaku*, 1965, **14**, 843; *Chem. Abstr.*, 1965, **63**, 17138.
127. T. Okubo, *ibid.*, 1963, **12**, 937; *Anal. Abstr.*, 1965, **12**, 673.
128. V. A. Galosnitskaya and V. I. Petrashen', *Zh. Analit. Khim.*, 1962, **17**, 878; *Anal. Abstr.*, 1963, **10**, 2264.
129. G. Reusmann, *Z. Anal. Chem.*, 1967, **226**, 346.
130. S. Uchikawa, *Bull. Chem. Soc. Japan*, 1967, **40**, 798; *Chem. Abstr.*, 1967, **67**, 29068.
131. A. K. Babko and P. V. Marchenko, *Zavodsk. Lab.*, 1960, **26**, 1202; *Anal. Abstr.*, 1961, **8**, 2419.
132. I. A. Blyum, T. K. Dushina, T. V. Semenova and I. Ya. Scherba, *ibid.*, 1961, **27**, 644; *Anal. Abstr.*, 1962, **9**, 576.
133. P. V. Marchenko, *ibid.*, 1961, **27**, 801; *Anal. Abstr.*, 1962, **9**, 618.
134. L. Ducret and H. Maurel, *Anal. Chim. Acta*, 1959, **21**, 74.
135. R. E. Stanton and A. J. McDonald, *Analyst*, 1964, **89**, 767.
136. J. J. Markham, *Anal. Chem.*, 1967, **39**, 241.
137. E. I. Savichev, E. I. Iskhakova and L. F. Flyazhnikova, *Zavodsk. Lab.*, 1962, **28**, 412; *Anal. Abstr.*, 1962, **9**, 4658.
138. Y. Yamamoto, S. Uchikawa and K. Akabori, *Bull. Chem. Soc. Japan*, 1964, **37**, 1718.
139. V. I. Kuznetsov, *Dokl. Akad. Nauk SSSR*, 1943, **41**, 113; *Chem. Abstr.*, 1944, **38**, 3925.

140. *Idem*, *Zh. Analit. Khim.*, 1947, **2**, 373; *Chem. Abstr.*, 1948, **43**, 7372.
141. V. I. Kuznetsov and L. S. Kozyreva, *Tr. Komiss. Anal. Khim. Akad. Nauk SSSR Otdel. Khim. Nauk*, 1954, **5**, 86; *Chem. Abstr.*, 1955, **49**, 12192.
142. L. Ducret and H. Maurel, *Anal. Chim. Acta*, 1959, **21**, 79.
143. L. Ducret, *ibid.*, 1957, **17**, 213.
144. L. C. Pásztor and J. D. Bode, *ibid.*, 1961, **24**, 467.
145. O. B. Skaar, *ibid.*, 1965, **32**, 508.
146. L. Ducret and M. Drouillas, *ibid.*, 1959, **21**, 86.
147. L. Ducret and M. Ratouis, *ibid.*, 1959, **21**, 91.
148. I. Iwasaki, S. Utsumi and C. Kang, *Bull. Chem. Soc. Japan*, 1963, **36**, 325; *Anal. Abstr.*, 1964, **11**, 1979.
149. A. T. Pilipenko and N. M. Shinh, *Ukr. Khim. Zh.*, 1966, **32**, 1211; *Anal. Abstr.*, 1968, **15**, 750.
150. *Idem*, *Zavodsk. Lab.*, 1967, **33**, 1074; *Anal. Abstr.*, 1968, **15**, 7276.
151. G. Pokorny and W. Likussar, *Anal. Chim. Acta*, 1968, **42**, 253.
152. A. G. Fogg, C. Burgess, and D. T. Burns, *Analyst*, 1970, **95**, 1012.
153. C. H. Giles and J. J. Greczek, *Textile Res. J.*, 1962, 506.
154. G. O. Kerr and G. R. E. C. Gregory, *Analyst*, 1969, **94**, 1036.
155. W. Z. Jablonski and C. A. Watson, *ibid.*, 1970, **95**, 131.
156. A. G. Fogg, C. Burgess and D. T. Burns, unpublished work.
157. T. Vickerstaffe, *The Physical Chemistry of Dyeing*, 2nd Ed., Ch. 2. Oliver and Boyd, Edinburgh, 1954.
158. *The British Pharmacopoeia*, p. 131. Pharmaceutical Press, London, 1968.
159. M. Rebek and M. K. Semlitsch, *Monatsh.*, 1961, **92**, 214.
160. *Idem*, *J. Soc. Dyers Colourists*, 1961, **77**, 566.
161. A. Bolliger, *Analyst*, 1939, **64**, 416.
162. S. R. Trotman and T. B. Frearson, *J. Soc. Dyers Colourists*, 1931, **47**, 344.
163. T. Ogawa, *Denki Kagaku*, 1957, **25**, 613.
164. *Idem*, *ibid.*, 1958, **26**, 406.
165. V. Mareš and Z. Stejskal, *Ceskosl. Farm.*, 1962, **11**, 354; *Anal. Abstr.*, 1963, **10**, 1175.
166. E. Knecht and E. Hibbert, *New Reduction Methods in Volumetric Analysis*, Longmans, London, 1918.
167. W. S. Calcott and F. L. English, *Ind. Eng. Chem.*, 1923, **15**, 1042.
168. J. S. Parsons and W. Seaman, *Anal. Chem.*, 1955, **27**, 210.
169. M. Matrka and Z. Ságner, *Chem. Prumysl*, 1958, **8**, 22.
170. J. P. Tandon and R. C. Mehrotra, *Z. Anal. Chem.*, 1957, **158**, 189.
171. J. P. Tandon, *ibid.*, 1962, **188**, 161.
172. M. Munemori, *Talanta*, 1958, **1**, 110.
173. *Allen's Commercial Organic Analysis*, 4th Ed., p. 627. Churchill, London, 1928.
174. M. Matrka, *Chem. Prumysl*, 1958, **8**, 583.
175. G. A. Vaisman and A. R. Filenko, *Aptechn. Delo*, 1956, **5**, 23; *Anal. Abstr.*, 1957, **4**, 189.

Talanta, 1971, Vol. 18, pp. 1197 to 1208. Pergamon Press. Printed in Northern Ireland

A NEUTRON-ACTIVATION SCHEME DEVELOPED FOR THE DETERMINATION OF 42 ELEMENTS IN LUNAR MATERIAL

A. O. BRUNFELT
Mineralogical-Geological Museum, University of Oslo, Oslo, Norway

E. STEINNES
Institutt for Atomenergi, Isotope Laboratories, Kjeller, Norway

Summary—A neutron-activation scheme designed for the determination of 42 elements in lunar rocks and fines is described. The scheme is based on seven different irradiations, four of which are followed by direct γ-spectrometry, and three by radiochemical separation systems. The total sample consumption for duplicate analysis is about 800 mg. The scheme has been tested on basalt BCR-1, and results for this standard rock are presented. Analytical experience obtained from analyses of lunar samples and BCR-1 is discussed.

WHEN the chemical composition of scarce materials such as meteorites or lunar samples is to be established, it is often important to have a method facilitating the determination of a large number of elements in a small sample. On the other hand, it is highly desirable that the results be as accurate as possible. Neutron-activation analysis, when used properly, is capable of satisfying these requirements, and this technique has therefore played an important role in the determination of the elemental composition of lunar material.[1]

In the authors' laboratories a programme comprising the determination of 42 elements in lunar rocks and fines from the Apollo 12 mission has been carried out.[2] When this work was initiated, it was decided to design a system based on methods largely developed by the authors, rather than to adapt previously published neutron-activation schemes for geological material[3–6] for the purpose. The resulting system uses purely instrumental analysis for 21 elements, and radiochemical separations are used in analysing for the other 21 elements. The instrumental procedures are similar to those described by Gordon and co-workers,[7,8], and Brunfelt and Steinnes.[9] The radiochemical part of the scheme has been constructed mainly on the basis of methods previously developed by the authors and co-workers for single elements[10–14] or for a group of elements.[15]

The standard rock basalt BCR-1 was selected as a test material for the present scheme, because it is to some extent similar in composition to the lunar samples, and has been fairly extensively analysed in a number of investigations. After the determination of the elements of interest in BCR-1, this rock was used as a standard for most of these elements in the subsequent analyses of lunar material.

OUTLINE OF THE SCHEME

The analytical scheme proposed in this paper is based on seven different irradiations (*A*–*G*) involving five independent portions of the sample, as indicated in Table I. Four of these runs are based on purely instrumental work, the remaining three irradiations are followed by radiochemical separations. Most radioactivity measurements are carried out by Ge(Li) γ-spectrometry. For some elements, the sensitivity

TABLE I.—SURVEY OF EXPERIMENTS INCLUDED IN THE SCHEME

Experiment	Irradiation	Irradiation time	Delay before start of experiment	Type†	Detector used	Approximate sample weight
A	Thermal*	30 sec	No delay	ND	Ge(Li)	10 mg
B	Thermal	5 min	2 hr	ND	Ge(Li)	Samples from (*A*)
C	Epithermal	2 d	3–5 d	ND	Ge(Li)	100 mg
D	Thermal	1 d	5 d	ND	Ge(Li)	Samples from (*C*)
E	Thermal	15 min	20 min	RC	NaI + Ge(Li)	50 mg
F	Thermal	20 hr	30 hr	RC	NaI + Ge(Li)	50 mg
G	Thermal	7 d	7 d	RC	NaI + Ge(Li)	200 mg

* Irradiation with the total reactor neutron energy spectrum.
† ND = Non-destructive; RC = Radiochemical.

is improved by means of a well-type NaI detector. Results for some elements are obtained in more than one of the groups. The seven groups can be outlined as follows.

A. Determination of elements with short-lived isotopes (Al, Ti, V, Ca) by a procedure similar to those previously described.[6,8]

B. Determination of Mn and Na on samples from (*A*) after further irradiation, using standard Ge(Li) spectrometry. Dy may also be determined.

C. Epithermal activation analysis mainly according to a previously published method;[9] determination of Fe, Br, Sr, Ba, Tb, Hf, Ta, and Th. Results for Ca, Sc, Co, Rb, Sb, Cs, La, Sm, Eu, Au and U may also be obtained.

D. Further activation of samples and standards from (*C*), without a cadmium cover. Results for Sc, Cr, La, Ce, Eu, Yb, and Lu are obtained, as previously described by Gordon *et al.*[7] In addition, Fe and Co may be determined.

E. Determination of Cl, In and some rare earths(RE) after a 15-min irradiation, largely based on previous methods for Cl[12] and In.[10] After alkaline fusion, chlorine is first removed as AgCl, whereafter a hydroxide precipitation is carried out, followed by dissolution of the precipitate in hydrobromic acid. Indium is separated by ethyl ether extraction, and an apparently pure fraction of RE-nuclides is obtained by a single fluoride precipitation with Dy as carrier. Chemical yield for Cl is determined by weighing; for In and Dy by re-activation. Of the RE elements, Sm, Dy, Ho and Er are determined in this group. Chemical yield for Cl, In and Dy is 50–80%.

F. This group is based on separation of medium and long half-life nuclides by anion-exchange in hydrochloric acid media after hydrofluoric acid decomposition of the sample, and is an extension of the method by Johansen and Steinnes,[15] where an NaI detector was used for the γ-spectrometric measurements of the eluted fractions. In the present work, by the use of a Ge(Li) detector, activities of ^{76}As, ^{122}Sb, ^{182}Ta, ^{233}Pa, and ^{239}Np were also observed in certain fractions, in addition to the activities involved in the previous work. The behaviour of ^{233}Pa was not reproducible, while the other nuclides seemed to behave more equally from sample to sample. A tracer investigation was carried out in order to study in more detail the distribution of these four nuclides in the separation sequence. Carriers were not added. Eight separate runs were performed with a mixture of the activities, and the results are shown in Table II. On the basis of this experiment, determination of U and As was also included in this part of the scheme. Sb might also be determined, but the method

TABLE II.—DISTRIBUTION (%) OF SOME ELEMENTS BETWEEN DIFFERENT ELUTION PHASES IN THE ANION-EXCHANGE SEPARATION SEQUENCE OF GROUP *F*.

Element	9*M* HCl	4*M* HCl	3*M* HCl	0·5*M* HCl	1*M* NH_4OH	Resin
As*	7 ± 5	85 ± 6	0·9 ± 0·5	<0·2	<0·2	7 ± 3
Sb	<0·1	<0·1	0·1 – 0·4	2·6 ± 0·7	5·6 ± 2·2	91 ± 3
Ta	19 ± 6	22 ± 6	16 ± 4	13 ± 5	3 ± 2	27 ± 7
Np	<0·2	64 ± 7	8 ± 1	1 – 2	0 – 1	28 ± 7

* Does not include loss during the dissolution step.

with group *G* was thought to give slightly better results for this element. Ta was found in all fractions, and its determination here did not seem advantageous. It should be noted that a certain fraction of ^{76}As is lost during the dissolution step; this loss is not prevented by carrier addition. It was found, however, that for samples dissolved in the same experimental run, the As results for duplicates were in reasonable agreement, thus indicating that the loss may be kept fairly constant by similar treatment of the samples during dissolution.

Besides As and U, K was included in this part of the scheme by introducing a hydroxide scavenging followed by a tetraphenylborate precipitation on the fraction passing the column in the sorption step. More than 97% of the ^{42}K activity is found in the tetraphenylborate precipitate.

The elements determined in this experiment are Co, Cu, Zu, Ga and W, in addition to those already mentioned. Fe may also be determined with good results. For W, chemical yield was determined by re-activation (about 40%). For Co, Cu, Zu and Ga, the yield has previously been established to be ≥97% by this procedure,[15] and for these four elements and K, U and As, the results are based on assumed equal yield for samples and standards run simultaneously.

G. This group includes the low-abundance elements Se, Rb, Ag, Sb, Cs, Ir and Au, and is based on hydrofluoric/nitric acid decomposition followed by a combination of specific separation steps previously used for the determination of single elements in rocks. Ag is precipitated as AgCl, which is dissolved in ammonia solution and further purified.[14] After oxidation with bromine, Sb and Au are extracted into isopropyl ether from 6*M* hydrochloric acid, back-extracted into 10*M* hydrochloric acid and selectively precipitated. Se is isolated by reduction and subsequent distillation.[11] After removal of most of the ^{51}Cr activity by a hydroxide scavenging in ammoniacal medium, Ir(III) is oxidized with hydrogen peroxide and further purified by anion-exchange.[16] After another hydroxide scavenging, Rb and Cs are precipitated with tetraphenylborate.[17] Chemical yields are established by re-activation, except for Ag, where weighing is used. The following yields are observed: Se, 60–80%; Rb and Cs, 30–80%; Ag, 40–60% Sb, 20–50%; Ir, 25–30%; Au, 70–80%.

EXPERIMENTAL

Preparation of samples and standards

Samples of BCR-1 and lunar materials were irradiated in 10 × 10 mm polyethylene envelopes (groups *A* and *B*), 1-ml cylindrical polyethylene vials (group *E*), or wrapped in 30 × 30 mm sheets of aluminium foil (groups *C*, *D*, *F* and *G*). The approximate weight used for each group is indicated in Table I. Standards for the BCR-1 analyses were prepared in the following way.

Al, Ti, Ca. Weighed amounts of Al metal, TiO_2 and $CaCO_3$ were sealed separately in 10 × 10 mm polyethylene envelopes.

V, Mn. Aliquots of standard solutions were evaporated to dryness on small sheets of polythylene foil and sealed in 10 × 10 mm envelopes. For *Na*, the same procedure was used, except that the preparation was done after irradiation of the standard solution.

Cl, In, Dy, Er, Ho, Sm. Standard solutions were irradiated in sealed polyethylene tubes, and aliquots were withdrawn and prepared for counting at the same geometry as the corresponding sample fractions.

Remaining elements. Standards of group *C*, *D*, *F* and *G* elements (*cf.* Table III) determined in BCR-1 were prepared by evaporating aliquots of dilute standard solutions on 30 × 30 mm sheets of aluminium foil, which were afterwards carefully folded.

For the lunar sample analyses, BCR-1 was used as standard for most elements (Table III). For the rest of the elements, standards were applied as described above.

Irradiation

Irradiations were carried out in the JEEP-II reactor (Kjeller, Norway). For short irradiations (groups *A–C*) the pneumatic tube facility, with a thermal neutron flux of $1{\cdot}5 \times 10^{11}$ n.mm^{-2}.sec^{-1} was employed. The longer irradiations (groups *D–G*) were carried out at a position in one of the vertical isotope channels where the thermal neutron flux was about $1{\cdot}5 \times 10^{11}$ n.mm^{-2}.sec^{-1} and the cadmium ratio of gold was about 3.

Activity measurements

Most activity measurements were carried out by means of a Ge(Li) detector system consisting of the following components: an ORTEC 20-ml Ge(Li) detector with associated electronics, a Hewlett-Packard 200 MHz ADC, and a NORD-I digital computer (4K, 16 bit). An ORTEC pulser was used for determination of counting time as well as for dead-time correction, in a similar manner to that described by Anders.[21] Peak areas were calculated by the computer according to a modified Covell[22] procedure, using two channels, instead of one, on each side of the peak to construct the baseline. In some cases, a 400-channel gamma-spectrometer with a well-type 75 × 75 mm NaI(Tl) crystal was used. The various radionuclides involved and the γ-energies of each nuclide made the basis for the analyses are listed in Table III. In cases where two different energies are listed, average values based on both peaks were calculated.

Experimental procedure

The irradiation time and delay before starting the post-irradiation procedure is given in Table I, for each of the seven groups.

Group A. Samples for the BCR-1 analyses were irradiated one by one together with a set of standards. For the lunar material analyses, each sample was irradiated together with a BCR-1 sample and a Ca standard. Al was measured 2–5 min after the end of the irradiation; V, Ti and Ca after 12–16 min at a position closer to the Ge(Li) detector. A stopwatch was used to measure time intervals between different countings. Care was taken to avoid errors due to different dead-times for samples and standards.

Group B. Between 10 and 20 samples from group *A* analyses were irradiated together with appropriate standards after the decay of short-lived activities from the first irradiation was complete. Mn was measured after 2–3 hr, Na after *ca.* 20 hr, in both cases with the Ge(Li) detector.

Group C. Samples and standards were irradiated in a 1·0-mm thick cylindrical cadmium box, of 14 mm internal diameter and 10 mm internal height. Standards of Ce and Ca, to be used in group *D*, were also included. Before the activity measurements, the rock samples were accurately weighed into new sheets of aluminium foil. Ge(Li) detector measurements were made after 5–6 days and after 20 days, respectively.

Group D. After the group *C* measurements had been finished, samples and standards were re-irradiated, without cadmium cover. Change of aluminium foil was again performed. Ge(Li) detector measurements for Yb and Lu were carried out after 7 days; the rest of the elements were determined by means of countings performed after *ca.* 20 days. For Eu, it proved advantageous to carry out an additional measurement after 50–60 days.

Group E. The irradiated samples were transferred to nickel crucibles containing the following carriers, evaporated to dryness in the presence of sodium hydroxide; In, 5 mg; Dy, 10 mg; Cl^-, 20 mg. After fusion with 2 g of sodium hydroxide pellets with the aid of an electrothermal bunsen, the samples were treated according to the following procedure.

(*a*) The fusion cake is dissolved in water, transferred to a 250-ml beaker and acidified with nitric acid. Possible undissolved matter is removed by passing the solution through a membrane filter.

(*b*) Silver chloride is precipitated with 2-ml of 1*M* silver nitrate, and the solution is centrifuged. The supernatant liquid is saved for step (*c*). The precipitate is washed twice with "wash solution"

[1*M* nitric acid containing 1 mg of Mn(II) per ml] and dissolved in a few ml of concentrated ammonia solution. The solution is passed through a membrane filter, then acidified with nitric acid, and filtered through a blue-ribbon filter. The AgCl precipitate is washed several times with wash solution, acetone and ether, and finally transferred to a counting vial.

(*c*) The supernatant solution from (*b*) is neutralized with ammonia solution. The precipitate is centrifuged, washed with water, and subsequently dissolved in 10 ml of 9*M* hydrobromic acid. This solution is extracted with two 30-ml portions of diethyl ether. The aqueous phase is saved for step (*d*). The organic phase containing In is washed with two 5-ml portions of 4·5*M* hydrobromic acid, and back-extracted with two 5-ml portions of 6*M* hydrochloric acid. The combined hydrochloric acid phases are washed with 15 ml of diethyl ether and then taken for counting.

(*d*) To the aqueous phase from (*c*) 1–2-ml of concentrated hydrofluoric acid is added. The resulting precipitate is centrifuged, washed twice with "wash solution," dissolved in 10 ml of 6*M* nitric acid containing 30 mg of boric acid, and taken for measurements of RE activities.

The Cl and In activities were measured as soon as possible after finishing the separations, with the NaI detector and the Ge(Li) detector, respectively. The RE samples were measured twice with the Ge(Li) detector; after 3–4 hr for Dy, and after about 20 hr for Ho, Er, and Sm. Chemical yields were determined by re-activation for In and Dy, and by weighing for Cl.

Group F. The irradiated samples were transferred to a 250-ml polypropylene beaker containing 5 ml of concentrated hydrofluoric acid, 5 ml of concentrated nitric acid and the following carriers: K, 5 mg; Co, 5 mg; Cu, 2 mg; Fe, 5 mg; Ga, 0·5 mg; W, 1 mg; Zn, 5 mg. After evaporation of the solution to dryness on a water-bath, an additional 5 ml of concentrated hydrofluoric acid were added, and the mixture was evaporated to dryness again. The residue was dissolved in 10 ml of 9*M* hydrochloric acid + 1 ml of 2% boric acid solution.

After the solution had been allowed to stand for about 2 hr, it was applied to a column of Dowex 1-x8 (100–200 mesh), pre-equilibrated with 9*M* hydrochloric acid. The column had an internal diameter of 12 mm, and the height of the resin bed was 85 ± 5 mm. After the sorption step the column was washed with three 5-ml portions of 9*M* hydrochloric acid. The combined effluents were stored for K determination. The following elution sequence was then performed:

3 × 5 ml of 4*M* hydrochloric acid: Co, As, Np
4 × 5 ml of 3*M* hydrochloric acid: Cu, W
4 × 5 ml of 0·5*M* hydrochloric acid: Ga, (Fe)
4 × 5 ml of 1*M* ammonia solution: Zn

All eluates were collected in 100-ml screwcap bottles for measurements with the Ge(Li) detector. In some cases ^{122}Sb was measured on the resin. The effluent from the sorption step was made alkaline (pH 13–14) with sodium hydroxide solution, and the precipitated hydroxides were removed by filtration. Potassium was then precipitated with 15 ml of a 1% sodium tetraphenylborate solution in 1*M* sodium hydroxide. The precipitate was filtered off on a membrane filter, washed with several portions of 1*M* sodium hydroxide and counted with the NaI detector.

Chemical yield for W was determined by re-activation, as described previously.[15] For the other elements, equal chemical yields for lunar samples and the BCR-1 standards were assumed.

Group G. The irradiated samples were transferred to 250-ml polypropylene beakers containing 2 ml of concentrated nitric acid, 5 ml of concentrated hydrofluoric acid and the following carriers: Ag, 50 mg; Au, 5 mg; Cs, 10 mg; Cr, 20 mg (hold-back); Ir, 2 mg; Rb, 5 mg; Sb, 5 mg; Se, 20 mg. After evaporation to dryness on a water-bath and addition of 5-ml of concentrated hydrofluoric acid and 2 ml of concentrated nitric acid, the mixture was again evaporated to dryness, and then treated according to the following separation procedure.

(*a*) The residue is treated with a mixture consisting of 5 ml of concentrated hydrochloric acid + 5 ml of concentrated nitric acid + 2 ml of a 3% boric acid solution, and evaporated to a volume of about 0·5 ml. Then 10 ml of 6*M* hydrochloric acid + 0·5 ml of concentrated nitric acid are added. The silver chloride precipitate is removed by centrifuging and washed with 10 ml of 6*M* hydrochloric acid. The hydrochloric acid solutions are combined and stored for further steps. The precipitate is dissolved in a few ml of concentrated ammonia solution, undissolved matter is removed by filtration, and silver chloride is reprecipitated by acidifying the solution with nitric acid. The precipitate is filtered off on a blue-ribbon filter, washed repeatedly with dilute nitric acid, acetone and ether, and finally transferred to a counting vial.

(*b*) The combined hydrochloric acid phases from (*a*) are heated with 1 or 2 drops of bromine, and then extracted with 25 ml of di-isopropyl ether. The organic phase is washed with two 5-ml portions of 6*M* hydrochloric acid. The hydrochloric acid phases are combined and set aside for further steps. Au and Sb are stripped with two 10-ml portions of 10*M* hydrochloric acid. After dilution with 80 ml of 2*M* hydrochloric acid and removal of traces of di-isopropyl ether by evaporation, Au is reduced to the metal by addition of 200 mg of ascorbic acid, and collected on a membrane filter. The filtrate is

TABLE III.—RESULTS OBTAINED FOR THE U.S.G.S. STANDARD BASALT BCR-1 BY THE PRESENT ANALYTICAL SCHEME

Element and concentration units	Determined in group							Radionuclide measured	γ-energy* used, *keV*	Single values	Mean value	Standard for lunar material analysis†
	A	*B*	*C*	*D*	*E*	*F*	*G*					
Na,%		$\underline{x}$						^{24}Na	1369, 2754	2·40, 2·44, 2·41, 2·38, 2·47	2·42	B
Al,%	$\underline{x}$							^{28}Al	1780	7·43, 7·45, 7·43, 7·40, 7·30	7·37‡	B
Cl,ppm					$\underline{x}$			^{38}Cl	2170	52, 55, 54	54	S
K,%						$\underline{x}$		^{42}K	1524	1·32, 1·32, 1·36, 1·33, 1·30	1·33	B
Ca,%	$\underline{x}$		(x)					^{49}Ca (^{47}Sc)	3090 (160)	5·39, 5·45, 4·54, 4·71, 4·89	4·99	S
Sc,ppm			$\underline{x}$	$\underline{x}$				^{46}Sc	889, 1120	31·4, 30·7, 31·3, 30·2, 29·9	30·7	B
Ti,%	$\underline{x}$							^{51}Ti	320	1·22, 1·38, 1·19, 1·33, 1·36	1·29	B
V,ppm	$\underline{x}$							^{52}V	1434	464, 464, 482, 487, 470	476	B
Cr,ppm				$\underline{x}$				^{51}Cr	320	10·3, 10·6, 9·8, 10·9, 11·2	10·6	S
Mn,ppm		$\underline{x}$						^{56}Mn	847	1427, 1424, 1416, 1398, 1434	1420	B
Fe,%			$\underline{x}$	x		x		^{59}Fe	1095, 1292	—	9·38 [14]	B
Co,ppm			x	x		$\underline{x}$		^{60}Co	1173, 1332	—	36·2 [14]	B
Cu,ppm						$\underline{x}$		^{64}Cu	511	—	15·7 [14]	B
Zn,ppm						$\underline{x}$		^{69m}Zn	439	—	127·4 [14]	B
Ga,ppm						$\underline{x}$		^{72}Ga	835	—	22·2 [14]	B
As, ppm						$\underline{x}$		^{76}As	559	—	0·67 [17]	B
Se,ppM							$\underline{x}$	^{75}Se	401	125, 118, 117, 119, 124	121	S
Br,ppm			$\underline{x}$					^{82}Br	777	<0·2	<0·2	S
Rb,ppm			$\underline{x}$				$\underline{x}$	^{86}Rb	1078	49, 51, 51	50	S
Sr,ppm			$\underline{x}$					^{85}Sr	514	314, 312, 317, 315, 302	312	B

Ag,ppM						$\underline{x}$	^{110m}Ag	658	32, 28, 27, 26, 26	28	S
In,ppM				$\underline{x}$			^{116m}In	417	94, 108, 108	103	S
Sb,ppm		x			x	$\underline{x}$	^{122}Sb	564	—	0·63 [17]	S
Cs,ppm		x				$\underline{x}$	^{134}Cs	605, 796	0·94, 1·02, 0·93, 0·99	0·97	S
Ba,ppm		$\underline{x}$				(x)	^{131}Ba (^{131}Cs)	496 (30)	579, 540, 570, 575, 637	580	B
La,ppm		x	$\underline{x}$				^{140}La	1596	23·6, 23·3, 24·4, 23·2, 24·0	23·7	B
Ce,ppm			$\underline{x}$				^{141}Ce	145	—	53 [18]	B
Sm,ppm		x		$\underline{x}$			^{153}SM	103	6·48, 6·24, 6·34, 6·84, 7·08	6·60	B
Eu,ppm		x	$\underline{x}$	(x)			^{152}Eu(^{152m}Eu)	122	1·99, 1·91, 1·92, 1·99, 1·91	1·94	B
Tb,ppm		$\underline{x}$					^{160}Tb	298	—	0·96 [8]	B
Dy,ppm	x			$\underline{x}$			^{165}Dy	95	5·56, 5·40, 5·43, 6·02, 5·82	5·65	B
Ho,ppm				$\underline{x}$			^{166}Ho	81	1·23, 1·23, 1·09, 1·20, 1·24	1·20	B
Er,ppm				$\underline{x}$			^{171}Er	308	5·7, 2·4, 5·4, 3·9, 5·2	4·5	S
Yb,ppm			$\underline{x}$				^{175}Yb	396	3·13, 3·37, 3·17, 3·21, 3·19	3·21	B
Lu,ppm			$\underline{x}$				^{177}Lu	208	0·538, 0·578, 0·525, 0·519, 0·516	0·535	B
Hf,ppm		$\underline{x}$					^{181}Hf	482	—	4·72 [8]	B
Ta,ppm		$\underline{x}$					^{182}Ta	222, 1221	0·74, 0·74, 0·75, 0·72, 0·74	0·74	B
W,ppM					$\underline{x}$		^{187}W	480, 686	0·371, 0·400, 0·390, 0·364	0·381	B
Ir,ppM						$\underline{x}$	^{192}Ir	317	$<0·1$	$<0·1$	S
Au,ppM		x				$\underline{x}$	^{198}Au	412	0·50, 0·68, 0·69, 0·60, 0·77	0·65	S
Th,ppm		$\underline{x}$					^{233}Pa	312	5·35, 5·38, 4·79, 4·82, 4·55	4·98	B
U,ppm		x			$\underline{x}$		^{239}Np	278	1·71, 1·71, 1·62, 1·75, 1·61	1·68	B

* Taken from Filby *et al.* [20]

† B = BCR-1 used as standard; S = separate standard.

‡ Corrected for contribution from the ^{28}Si(n, p) reaction.

heated, and 100–200 mg of thioacetamide are added in order to precipitate Sb_3S_3, which is collected on another membrane filter. Both precipitates are washed with several portions of 2*M* hydrochloric acid and water before transfer to counting vials.

(*c*) To the hydrochloric acid solution from (*b*) is added 200 mg of $NaHSO_3$ and the whole is heated for some minutes. The resulting selenium precipitate is removed by filtration through a membrane filter. The filtered solution is stored for further steps. The filter is transferred to a distillation apparatus and dissolved in a mixture of 5 ml of concentrated nitric acid and 5 ml of concentrated sulfuric acid. Distillation is then carried out until white fumes of SO_3 are visible. The nitric acid distillate is discarded. After cooling of the distillation flask, 10 ml of a 1:1 mixture of concentrated hydrochloric and hydrobromic acids is added, and the solution is again heated to incipient fumes of SO_3. The distillate is transferred to a beaker, and Se is precipitated by addition of 200 mg of $NaHSO_3$. The precipitate is collected on a tared membrane filter, washed with dilute hydrochloric acid and water, and after drying for 10 min at 110° and weighing, is transferred to a counting vial.

(*d*) The first filtrate from (*c*) is adjusted with concentrated ammonia solution to pH $\sim$ 7 and filtered through a blue-ribbon filter. To the filtrate are added 10 ml of concentrated hydrochloric acid and 5 ml of 30% hydrogen peroxide. Upon heating the solution, the brown colour of Ir(IV) appears. The solution is passed through a column of Dowex 1-x8, 100–200 mesh, height of resin bed 50 mm, pre-equilibrated with 6*M* hydrochloric acid. The effluent is stored for step (*e*). After washing of the column with two 5-ml portions of 6*M* hydrochloric acid and four 5-ml portions of water, Ir is eluted with three 10-ml portions of 5% ascorbic acid in 3*M* hydrochloric acid followed by three 10-ml portions of 10*M* hydrochloric acid. The combined eluates are collected in a 200-ml Erlenmeyer flask for counting.

(*e*) To the effluent from the sorption step of (*d*) are added 50 mg of Fe(III), and the solution is made alkaline with an excess of 3*M* sodium hydroxide. The solution is then boiled on a hot-plate down to a volume of about 30 ml, in order to remove ammonia, which interferes in the succeeding Rb-Cs precipitation step. The hydroxide precipitate is removed by filtration. Fifteen ml of a 1% solution of sodium tetraphenylborate in 1*M* sodium hydroxide are then added. The Rb-Cs precipitate is filtered off on a membrane filter, washed with several portions of 1*M* sodium hydroxide, and finally dissolved in 25 ml of acetone in a volumetric flask before counting.

The fractions containing Sb, Au, Ir, and Rb-Cs were analysed by Ge(Li) γ-spectrometry, while the NaI well detector was used for Ag and Se.

Chemical yield was determined by weighing (Ag, Se), or by re-activation (Au, Sb, Ir, Cs). The Au and Sb_2S_3 precipitates were dissolved in 5-ml of *aqua regia* and concentrated hydrochloric acid respectively, and further diluted to a suitable concentration with water and 0·4*M* citric acid, respectively. The Ir and Rb-Cs fractions were diluted to appropriate volumes with water and acetone respectively. For the re-activation, exact volumes (250–500 μl) were transferred by pipette into small polyethylene tubes, which were sealed, and irradiated for 2 min (Cs, Au, Sb) or 30 min (Ir). The Cs yield was based on measurement of the 129 keV γ-ray of ^{134m}Cs, and equal yields were assumed for Rb and Cs.

RESULTS AND DISCUSSION

In Table III are summarized the most significant results relevant to the present analytical scheme. The subdivision of the 42 elements within the seven groups *A–G* is outlined. For elements which can be determined satisfactorily in more than one group, the group in which the best determination was achieved in the lunar material analyses is emphasized by underlining.

Single values as well as the mean value obtained for BCR-1 when testing the scheme are also listed in the Table. For some elements where recent results from the authors' previous work[9,15,18,19] were available, additional results were not recorded in the present work, and the previous values were used for the lunar sample work. The mean values from the present work are in most cases in good agreement with data from the compilation by Flanagan[23] as well as with values from recent investigations similar to the present work.[29–32]

The scheme has been employed for duplicate analyses of five 1-g samples of lunar material, the results of which are published elsewhere.[2] The analytical experience obtained from the investigation of lunar samples as well as from the BCR-1 work is briefly discussed in the following.

Al, Na, Mn. These elements are determined with similar precision and accuracy by Ge(Li) γ-spectrometry as by NaI-detectors.[24–26] For Na, the precision appears to be as good as ± 2–3% for sodium contents at the 0·2% level.

Cl. The most serious interfering activity in the Cl determination is presumably ^{56}Mn. Good results have been obtained, however, in lunar samples with a Cl content as low as 5 ppm and containing about 2000 ppm Mn.

K. For this element very precise results have been obtained, even at the 0·05% level.

Ca. The precision obtained by measurement of the 3·09 MeV γ-ray of ^{49}Ca is poor, although somewhat more precise results may be obtained by measurements following the 5-min irradiation, using a suitable lead absorber. Measurement of the 160 KeV γ-ray of ^{47}Sc following the epithermal activation (group *C*) yields better precision, but the results tend to be low when based on a pure Ca standard, presumably because of interfering peaks near the boundaries of the ^{47}Sc peak for the samples. Introduction of detectors with high resolution for low-energy γ-rays should probably facilitate a satisfactory group-*C* determination of Ca.

Cr. The value obtained for BCR-1 is significantly low, compared with radiochemical neutron-activation results,[28] probably because of the unfavourable ^{51}Cr/^{233}Pa ratio in this sample. For the lunar rock analyses, a separate Cr standard was therefore used.

Sc, Fe, Co. These elements are all determined satisfactorily by neutron activation and Ge(Li) γ-spectrometry,[7] corresponding to group *D* in the present work. For Fe, however, we have found the group *C* results to be slightly better, mainly because of the enrichment of ^{59}Fe relative to ^{46}Sc (a factor of 2·9 under the present conditions) obtained by epithermal activation. For Co, the radiochemical values of group *F* are more precise than are those based on purely instrumental analysis.

Cu, Ga, Zn. For these elements, introduction of a Ge(Li) detector clearly represents an advantage, although NaI detectors may also be fully satisfactory when the present anion-exchange separation is used.[15] Better determination of Ga can be carried out in samples with unfavourable ^{72}Ga/^{59}Fe ratios. Similarly the possible interferences from ^{187}W and ^{198}Au in the measurement of respectively ^{64}Cu and ^{69m}Zn are avoided. Good experience has been obtained with lunar samples, where the abundance of these three elements is as low as about 5 ppm.

As. Although the determination of this element according to the group *F* procedure is encumbered with considerable uncertainty, experience so far indicates that the figures obtained may be regarded as more meaningful than just orders of magnitude.

Se. In the lunar samples, with an Se content of about 0·2 ppm, a precision of 5 or better was observed for this element.

Br. Bromine may be determined in common basaltic rocks by epithermal activation analysis if its concentration is higher than about 0·2 ppm. The value for BCR-1 in Table III is relative to W-1 with an assigned value of 0·5 ppm.[27] For future Br determination, a rock standard with relatively high Br content is intended to be used.

Rb, Cs. These elements can be favourably determined by instrumental activation analysis with epithermal neutrons[9] if their concentrations are above 10 ppm and 0·2 ppm, respectively. For the lunar rock analyses, however, it was necessary to include a radiochemical step (group *G*) in order to facilitate determination of the low amounts of Rb and Cs present in these samples. If the iridium determination [step (*d*)] was excluded from the group *G* procedure, the chemical yields for Rb and Cs would probably be constant and about 90%.

Sr, *Ba*. For Sr and Ba, epithermal activation represents an advantage if these elements are to be determined by purely instrumental analysis, and adequate results can be obtained on common silicate rocks.[9] For lunar rocks, however, with Sr and Ba contents of the order of 100 ppm, the results obtained seem to be more uncertain.

Barium may also be determined in the Rb-Cs fraction of group *G*, *via* the 31-keV γ-ray of ^{131}Cs, the daughter nuclide of ^{131}Ba. This implies that Ba and Cs should be completely separated in a single separation step, which should be performed simultaneously for samples and standards. In the present method, provided that Ba carrier has been added, this separation would take place in step (*e*) of the group *G* procedure. The use of ^{131}Cs in the determination of Ba in geological material has not been previously reported in the literature.

Ag, *Au*, *Ir*. For Ag and Au, the sensitivity is adequate for lunar sample work. For Ir, however, the practical detection limit is 0·1 ppM (parts per milliard), and modification of the scheme would be necessary in order to permit quantitative determination in some lunar rocks. Au contents down to a few ppM may also be determined instrumentally after epithermal activation.

Sb. The epithermal activation works well for concentrations above 0·1–0·2 ppm. For the lunar samples, however, the radiochemical separation of group *G* was found necessary.

RE elements. La, Ce, Yb and Lu are favourably determined in lunar rocks by instrumental activation analysis with thermal neutrons (group *D*). Sm may also be added to this group as far as lunar samples are concerned. For some terrestrial rocks, however, peaks due to ^{239}Np, ^{233}Pa and ^{182}Ta may cause some trouble, and a radiochemical determination like that of group *E* may be preferable. For Tb, epithermal activation appears to be advantageous.[9] Dy may also be determined instrumentally (group *B*), but the radiochemical separation of group *E* gives better results. This group separation also yields fair Ho results, while the Er values for BCR-1 seem to be of little value. For the lunar samples analysed, however, considerably better Er determinations are obtained, mainly because of the Eu depletion relative to the other RE elements and the correspondingly more favourable ^{171}Er/^{152m}Eu ratio of the separated fractions.

Hf, *Ta*, *W*. The epithermal activation facilitates good determinations for Hf and Ta. The W determinations of this work are improved compared to the previous ones[15] by NaI detector.

Th. The instrumental determination of this element in lunar samples was very difficult because of the high content of Cr (about 3000 ppm) compared to a Th content of the order of 1 ppm or less, and the corresponding interference of the 320-keV γ-ray of ^{51}Cr to the 312-keV γ-ray of ^{233}Pa. By epithermal activation, this interference is reduced by approximately a factor of 12, but the thorium results obtained for the lunar rocks are still not satisfactory.

U. The limit of detection for U in rocks is about 0·1 ppm by instrumental activation analysis based on epithermal neutrons. As the lunar samples analysed by the authors appeared to have U contents down to this level, the radiochemical values of Group *F* were preferred. If the content is above 0·5–1 ppm, however, the values obtained from group *C* will probably be equally or even more accurate than those from the radiochemical group separation.

The present scheme provides the determination of 42 elements in duplicate, with a total sample consumption of only 800 mg. Although especially designed for lunar sample, the scheme should be applicable to stony meteorites as well as to most terrestrial rocks. For most of the elements, the accuracy obtained by application of this multi-element scheme should probably be equally good as that observed when a single-element neutron-activation method is used on routine series.

Acknowledgement—This work is supported by the Royal Norwegian Council of Scientific and Industrial Research (Research Contract B 1206.3070).

Zusammenfassung—Ein Neutronenaktivierungsschema zur Bestimmung von 42 Elementen in Mondgesteinen und -stäuben wird beschrieben. Das Schema beruht auf 7 verschiedenen Bestrahlungen, wovon vier direkt durch Gamma-Spektrometrie überwacht werden, die anderen drei mit radiochemischen Abtrennungs-Systemen. Der Gesamt-Probenverbrauch für eine Doppelanalyse beträgt etwa 800 mg. Das Schema wurde an dem Basalt BCR-1 erprobt; Ergebnisse für dieses Standardgestein werden mitgeteilt. An Mondproben und an BCR-1 gewonnene analytische Erfahrungen werden diskutiert.

Résumé—On décrit un schéma d'activation de neutrons destiné à la détermination de 42 éléments dans les roches et poussières lunaires. Le schéma est basé sur sept irradiations différentes, dont quatre sont suivies par une spectrométrie γ directe et troispar des systèmes de séparation radiochimique. La consommation totale d'échantillon pour une analyse en double est d'environ 800 mg. Le schéma a été essayé sur le basalte BCR-1, et l'on présente les résultats pour cette roche étalon. On discute de l'expérience analytique obtenue d'analyses d'échantillons lunaires et de BCR-1.

REFERENCES

1. Proc. Apollo 11 Lunar Science Conference, *Geochim. Cosmochim. Acta*, 1970, *Supplement I*, Vol. 2.
2. A. O. Brunfelt, K. S. Heier and E. Steinnes, *Proc. Apollo 12 Lunar Science Conference*, Pergamon Press, in the press.
3. O. Landstrøm, K. Samsahl and C. G. Wenner, *Rept.* AE-296, Aktiebolaget Atomenergi, Stockholm, 1967.
4. G. H. Morrison, J. T. Gerard, A. Travesi, R. L. Currie, S. F. Peterson and N. M. Potter, *Anal. Chem.*, 1969, **41**, 1633.
5. J. C. Laul, D. R. Case, M. Wechter, F. Schmidt-Bleek and M. E. Lipschutz, *J. Radioanal. Chem.*, 1970, **4**, 241.
6. R. H. Filby, W. A. Haller and K. R. Shah, *ibid.*, 1970, **5**, 277.
7. G. E. Gordon, K. Randle, G. G. Goles, J. B. Corliss, M. H. Beeson and S. S. Oxley, *Geochim. Cosmochim. Acta*, 1968, **32**, 369.
8. G. E. Gordon, J. C. Dran, P. A. Baedecker and C. F. L. Anderson, *Modern Trends in Activation Analysis.* NBS Special Publ. 312, 1969, Vol. 1, p. 399.
9. A. O. Brunfelt and E. Steinnes, *Anal. Chim. Acta*, 1969, **48**, 13.
10. O. Johansen and E. Steinnes, *Talanta*, 1966, **13**, 1177.
11. A. O. Brunfelt and E. Steinnes, *Geochim. Cosmochim. Acta*, 1967, **31**, 283.
12. O. Johansen and E. Steinnes, *ibid.*, 1967, **31**, 1107.
13. A. O. Brunfelt and E. Steinnes, *Analyst*, 1968, **93**, 286.
14. *Idem*, *Radiochem. Radioanal. Letters*, 1969, **1**, 219.
15. O. Johansen and E. Steinnes, *Talanta*, 1970, **17**, 407.
16. P. A. Baedecker and W. D. Ehmann, *Geochim. Cosmochim. Acta*, 1965, **29**, 329.
17. K. Tomura, H. Higuchi, H. Takahashi, N. Onuma and H. Hamaguchi, *Anal. Chim. Acta*, 1968, **43**, 523.
18. E. Steinnes, unpublished work, 1970.

19. A. O. Brunfelt and E. Steinnes, *Chem. Geol.*, 1967, **2**, 199.
20. R. H. Filby, A. I. Davis, G. G. Wainscott, W. A. Haller and W. A. Cassatt, *Rept.* WSUNRC 97 Washington State University, 1969.
21. O. U. Anders, *Nucl. Instr. Methods*, 1969, **68**, 205.
22. D. F. Covell, *Anal. Chem.*, 1959, **31**, 1785.
23. F. J. Flanagan, *Geochim. Cosmochim. Acta*, 1969, **33**, 81.
24. E. Steinnes, *Rept.* KR-131, Institutt for Atomenergi, Kjeller, Norway, 1969.
25. R. B. Parker and A. O. Brunfelt, *Chem. Geol.*, 1968, **3**, 213.
26. O. Johansen and E. Steinnes, *Anal. Chim. Acta.* 1968, **40**, 201.
27. R. H. Filby, *Geochim. Cosmochim. Acta*, 1965, **29**, 49.
28. A. O. Brunfelt and E. Steinnes, *Anal. Chem.*, 1967, **39**, 833.
29. R. O. Allen, L. A. Haskin, M. R. Anderson and O. Müller, *J. Radioanal. Chem.*, 1970, **6**, 115.
30. E. B. Denechaud, P. A. Helmke and L. A. Haskin, *ibid.*, 1970, **6**, 97.
31. P. Rey, H. Wakita and R. A. Schmitt, *Anal. Chim. Acta*, 1970, **51**, 163.
32. R. A. Schmitt, T. A. Linn Jr. and H. Wakita, *Radiochim. Acta*, 1970, **13**, 200.

Talanta, 1971, Vol. 18, pp. 1209 to 1216. Pergamon Press. Printed in Northern Ireland

ELECTROCHEMICAL BEHAVIOUR OF ALUMINIUM(III) AND BERYLLIUM(II) PERCHLORATES IN DIMETHYLFORMAMIDE

M. GALOVÁ
Department of Analytical Chemistry, Technical University
Svermová 3, Kosice, Czechoslovakia

D. A. PANTONY
Department of Metallurgy, Imperial College of Science and Technology, London, S.W.7, U.K.

(*Received* 16 *February* 1971. *Accepted* 14 *July* 1971)

Summary—Well defined voltammetric peaks of Al(III) and Be(II) were obtained in DMF at the HMDE, and the nature of the electrochemical process in this medium was investigated. Adsorption and chemical reaction coupled with the charge transfer were observed in both cases. The optimum depolarizer concentration and scan-rate for analytical determination were established. Close similarities were found in the electrochemical behaviour of Al(III) and Be(II), and differences were in degree rather than of kind.

THE AQUEOUS polarographic reduction wave of Al(III), described in 1931 by Prajzler,[1] has been used for analytical purposes.[2-8] However, the direct determination of aluminium in aqueous solution was difficult owing to the anomalous behaviour of its wave. In 1960 M. Heyrovský[9,10] proved that the polarographic wave of aluminium ions is due to the reduction of three protons of the hexaquoluminium ion:

$$[Al(H_2O)_6]^{3+} + 3e \rightarrow Al(OH)_3 + 3H_2O + 1{\cdot}5H_2$$

The electrode reaction is catalysed by the reaction product, aluminium hydroxide, which is adsorbed at the electrode surface.

It is well known in technical electrochemistry[11] that direct electro-deposition of aluminium from aqueous solution is impossible. This led to an attempt to use non-aqueous organic solvents such as dimethylformamide (DMF) and dimethylsulphoxide (DMSO) as media for electro-deposition of the element. Aluminium, as an oxinate in DMF in the presence of iron and titanium, has been determined polarographically.[12] When aluminium chloride was polarographed in a mixture of DMSO + 10% v/v acetylacetone, the waveheight was found to be proportional to the concentration over a wide range, and the process was shown to be diffusion-controlled.[13] Estimates of aluminium contents of alloys such as ferrotitanium, magnet alloys, and of magnesium, DMF solutions being used, were carried out with normal polarographic reproducibility by Kumar and Pantony.[14] These authors also gave micro- and macrocoulometric data for electro-deposition of aluminium and other elements from DMF.

Polarographic investigations of beryllium in water were carried out first by Heyrovský and Berezický,[15] but the interference of a hydrogen wave caused by the hydrolysis of Be(II) salts made it impossible to obtain the pure Be(II) reduction wave. Later Kemula and Michalski[16] and more recently Györbiró[17,18] investigated the reduction of Be(II) in water. In all cases the interference of a hydrogen wave was observed.

In the present work the electrochemical behaviour of Al(III) and Be(II) as perchlorates in DMF and the optimum conditions for their determination were investigated. Observations and correlations found in their electrochemical properties are presented and discussed. Applications will be discussed elsewhere.

EXPERIMENTAL

Cyclic voltammetry at the HMDE was carried out with a Tektronix 564 oscilloscope and SSP-2 sweep polarographic analyser. The three-electrode system included a DMF–silver/silver chloride half-cell[19] as reference electrode and a tungsten wire as counter electrode. A methylcellulose bridge[19] connected the working solution with the reference electrode. Alternatively, a similar bridged DM–Ag/AgCl electrode can be used as anode if desired. (HMDE = hanging mercury drop electrode.)

Aluminium and beryllium perchlorates were prepared by the action of 70% perchloric acid on 99·99% pure aluminium wire and spectroscopically pure beryllium oxide, respectively. The products were dried in a vacuum oven at 50–60° for 48 hr after a number of evaporations. The perchlorates were weighed, handled and dissolved swiftly and under dry conditions according to methods already described.[14,19] These procedures had been shown not to introduce sufficient water to affect the electrolysis.

Dimethylformamide was purified as follows: commercial DMF was shaken with solid potassium carbonate for 48 hr and filtered. It was then treated in the same way successively with potassium hydrogen sulphate, again with potassium carbonate and then with molecular sieves, and twice distilled under reduced pressure (~13 mbar) at 55°. The purified DMF was stored over molecular sieves.

Before electrolysis the solution was deaerated with oxygen-free nitrogen, or argon, that had been dried and purified by passage through silica gel, magnesium perchlorate, soda-lime and then through a titanium furnace at 750°.

RESULTS AND DISCUSSION

General aspects of voltammetry of Al(III) *and* Be(II) *perchlorates in DMF*

The cyclic voltammogram of aluminium perchlorate in DMF shows two peaks (Fig. 1). Their position on the potential axis as well as the ratio of their heights varies with concentration of Al(III) in solution and with scan-rate but the separation of peaks remains constant, $\Delta E_p \sim 0{\cdot}32$ V. No peaks appear on the anodic sweep. In the second and following cycles a slight anodic shift in potential of both peaks occurs and the heights of the peaks change with successive cycles: the more positive peak disappears completely immediately after the first cycle while the negative peak decreases rapidly and after a few cycles disappears almost completely. These effects are caused partly by the depletion of the diffusion layer (thus, by repeating the sweep after a pause of several minutes, a restoration of peak-height results), and partly by the fact that no reversible process occurs during the anodic sweep in the applied potential range, so no material is provided for the next cycle.

The cyclic voltammograms of Be(II) perchlorate in DMF are very similar to those of Al(III) perchlorate. Two irreversible peaks on the cathodic sweep decrease with successive cycles even more rapidly than in the case of the aluminium system. The potentials of the peaks do not change appreciably with concentration of Be(II) in solution and at the scan-rate of 1 V/sec are: $E_{\mathrm{ppos}} = -1{\cdot}8$ V, $E_{\mathrm{pneg}} = -2.4$ V, both *vs.* the DMF–Ag/AgCl electrode. The separation potential, ΔE_p, is 0·6 V and is therefore larger than that for Al(III), and the shape of the negative peak is sharper.

Dependence of peak-heights on the bulk concentration of Al(III) *and* Be(II) *perchlorates*

The concentration dependence was followed in the range 5×10^{-5}–$10^{-3}M$ aluminium perchlorate and 5×10^{-5}–$1.67 \times 10^{-3}M$ beryllium perchlorate.

In Fig. 2 the currents in the first cycle for negative peaks of Al(III) and Be(II) are shown as a function of concentration. In both cases the peak-height follows the Randles-Ševčík equation for diffusion-controlled current down to $10^{-4}M$ for Al(III)

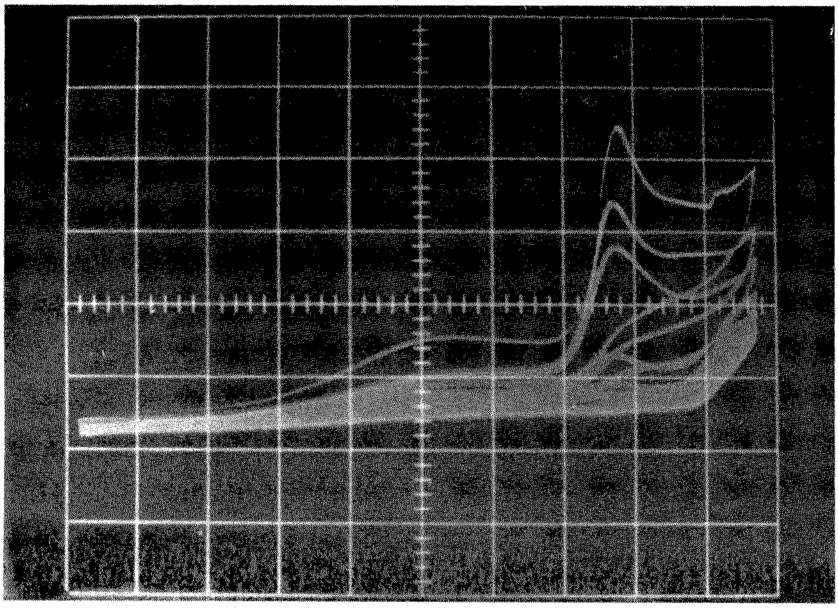


FIG. 1.—Cyclic polarograms of aluminium perchlorate ($10^{-3}M$) in dimethylformamide containing $0{\cdot}1M$ TEAP as supporting electrolyte. Scanned from -1 to -3 V at 1 V/sec, 2 μA per division current sensitivity. Current decreasing with consecutive sweeps.

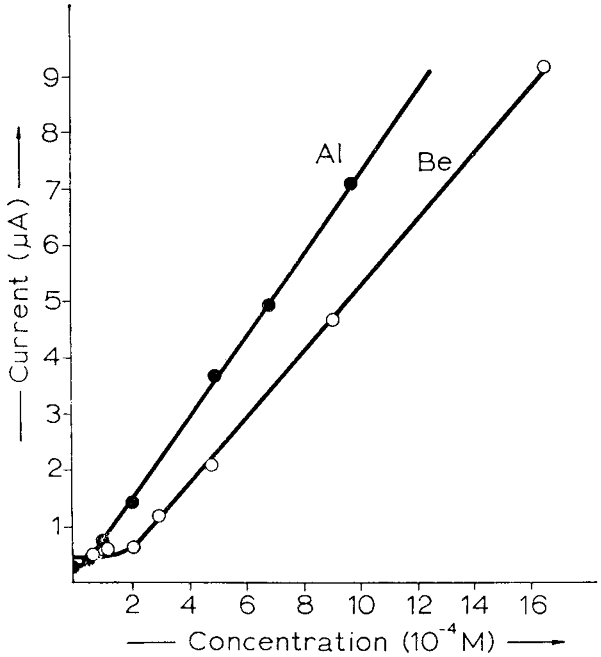


Fig. 2.—The negative-peak currents for Al(III) and Be(II) in DMF as a function of bulk concentration of depolarizer.

and $2 \times 10^{-4}M$ for Be(II). Below these concentrations the decreases in peak-heights are apparently smaller than theoretically expected.

If the electrochemical reactions were simple reductions to elemental metals, the ratio of Be(II) to Al(III) reduction peak currents at the same molar concentrations of depolarizer would be given by the Randles-Ševčík equation as follows:

$$i_{\mathrm{Be}}/i_{\mathrm{Al}} = 0{\cdot}537 D_{\mathrm{Be}}^{1/2}/D_{\mathrm{Al}}^{1/2}$$

If the differences in diffusion coefficients cannot be neglected, the ratio will differ from the value 0·537 but should remain constant over a reasonable concentration range.

From Table I it can be seen that the experimental values of the $i_{\mathrm{Be}}/i_{\mathrm{Al}}$ ratio approach the theoretical value only at low concentrations and they increase with

Table I.—Ratio $i_{\mathrm{Be}}/i_{\mathrm{Al}}$ for various bulk concentrations of depolarizers

Concentration of both depolarizers, *M*	$i_{\mathrm{Be}}/i_{\mathrm{Al}}$
2×10^{-4}	0·53
5×10^{-4}	0·63
7×10^{-4}	0·70
$8{\cdot}5 \times 10^{-4}$	0·72
$1{\cdot}0 \times 10^{-3}$	0·74
$1{\cdot}13 \times 10^{-3}$	0·74
$1{\cdot}25 \times 10^{-3}$	0·75

increasing concentration of depolarizer. The deviation indicates that the process is not entirely diffusion-controlled over the whole range of experimental conditions. This observation will be discussed in the following section in the light of the results obtained from voltage scan-rate investigations.

The behaviour of the positive peaks in the first cycle with changing concentration is shown in Fig. 3. At lower concentrations [up to approximately $5 \times 10^{-4}M$ for Al(III)] the peak-height increases proportionally with the concentration. At higher concentrations the peak-height reaches a limiting value and becomes independent of further increase of concentration. The positive peak of Be(II) shows a similar behaviour, the current steps increasing at a higher concentration than for aluminium.

The shape of both curves is characteristic of an adsorption process. In the low concentration range the diffusion of depolarizer is not sufficient to provide enough material to cover the whole electrode surface and the adsorption current is controlled by the rate of diffusion. The range where peak current is independent of concentration represents a situation where the whole surface is covered by adsorbed material and no further increase in peak-height is possible.

The curve for beryllium perchlorate reaches its saturated surface concentration at higher bulk concentration than does aluminium perchlorate. This is probably caused by the differences in the ionic radii: the ionic radius for Be(II) is 0·031 nm, while for Al(III) it is 0·05 nm. Therefore a lower concentration of Al(III) is necessary to cover the whole surface of the drop and the ratio of concentrations at which "limiting" conditions is reached is in keeping with the ratio of the squares of the ionic radii.

The adsorption character of the process is confirmed by the earlier observation that the positive peak disappears after the first cycle while the negative peak does so only after several cycles. No desorption peak was noticed in the potential range

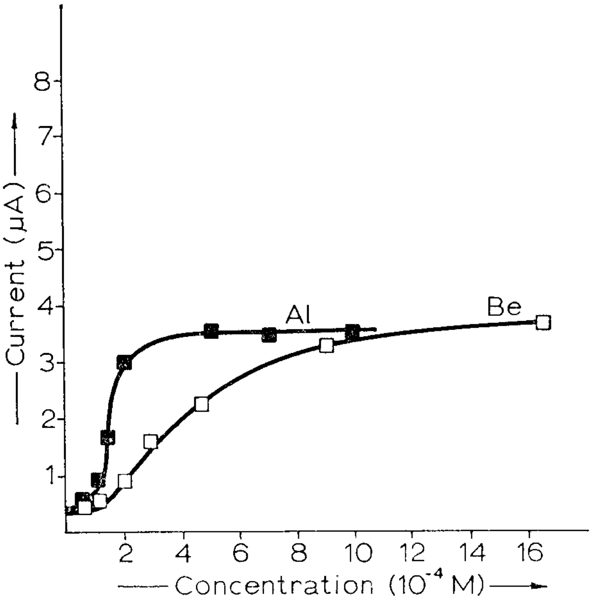


Fig. 3.—The positive-peak currents for Al(III) and Be(II) in DMF as a function of the bulk concentration of depolarizer.

used; this means that the stationary electrode surface is occupied by the product of the previous adsorption after the first cycle.

Since the adsorption peak is separated from the diffusion peak and is placed in a relatively more positive position, the conclusion can be drawn that a strong adsorption of the product of electrochemical reaction takes place.[20,21] From the respective values of ΔE_p for both ions it follows that the adsorption of product is stronger after the electrochemical reduction of Be(II) than of Al(III).

With increasing bulk concentration of the depolarizer the influence of the adsorption on the overall electrode process is less. This can be seen in Fig. 4 where the ratio of positive to negative peak-height is plotted *vs.* concentration. At low concentrations the adsorption peak increases in size faster than the diffusion peak. The maximum for both curves coincides with the inflexion of the adsorption current/concentration curves. Further major increases in concentration result in a decrease in the ratio since only the diffusion peak increases.

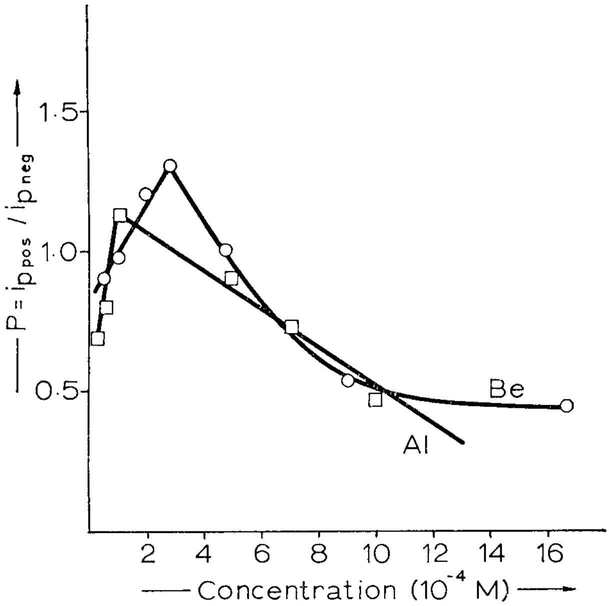


FIG. 4.—The ratio of positive to negative peak currents for Al(III) and Be(II) in DMF as a function of bulk concentration of depolarizer.

Dependence of peak heights and potentials on the voltage scan-rates

With an increase in scan-rate the potentials of both positive and negative peaks shift to more negative values, as expected for irreversible charge transfer.[22]

The dependence of the current function $i_p/v^{1/2}$ on the rate of voltage scan is demonstrated in Fig. 5. It shows that at lower scan rates the electrode reaction is not diffusion-controlled. Up to the scan-rate of 2 V/sec a chemical reaction, which at higher scan-rates has no chance to proceed, is coupled with the charge transfer. The shape of both curves indicates a catalytic reaction with reoxidation of the primary product. The chemical reaction with beryllium proceeds faster than that with aluminium. This is well in agreement with the results presented in Table I. The increasing

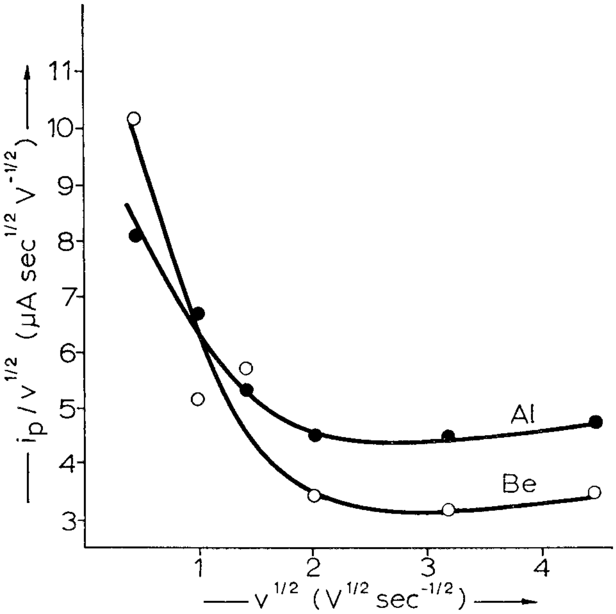


FIG. 5.—The current function $i_p/v^{1/2}$ for negative peaks of Al(III) and Be(II) in DMF as a function of the voltage scan-rate.

deviation of the ratio i_{Be}/i_{Al} from the theoretical value for diffusion-controlled current with increasing but equal concentrations of the depolarizers is caused by the differences in the reaction rates of the catalytic reactions for Al(III) and Be(II).

In the presence of perchlorate in solution the possibility arises of oxidation of the primary product of the electrode reaction back to the original depolarizer. The bulk concentration of perchlorate as supporting electrolyte is high (0·1*M*), and therefore it can be assumed that its concentration in the vicinity of the electrode remains constant during the whole process. The homogeneous oxidation of product would be pseudo-unimolecular and its rate would depend only on the concentration of the reaction product.

The number of electrons transferred in the electrochemical process for Al(III) as determined by coulometric analysis carried out under potentiostatic conditions was found to be 3. The primary product of the electrode reaction is therefore Al. The fact that this product, which is being oxidized chemically in solution to Al(III), cannot be oxidized electrochemically on the anodic sweep to yield a reversible wave appears to be anomalous. The most probable explanation is to be found in the adsorption process on the electrode surface, which hinders the electron transfer between the electrode and the depolarizer (the first product, Al).

The behaviour of the positive adsorption peaks of both elements with changing scan-rate was investigated and the results are given in Fig. 6. No remarkable changes occur in either curve when the scan-rate is increased. The concentration of depolarizer in both cases [$10^{-3}M$ Al(III) and $2 \times 10^{-3}M$ Be(II)] is such that the adsorption process does not influence the overall electrochemical reduction process to any high degree. Only at very high scan-rates is there observed a small decrease in both

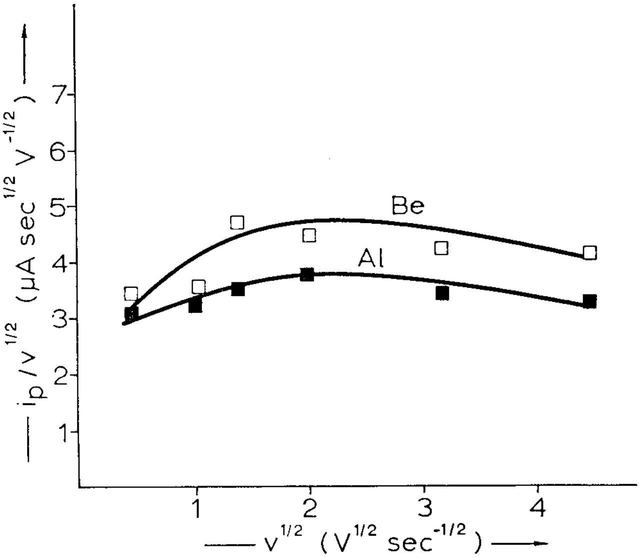


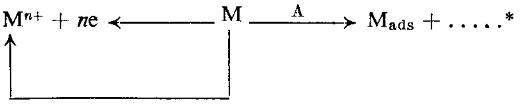
FIG. 6.—The current function $i_p/v^{1/2}$ for positive peaks of Al(III) and Be(II) in DMF as a function of the voltage scan-rate.

curves, which is caused by the inability of the diffusion process to allow coverage of the whole electrode surface during the life of the adsorption peak.

CONCLUSIONS

1. The main obstruction to the polarographic determination of aluminium and beryllium in water—the interference of the hydrogen wave—has no influence on the electrochemical reaction of these ions in certain organic media, especially aprotic solvents such as DMF. The peaks obtained in sweep or cyclic voltammetry can be used for analytical purposes.

2. The nature of the processes in the electrochemical reduction of aluminium and beryllium perchlorates in DMF can be described as follows:



$$M^{n+} + ne \longleftarrow M \xrightarrow{A} M_{ads} + \ldots\ldots^{*}$$

chemical oxidation, perhaps by perchlorate, B

* a further oxidation process to oxides cannot be excluded.

Reaction A proceeds until the whole electrode surface is covered. Reaction B proceeds only at scan-rates lower than 2 V/sec.

3. The optimum conditions for analysis are as follows.

Scan-rate: greater than 2 V/sec.

Concentration: the lower limit of concentration is given by the extent of the of the Randles equation, *viz.* $10^{-4}M$ for Al(III) and $2 \times 10^{-4}M$ for Be(II).

Solution preparation: examples have been described earlier.[14]

4. Comparison of the electrochemical behaviour of Al(III) and Be(II)shows similarities. The differences are in degree and not of kind. The results are a verification of the diagonal relationship of, particularly, electrochemical properties in the periodic system.

Zusammenfassung—Wohldefinierte voltametrische Peaks von Al(III) und Be(II) wurden in DMF an der HMDE gefunden und es wurde die Natur des elektrochemischen Prozesses in diesem Medium untersucht. In beiden Fällen wurde beobachtet, daß gekoppelt mit dem Ladungsübergang Adsorption und chemische Reaktion stattfinden. Die optimale Depolarisatorkonzentration und die beste Durchlaufgeschwindigkeitz ur analytischen Bestimmung wurden ermittelt. Im elektrochemischen Verhalten von Al(III) und Be(II) wurden enge Ähnlichkeiten gefunden; die Unterschiede waren mehr quantitativ als qualitativ.

Résumé—On a obtenu des pics voltammétriques bien définis de Al(III) et Be(II) en DMF au HMDE, et l'on a étudié la nature du processus électrochimique dans ce milieu. Dans les deux cas, on a observé une adsorption et une réaction chimique couplée avec le transfert de charge. On a établi la concentration optimale en dépolarisant et la vitesse d'examen pour la détermination analytique. On a trouvé des similitudes étroites dans le comportement électrochimique de Al(III) et Be(II), et les différences sont dans le degré plutôt que dans la nature.

REFERENCES

1. I. Prajzler, *Collection Czech. Chem. Commun.*, 1931, **3**, 406.
2. I. P. Gokhstein, *Zavodsk. Lab.*, 1936, **5**, 28, 158.
3. B. A. Heller and A. M. Zanko, *ibid.*, 1939, **8**, 1030.
4. A. A. Kozlova and M. A. Portnov, *ibid.*, 1940, **9**, 287.
5. H. W. Hodgson and I. H. Glover, *Analyst*, 1951, **76**, 706.
6. M. Ishibashi and T. Fujinaga, *Nippon Kagaku Zasshi*, 1952, **73**, 5381.
7. G. F. Reynolds and T. I. Weber, *Anal. Chim. Acta*, 1958, **19**, 293, 406.
8. M. Perkins and G. F. Reynolds, *ibid.*, 1958, **8**, 616.
9. M. Heyrovský, *Advan. Polarog.*, 1960, **3**, 854.
10. Idem, *Collection Czech. Chem. Commun.*, 1960, **25**, 3120.
11. S. Field, *The Principles of Electrodeposition*, 2nd Ed., p. 102. Pitman, London, 1949.
12. H. Dehn, G. Gritzner and V. Gutmann, *Microchim. Acta*, 1967, 426.
13. H. Dehn, V. Gutmann and G. Schöber, *ibid.*, 1962, 959.
14. G. P. Kumar and D. A. Pantony, *J. Polarog. Soc.*, 1968, **14**, 84.
15. J. Heyrovský and S. Berezický, *Collection Czech. Chem. Commun.*, 1929, **1**, 19.
16. W. Kemula and M. Michalski, *ibid.*, 1933, **5**, 536.
17. K. Györbíró, *Acta Chim. Acad. Sci. Hung.*, 1960, **22**, 225.
18. *Idem*, *Mag. Kem. Folyoirat*, 1959, **65**, 354.
19. G. P. Kumar and D. A. Pantony, *Proc. Third Intern. Congr. Polarography*, Ed. G. J. Hills, p. 1061. Macmillan, London, 1964.
20. D. S. Polcyn and I. Shain, *Anal. Chem.*, 1966, **38**, 370.
21. R. Brdička, *Collection Czech. Chem. Commun.*, 1947, **12**, 522.
22. R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.

Talanta, 1971, Vol. 18, pp. 1217 to 1223. Pergamon Press. Printed in Northern Ireland

INTERACTION OF COBALT(II) CHLORIDE WITH 2-NITROSO-1-NAPHTHOL IN A 96:4 BENZENE–ETHANOL SOLUTION

VINCENZO CARUNCHIO, ALESSANDRO BONDOLI and MARIA ANTONIA FOGAROLI
Institute of Analytical Chemistry, University of Rome, Rome, Italy

(*Received* 11 *May* 1971. *Accepted* 9 *June* 1971)

Summary—The cobalt(II) chloride–2-nitroso-1-naphthol system has been studied spectrophotometrically in a 96:4 (v/v) benzene–ethanol solution. Two species have been found, the M:L complexation ratios of which are 1:1 and 1:2. The concentration quotients of the formation equilibria are $K_1 = 1{\cdot}2 \times 10^3$ and $K_2 = 1{\cdot}4 \times 10^4$ respectively. The first step of the reaction is accompanied by a configurational change from a tetrahedral to an octahedral structure.

TETRAHEDRAL–OCTAHEDRAL equilibria of cobalt(II) compounds can be affected by several factors. Among these particular interest has been given to the donor power of the solvents and ligands as well as to the dielectric properties of the former.[1]

In ethanol the predominant species of cobalt(II) chloride has a tetrahedral co-ordination, according to the formula $[CoCl_2{\cdot}2(C_2H_5OH)]$.[2,3] The addition of 2-nitroso-1-naphthol to this solution produces a colour change from blue to pink, which can be attributed to the displacement of the configurational equilibrium to the octahedral form. To obtain information on the path of this reaction a spectrophotometric study on the composition and stability of the species present in solution has been conducted. A 96:4 (v/v) benzene–ethanol solution was used as a solvent; cobalt(II) chloride is almost insoluble in benzene and 4% represents the lowest quantity of ethanol required to yield a convenient concentration of this salt in solution. The use of such a mixture was preferred to that of absolute ethanol, since the co-ordination power of the benzene is almost insignificant. Thus the interaction between the solvent and the competitive ligand is less evident and the complex dissociation and autocomplex formation are negligible.[4] Moreover, the low dielectric constant of the mixture with respect to that of ethanol reduces the ionization of the complex species, even if the latter would be formed on autocomplexation. Thus the monomeric and non-ionized species should be predominant.

EXPERIMENTAL

Reagents

All chemicals were analytical grade commercial products.

Ethanol and benzene. These were dehydrated and purified by distillation over sodium.

Anhydrous cobalt(II) chloride. This was obtained by dehydration of the corresponding hexahydrate at 110° for 16 hr.

2-*Nitroso*-1-*naphthol.* Its purity was checked by ascending chromatography with absolute ethanol on a Whatman No. 2 paper.

The water content of the products used was determined by the dead-stop end-point method, using Karl Fischer reagent[5] and was less than 0·0005% in all cases. All solutions were prepared in a dry-box under an atmosphere of dry nitrogen.

Apparatus

Spectrophotometers. Ultraviolet and visible spectra were recorded at 25 ± 0·1° on Beckmann DU and DK-2A spectrophotometers, using 10·0-mm quartz cells.

RESULTS

The absorption spectra of cobalt(II) chloride and 2-nitroso-1-naphthol solutions are shown in Fig. 1, along with the spectrum of a 1:8 molar ratio mixture of the two (recorded after the maximum absorbance value in the 500 nm region had been reached, *i.e.* after at least 48 hr).

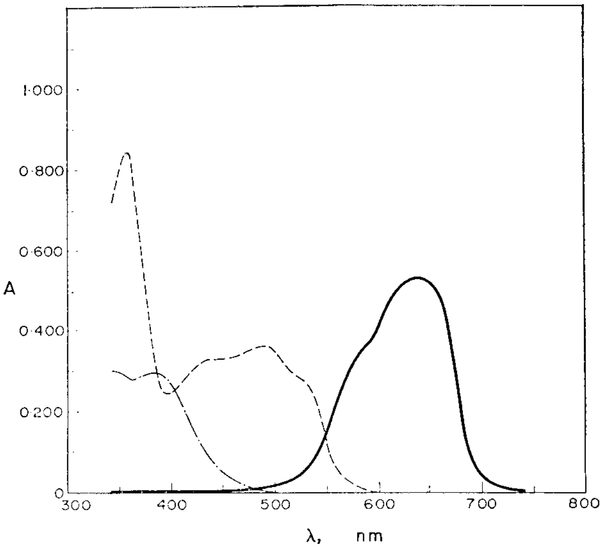


FIG. 1.—Absorption spectra in 96:4 benzene–ethanol mixture of:
————— $2{\cdot}5 \times 10^{-3}M$ $CoCl_2$ (blank—solvent)
— · — · — $8{\cdot}0 \times 10^{-5}M$ 2-nitroso-1-naphthol (blank—solvent)
– – – – – – $2{\cdot}4 \times 10^{-5}M$ $CoCl_2$ + $2{\cdot}0 \times 10^{-4}M$ 2-nitroso-1-naphthol (blank—$1{\cdot}5 \times 10^{-4}M$ 2-nitroso-1-naphthol, taking into account the ligand consumed in the complexation reactions).

The spectrophotometric investigation was performed at 510 nm, where the solutions containing either the metal or the naphthol do not show an appreciable absorbance. The method used was that of the straight-line, modified by Klausen and Langmyhr,[6] which permits the identification of the complex species in the solution and the calculation of their complexation indices as well as the concentration quotients of the equilibria. The choice of this method was suggested by the shape of the $A = f(C_L)_{C_M}$ curve (Fig. 2), which shows a large range where the complex species are dissociated.

Figures 3 and 4 show the curves of the Asmus function to detect the ligand index, when the initial molar ratio L/M is in the range from 0·4 to 10·0. The Asmus function for metal index is reported in Fig. 5, where the values refer to solutions with initial molar ratio M/L between 0·4 and 15·0. Examination of Figs. 3–5 indicates that two species are detectable with formation ratio M/L 1:1 and 1:2, respectively. Such species correspond to the intervals where the functions show a straight line. The predominance of one species over the other depends on the initial metal–ligand concentration ratio. Actually the 1:1 species prevails when $C_M/C_L \geq 1{:}0{\cdot}8$, while the 1:2 complex predominates when $C_M/C_L \leq 1{:}2{\cdot}3$. For the C_M/C_L ratios between these values neither species seems to prevail (*b* zones of the figures). These data quantitatively confirm the existence of two species which can be predicted by considering Fig. 2. Futhermore the complexation molar ratio M/L of the detected species was verified by the continuous variations method;[7] the results obtained (Fig. 6) are in perfect agreement with those described above.

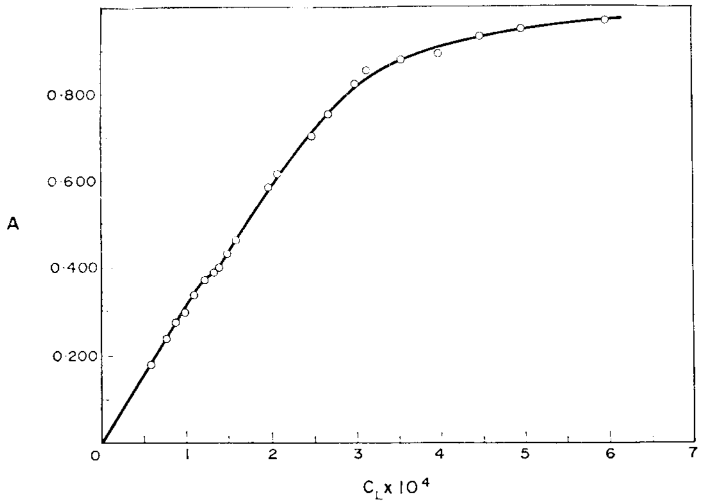


FIG. 2.—Mole-ratio method with constant metal concentration (λ = 510 nm, τ = 25°C) for the cobalt(II) chloride–2-nitroso-1-naphthol system in a 96:4 benzene–ethanol solution.
$C_M = 6{\cdot}0 \times 10^{-5}M$; $C_L = 0{\cdot}6–6{\cdot}0 \times 10^{-4}M$. Blank—solvent mixture.

The concentration quotients of the two complexes were determined by the straight line method[6] and gave $K_1 = 1{\cdot}2 \times 10^3$ and $K_2 = 2{\cdot}4 \times 10^4$, respectively.

DISCUSSION

The results show that, under the conditions described, the spectrophotometric method used permits detection of two compounds in the cobalt(II) chloride–2-nitroso-1-naphthol system in 96:4 benzene–ethanol solution, though no appreciable change in the shape of the absorption spectra of the solutions is observed as the ratio C_M/C_L is varied. Both compounds are characterized by the presence of two absorption maxima in the 450–550 nm range, which is typical of $CoCl_2X_4$ class compounds (X = solvent molecule). At the same time, the absence of the absorption band in the 600–700 nm region excludes the presence of tetrahedral species of the $CoCl_2X_2$ type.[2]

As the starting compound has been attributed the formula $[CoCl_2 . 2(C_2H_5OH)]$, the configurational change caused by addition of 2-nitroso-1-naphthol is imputable to the higher basicity of this ligand with respect to that of ethanol.

The analysis of the system gives evidence on the two steps of the reaction between

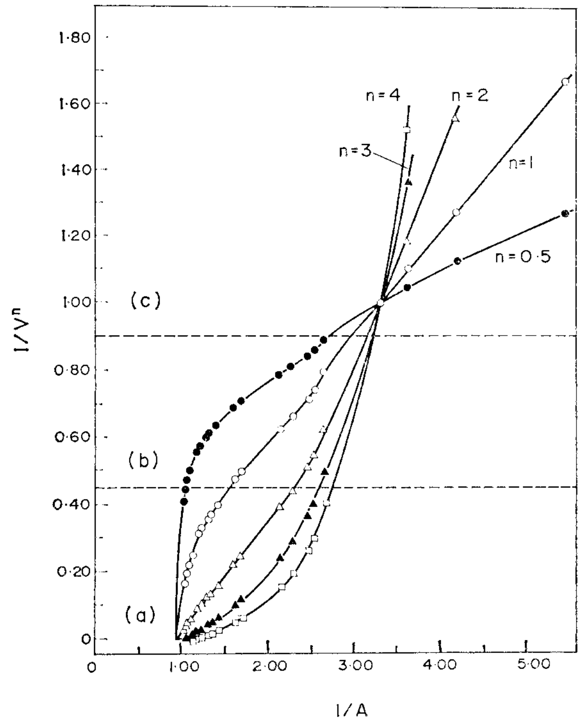


FIG. 3.—Straight-line method with constant metal concentration (λ = 510 nm, τ = 25°C) for the cobalt(II) chloride–2-nitroso-1-naphthol system in a 96:4 benzene–ethanol solution. $C_M = 6{\cdot}0 \times 10^{-5}M$; $C_L = 0{\cdot}6$–$6{\cdot}0 \times 10^{-4}M$. Blank—solvent mixture.

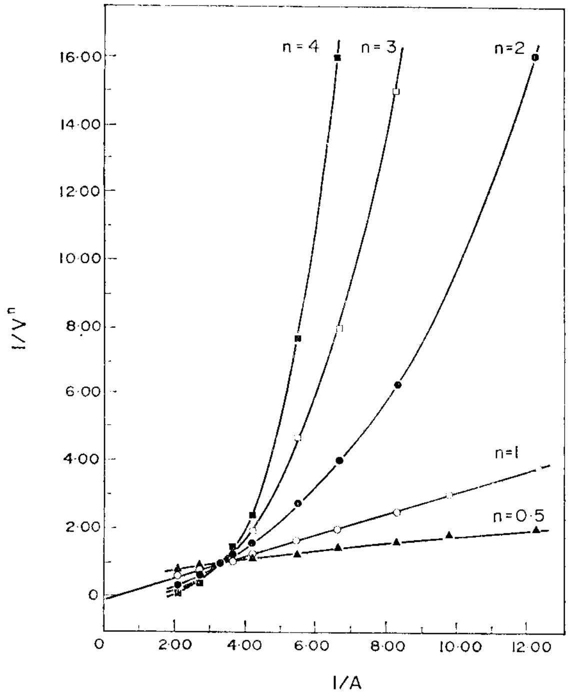


FIG. 4.—Straight-line method with constant metal concentration (λ = 510 nm, τ = 25°) for the cobalt(II) chloride–2-nitroso-1-naphthol system in a 96:4 benzene–ethanol solution. $C_M = 6{\cdot}0 \times 10^{-5}M$; $C_L = 0{\cdot}25$–$1{\cdot}60 \times 10^{-4}M$. Blank—solvent mixture.

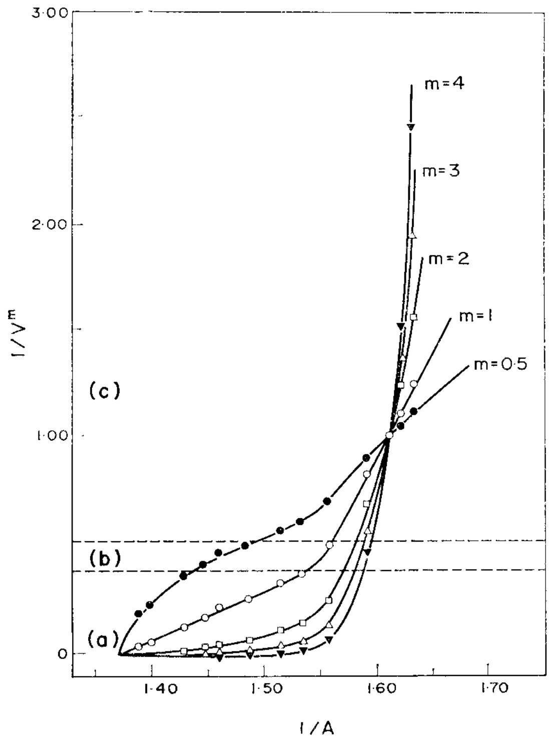


FIG. 5.—Straight-line method with constant ligand concentration (λ = 510 nm, τ = 25°C) for the cobalt(II) chloride–2-nitroso-1-naphthol system in a 96:4 benzene–ethanol solution.

C_M = 0·08–3·0 × $10^{-3}M$; C_L = 2·0 × $10^{-4}M$. Blank–solvent mixture.

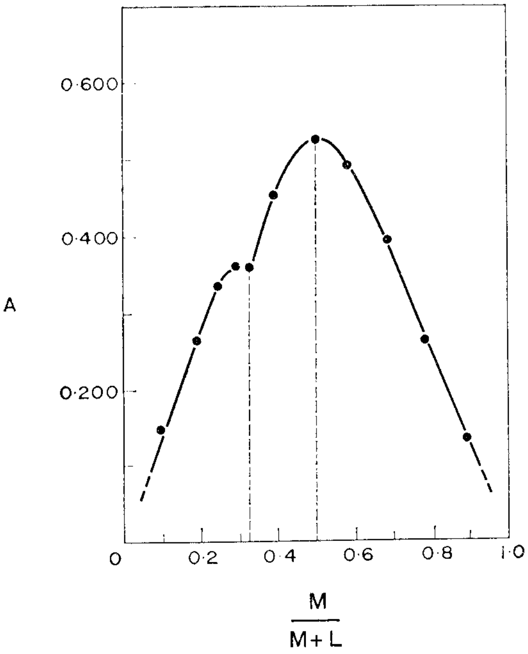
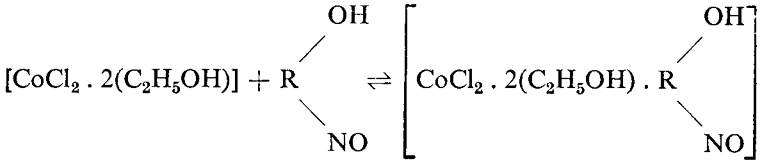


FIG. 6.—Continuous variations method for cobalt(II) chloride–2-nitroso-1-naphthol system in a 96:4 benzene–ethanol solution.

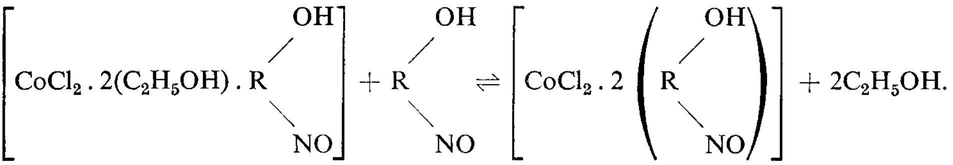
C_M + C_L = $10^{-4}M$. Blank—solvent mixture.

cobalt(II) chloride and 2-nitroso-1-naphthol. When the ligand is in deficit, it can be supposed that the addition reaction



$$[\mathrm{CoCl_2}\,.\,2(\mathrm{C_2H_5OH})] + \mathrm{R}\begin{array}{l}\diagup\mathrm{OH}\\ \diagdown\mathrm{NO}\end{array} \rightleftharpoons \left[\mathrm{CoCl_2}\,.\,2(\mathrm{C_2H_5OH})\,.\,\mathrm{R}\begin{array}{l}\diagup\mathrm{OH}\\ \diagdown\mathrm{NO}\end{array}\right] \tag{1}$$

[R(OH)NO is 2-nitroso-1-naphthol] takes place with the formation of a species in which naphthol acts as a bidentate chelating agent through an oxygen and a nitrogen donor atom. Increasing the amount of 2-nitroso-1-naphthol gives rise to the next step of the reaction, in which the following substitution occurs:



$$\left[\mathrm{CoCl_2}\,.\,2(\mathrm{C_2H_5OH})\,.\,\mathrm{R}\begin{array}{l}\diagup\mathrm{OH}\\ \diagdown\mathrm{NO}\end{array}\right] + \mathrm{R}\begin{array}{l}\diagup\mathrm{OH}\\ \diagdown\mathrm{NO}\end{array} \rightleftharpoons \left[\mathrm{CoCl_2}\,.\,2\left(\mathrm{R}\begin{array}{l}\diagup\mathrm{OH}\\ \diagdown\mathrm{NO}\end{array}\right)\right] + 2\mathrm{C_2H_5OH}. \tag{2}$$

It should be noted that the absorption spectra of the complexes found here in 96:4 benzene–ethanol exclude oxidation reactions of the central metal atom, since the band in the 500 nm region is split into two components, in a similar way to that of some other octahedral compounds of cobalt(II).[8]

On the basis of the scheme of reactions (1) and (2), K_1 can also be regarded as the concentration quotient of a configurational equilibrium, the determined value of which is of the same order as those known for similar complexes.[9]

The fact that K_1 is less than K_2 can be explained in terms of entropy variation, if the decreased stability of octahedral complexes with respect to tetrahedral ones is taken into account.[10]

The solvent mixture has low values for both its donor property and dielectric constant. These properties minimize the solvent-dependent side-reactions. Thus, it has been possible to determine the concentration quotients in the mixture used, whilst in an aqueous or partially aqueous media Callahan *et al.*[11] found a negative value for the formation constant of the system and attributed the failure to obtain the real value to the occurrence of hydrolysis, precipitation, oxidation or polymerization reactions.

The high molar absortivity of the complex species may raise consideration of the suitability of such a system for cobalt determination. Actually, in the 525 nm region ε is about $1{\cdot}5 \times 10^3$ $\mathrm{l.mole^{-1}.mm^{-1}}$, nearly equal to that obtained for the cobalt–nitroso R salt complex in water.[12] On the other hand, even if the latter method at 370 nm gives a molar absorptivity higher than that obtained with our system, the considerable ligand absorbance at this wavelength makes it unfavourable for analytical purposes.

Acknowledgment—This work was encouraged by Prof. G. De Angelis and supported by the financial aid of Consiglio Nazionale delle Ricerche (Roma), which also gave a grant for one of us (A. B.).

Zusammenfassung—Das System Kobalt(III)-chlorid-2-Nitroso-1-naphthol wurde spektrophotometrisch in einer Benzol-Athanol-lösung (96:4,v/v) untersucht. Zwei Spezies wurden gefunden mit den M:L-Verhältnissen 1:1 und 1:2. Die Konzentrations-quotienten des Bildungsgleichgewichts betragen $K_1 = 1.2 \cdot 10^3$ bzw. $K_2 = 1.4 \cdot 10^4$. Der erste Reaktionsschritt ist mit einer Konfigurationsänderung von tetraedrischer zu oktaedrischer Struktur verbunden.

Résumé—On a étudié spectrophotométriquement le système chlorure de cobalt(III)-2-nitroso 1-naphtol dans une solution benzène-éthanol 96:4 (v/v). On a trouvé deux espèces, dont les rapports de complexation M:L sont 1:1 et 1:2. Les quotients de concentration de l'équilibre de formation sont $K_1 = 1{,}2 \times 10^3$ et $K_2 = 1{,}4 \times 10^4$ respectivement. Le premier stade de la réaction est accompagné par un changement de configuration d'une structure tétraédrique en une structure octaédrique.

REFERENCES

1. For an extensive survey on the argument see: L. I. Katzin in R. L. Carlin, *Transition Metal Chemistry*, *Vol.* 3, p. 56. Dekker, New York, 1966.
2. L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, 1950, **72,** 5464.
3. C. Oldham, J. G. Oliver and I. J. Worrall, *Inorg. Nucl. Chem. Letters*, 1969, **5,** 241.
4. V. Gutmann, *Coordination Chemistry in Non-aqueous Solutions*, Chap. 2, Springer Verlag, New York, 1968.
5. I. Gyenes, *Titration in Nonaqueous Media*, p. 139. Van Nostrand, London, 1967.
6. K. S. Klausen and F. J. Langmyhr, *Anal. Chim. Acta*, 1963, **28,** 501.
7. P. Job, *Ann. Chim.*, 1928, **9,** 113.
8. C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, 1959, **9,** 397.
9. W. Libus and I. Uruska, *Inorg. Chem.*, 1966, **5,** 256.
10. L. E. Orgel, *An Introduction to Transition-Metal Chemistry, Ligand-Field Theory*, Chap. 5. Methuen, London, 1966.
11. C. M. Callahan, W. C. Fernelius and B. P. Block, *Anal. Chim. Acta*, 1957, **16,** 101.
12. G. C. Lalor, *J. Inorg. Nucl. Chem.*, 1969, **31,** 1783.

Talanta, 1971, Vol. 18, pp. 1225 to 1232. Pergamon Press. Printed in Northern Ireland

A CATALYTIC METHOD FOR THE DETERMINATION OF COBALT IMPURITIES IN REACTOR COOLING-WATER CIRCUITS

G. E. Batley
Australian Atomic Energy Commission, Research Establishment, Lucas Heights
N.S.W. Australia

(*Received* 17 *March* 1971. *Accepted* 15 *July* 1971)

Summary—Metal impurities in reactor cooling-water circuits must be kept to a minimum. A method is described for the determination of trace levels of cobalt in water samples, based on catalysis of the hydrogen peroxide oxidation of Alizarin Red S. The determination is carried out at pH 11·0 in a phosphate buffer under conditions where the reaction rate is a maximum. Interfering impurities are removed by an ion-exchange separation. The method enables cobalt to be determined in water samples down to 10^{-4} μg/ml, or 5×10^{-5} μg/ml in samples where an ion-exchange separation is not required.

Hydrogen peroxide oxidation reactions have formed the basis for a large number of catalytic methods of analysis.[1] These reactions involve compounds such as aminoazo dyes, hydroxyamines, halogens, hydroxyanthraquinones and fluorone derivatives, the oxidation of which proceeds slowly at room temperature. The hydrogen peroxide oxidation of these compounds is readily catalysed by trace quantities of many metal ions. Such reactions can form the basis of satisfactory methods for the determination of metal ions at the parts per milliard (ppM) level and have important applications in reactor technology.

It is of particular importance that metal impurities in reactor cooling-water circuits be controlled at a minimum level. Trace quantities of cobalt ion can accumulate on the fuel elements and form metal spinels. Resultant build-up of ^{60}Co in reactor components presents a severe hazard during reactor maintenance.

For the determination of cobalt at the ppM-level, the catalysed oxidation of *o*-dihydroxyanthraquinones by hydrogen peroxide or sodium perborate has received considerable attention, in particular by workers in Hungary and the U.S.S.R.[2–7] The mechanism of the reaction is still not fully understood.

An analytical procedure for the determination of cobalt, based on the oxidation of alizarin was first reported by Parkhomenko, Prik and Yatsimirskii[3] in 1961. The reaction conditions chosen by these workers did not offer the maximum sensitivity, and slight modifications can reduce the limit of detection by a factor of fifty.

Popa and Costache reported methods for cobalt, using 9-phenyl-2,3,7-trihydroxy-6-fluorone[7] and Bordeaux S.[8] Their methods are affected by many impurities but the lower limits of detection claimed are 8×10^{-11} and 3×10^{-9} g of cobalt/ml respectively. Peshkova *et al.*[6] reported methods using alizarin which have a lower limit of 5×10^{-11} g of cobalt/ml.

Methods using alizarin can be unreliable because of decomposition of the dye in the alkaline solutions which are necessary to dissolve it. As is true for most catalytic methods, they are also not specific for cobalt but are catalysed by a number of other metal ions.

Most of the methods so far reported are suitable only for the analysis of pure cobalt solutions unless rather elaborate precautions are taken to mask impurities. Unfortunately most masking agents seriously interfere with the catalytic reaction, while satisfactory separations often involve lengthy procedures.

We have found that the ion-exchange method described below provides a suitable means of removing those interfering impurities likely to be encountered in reactor cooling-water or tap-water samples. The dye used is Alizarin Red S (1,2-dihydroxyanthraquinone-3-sulphonic acid).

EXPERIMENTAL

Apparatus

A Cary 16 spectrophotometer with 10-mm silica cells was used for all absorbance measurements; pH measurements were made on a Vibron pH Meter Model 39A. All physical measurements were carried out in a laboratory maintained at 25° ± 1°.

Reagents

All chemicals used were analytical-reagent grade. Hydrogen peroxide was used as a $4\cdot41M$ solution. Recrystallized cobalt nitrate was used to prepare a $10^{-2}M$ cobalt solution from which stock solutions of $4 \times 10^{-5}M$ and $4 \times 10^{-7}M$ were prepared by dilution. Indicator-grade Alizarin Red S [ARS] was purified by several recrystallizations from 50% aqueous ethanol and used as a $1\cdot5 \times 10^{-3}M$ aqueous solution.

Buffer solutions were prepared from recrystallized sodium tetraborate decahydrate and anhydrous disodium hydrogen phosphate. Sodium hydroxide was further purified by controlled potential mercury cathode electrolysis of a $3M$ aqueous solution at $-1\cdot0$ V *vs.* S.C.E.

Distilled demineralized water was used throughout.

Ion-exchange separations were carried out on 3-mm-bore columns packed to a depth of 40 mm with Amberlite CG400 ion-exchange resin of 100–200 mesh.

Concentrated hydrochloric acid for use in the ion-exchange column was purified by passing it through a large column of the anion-exchange resin used in the standard method.

Measurement of reaction rates

The rate of oxidation of Alizarin Red S by hydrogen peroxide was followed by measuring the decrease in absorbance of the dye with time. The solution for each reaction was prepared by mixing, in a 25-ml volumetric flask, 5 ml of $0\cdot2M$ disodium hydrogen phosphate buffer, enough $2M$ sodium hydroxide to adjust the pH to 11, 1 ml of $1\cdot5 \times 10^{-3}M$ Alizarin Red S and the required volume of $4 \times 10^{-7}M$ cobalt solution. The mixture was diluted to about 20 ml with distilled water. Then 1 ml of $4\cdot41M$ hydrogen peroxide was added and the solution made up to volume with distilled water and shaken, and the timer started. The solution was transferred to the spectrophotometer cell and absorbance measurements were commenced as soon as possible, readings being recorded every 15 sec for 3 min. From plots (Fig. 1) of log absorbance *vs.* time for several cobalt concentrations in the range 1×10^{-9}–$2 \times 10^{-8}M$ a calibration curve of slope against cobalt concentration was prepared.

Ion-exchange method

To an aliquot of the cobalt-containing solution was added purified concentrated hydrochloric acid until the acid concentration was greater than $8M$. The mixture was then passed through the small column containing anion-exchange resin, which had previously been converted into the chloride form by washing with hydrochloric acid. The eluate was discarded. The cobalt retained on the column was eluted with 50 ml of distilled water, and the eluate evaporated to approximately 15 ml. The phosphate buffer (5 ml, $0\cdot2M$) was added, followed by 1 ml of $1\cdot5 \times 10^{-3}M$ Alizarin Red S. Sodium hydroxide solution was added to adjust the pH to 11·0. The hydrogen peroxide used in this work contained sulphuric acid as stabilizer and it was therefore necessary to add additional alkali so that the pH after peroxide was added would still be 11·0. This additional quantity was determined by trial and error. The solution was then treated as before, diluting to about 20 ml, then adding peroxide and making the volume up to 25 ml with distilled water.

It was necessary to prepare a calibration graph from the results obtained from passing standard cobalt solutions through the resin.

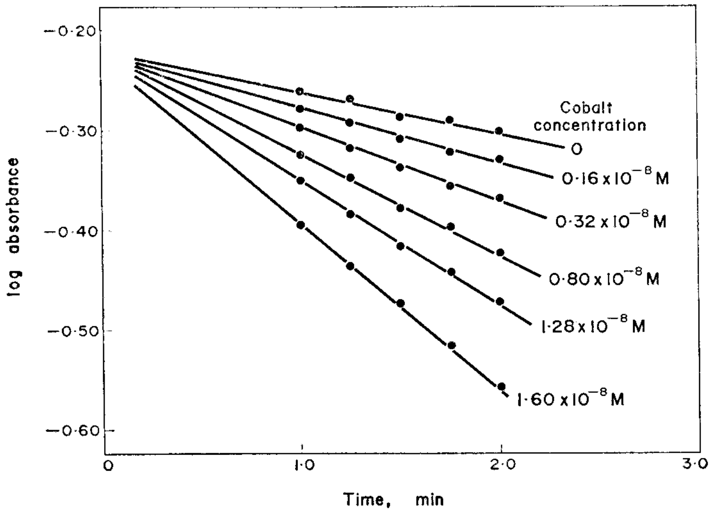


FIG. 1.—Variation of log absorbance with time for the cobalt-catalysed oxidation of Alizarin Red S.
$[H_2O_2] = 0{\cdot}176M$, $[ARS] = 6{\cdot}2 \times 10^{-5}M$, pH 11·0 phosphate buffer.

RESULTS AND DISCUSSION

The theory of the catalytic method of analysis has been thoroughly discussed.[1,9,10] In brief the method relies on the selection of conditions such that the reaction is pseudo first-order with respect to catalyst concentration. These conditions are: a hydrogen peroxide concentration which is large and effectively constant, a solution maintained at a constant pH, and a concentration of Alizarin Red S at least 1/50 that of the peroxide concentration. The rate of reaction of Alizarin Red S is followed spectrophotometrically. The rate constant, measured over the initial stages of the reaction from the slope of the plot of log absorbance against time, is usually expressed as $\tan \alpha$. The rate of the reaction in the absence of catalyst is referred to as $\tan \alpha_0$. The calibration plot follows the equation

$$-\tan \alpha = KC - \tan \alpha_0$$

where C is the cobalt concentration and K a constant.

The cobalt-catalysed reaction rate shows a marked dependence on the pH and on the purity and chemical composition of buffer solutions. Initially we examined a number of buffer solutions (Table I). Differences in purity of chemicals used were readily detectable by their effect on the rate of the non-catalysed reaction. The catalytic reaction was appreciably retarded in the presence of ammonia buffers while the use of potassium instead of sodium salts of the same anion produced almost a three-fold decrease in rates. Solutions of sodium hydroxide and sodium carbonate were found to be difficult to purify and gave very rapid reactions in both the presence and absence of cobalt. In these solutions the reactions departed from first-order dependence on cobalt concentration, making them unsuitable for analytical use.

The pH-dependence of the reaction rate was investigated in both phosphate and borate buffer systems in the pH range 9–12 (Fig. 2). In borate buffers there was no significant increase in $\tan \alpha$ until pH 9·5, and a maximum value was reached at

TABLE I.—RATE MEASUREMENTS OF COBALT-CATALYSED OXIDATION OF ALIZARIN RED S IN DIFFERENT BUFFER SYSTEMS

Buffer	$10^3 \times \tan\alpha$ Cobalt-catalysed	$10^3 \times \tan\alpha$ Non-catalysed	$10^3 \times \Delta\tan\alpha$
0·1*M* borax	1·8	1·0	0·8
0·1*M* Na_2HPO_4*	19·0	1·8	17·2
0·1*M* Na_2HPO_4†	47·0	17·0	30·0
0·1*M* K_2HPO_4	9·6	4·5	5·1
0·1*M* Na_2CO_3‡	99·0	10·0	89·0
0·1*M* NaOH‡	107·2	19·8	87·4
0·1*M* KOH‡	34·0	18·0	16·0

$[Co^{2+}] = 4{\cdot}8 \times 10^{-9}M$; $[H_2O_2] = 0{\cdot}088M$; $[ARS] = 6{\cdot}2 \times 10^{-5}M$.

* Prepared from B.D.H. anhydrous Na_2HPO_4.

† Prepared from recrystallized AR $Na_2HPO_4.12H_2O$ (Standard Laboratories, Australia).

‡ Measurements in high pH solutions showed departures from first-order rate.

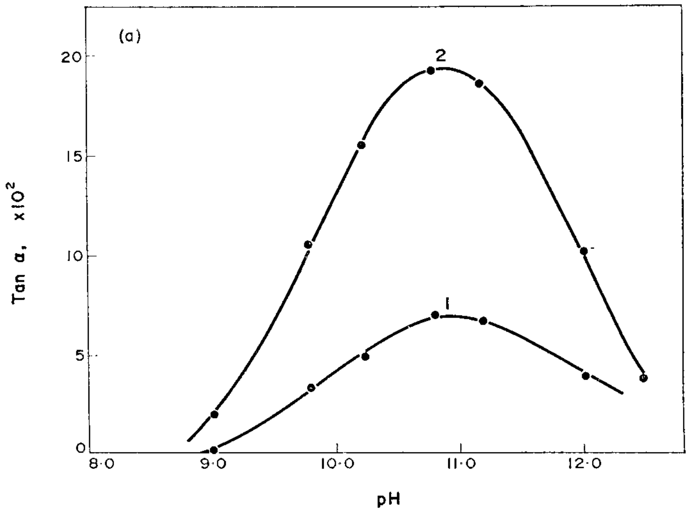
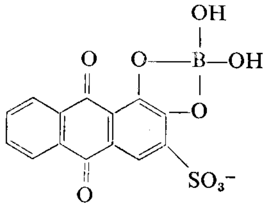


FIG. 2(a).

pH 10·8. In phosphate buffers the maximum rate occurred at pH 10·9 with measurable rate increases occurring from pH 8·9. It is known that borax forms complexes with *o*-diphenols.[11] The reaction between Alizarin Red S and borax leads to the formation of compound I.



I

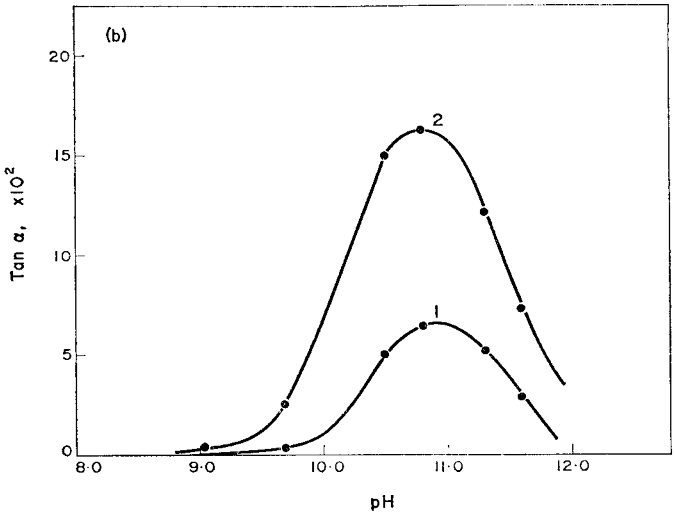


FIG. 2(b).

FIG. 2.—Effect of varying the pH on the catalysed oxidation of Alizarin Red S in phosphate buffer (2(a)) and in borax buffer (2(b)). In each case: $[H_2O_2] = 0{\cdot}172M$, $[ARS] = 6{\cdot}2 \times 10^{-5}M$.
(1) No cobalt
(2) $[Co] = 1{\cdot}6 \times 10^{-6}M$.

This complex is a weaker acid than the original dye, having p*K* values which we determined as 10·7 and 11·1 compared with 7·3 and 11·8 for the dye in the absence of borax.[12] Thus under the conditions chosen by Parkhomenko *et al.*[2] the use of a borax buffer is far from desirable. In the first instance their conditions (pH 9·2) were such that the rate of reaction was 1/80 or less of what it would be at pH 10·8. Also, at the wavelength of 430 nm used by these workers and at pH 9·2, Alizarin Red S exists as the yellow undissociated complex with molar absorptivity (ε) 750 $\text{l.mole}^{-1}.\text{mm}^{-1}$. At pH 11·0 in phosphate buffer, $\varepsilon = 1{\cdot}04 \times 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$ at 525 nm and $1{\cdot}50 \times 10^3$ at 555 nm. For maximum sensitivity it is preferable to work at wavelengths where the molar absorptivity, and therefore change in absorbance, is a maximum.

The rates of both the catalysed and non-catalysed reactions are shown in Fig. 2 as a function of pH. One would not expect the same variation in the rate of the non-catalysed reaction with pH and the changes observed are attributed to traces of cobalt present in these blank solutions.

As shown previously,[2] the dependence of reaction rates on hydrogen peroxide concentration is approximately first-order, reaching a limiting value beyond which further increase of concentration produces only small increases in rate. In our experiments the limiting value of hydrogen peroxide concentration was 0·176*M*, which was therefore used for most experiments (Fig. 3).

It was noted that small changes in salt concentration of the reacting solutions of the order likely to be encountered in pH adjustment of samples did not affect the reaction rate, but large increases appreciably slowed down the reaction (Table II) (possibly because of chloro-complex formation with cobalt).

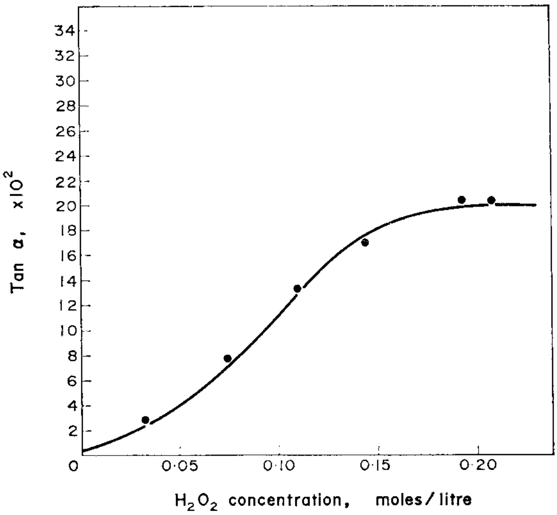


FIG. 3.—Dependence on H_2O concentration of the rate of the catalysed oxidation of Alizarin Red S.
[Co] = $1·6 \times 10^{-8}M$, [ARS] = $6·2 \times 10^{-5}M$, pH 11·0 phosphate buffer.

TABLE II.—EFFECT OF SALT CONCENTRATION ON THE COBALT-CATALYSED OXIDATION OF ALIZARIN RED S

NaCl added *M*	Ionic strength	$10^2 \times \tan\alpha$		$10^2 \times \Delta \tan\alpha$
		Cobalt-catalysed	Non-catalysed	
0	0·20	63·2	19·6	43·6
0·03	0·23	63·2	19·6	43·6
0·10	0·29	63·6	18·0	45·6
0·15	0·35	60·2	17·5	42·7
0·27	0·47	53·0	16·3	36·7
0·46	0·66	44·3	14·0	30·3

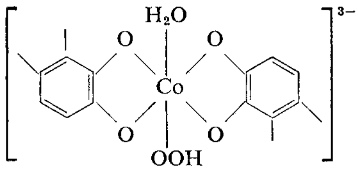
$[Co^{2+}] = 1·6 \times 10^{-8}M$; $[H_2O_2] = 0·088M$; [ARS] = $6·2 \times 10^{-5}M$; pH 10·9; 0·04*M* borax buffer + NaOH

Reaction mechanism

Despite many attempts in the literature to elucidate the mechanism of the catalysed oxidation of organic molecules by hydrogen peroxide, the explanation is still uncertain. The following observations summarize the current theories.

It is believed that metal ions which catalyse peroxide oxidations in alkaline solution are those which can readily change their oxidation state and by reaction with H_2O_2 liberate ·OH, ·OOH, O and OH^+ species. These ions and radicals are in fact the species which oxidize the organic moiety.[1] Further evidence[13] shows that the decomposition of peroxide is pH-dependent, reaching a maximum rate at pH 12. This decomposition is inhibited by alizarin or similar molecules and the presence of traces of cobalt ions both annuls this inhibition and hastens the decomposition of the peroxide. It is assumed that the greater reactivity of *o*-dihydroxy compounds over monohydroxy or *m*-dihydroxy compounds is associated with their ability to form metal complexes, rather than with any differences in ease of oxidation.

Bognar[14] believes that the reaction proceeds *via* an intramolecular attack by OOH^- on the dihydroxyanthraquinone. Both of these compounds are co-ordinated in a complex of the type



The catalytic reaction may involve oxidation of the metal ions although no evidence was provided to support this.

It is known that the addition of cobalt-complexing species to the solutions will inhibit the catalytic reaction. Indeed, attempts to determine cobalt in ammonia buffers failed because of the significant reduction in the catalytic effect of the metal, while in the same buffer solutions manganese can satisfactorily catalyse the oxidation; an analytical method has been based on this observation.[15] This is no doubt a result of the low stability of manganese (II) ammine complexes. Nevertheless the catalytic effect of manganese is still less than that of cobalt in phosphate buffers.

Interferences

A major obstacle to the general acceptance of catalytic methods of analysis has been the lack of specificity for one metal ion. Masking or separation of interfering metals has often proved difficult. Table III lists those ions likely to be encountered in significant concentrations in reactor cooling-circuits or tap-water samples, and the maximum amount of these ions in excess of cobalt which will not significantly interfere with the cobalt determination. Of major concern is the presence of high levels of alkaline earth metals.

TABLE III.—EFFECT OF ADDED METAL IONS ON THE COBALT-CATALYSED OXIDATION OF ALIZARIN RED S

Metal (M^{n+})	Maximum tolerable concentration, M	$\frac{[M^{n+}]}{[Co^{2+}]}$
Fe^{3+}	$1\cdot6 \times 10^{-5}$	2000
Cr^{3+}	$2\cdot4 \times 10^{-5}$	3000
Cu^{2+}	$4\cdot0 \times 10^{-6}$	500
Ca^{2+}	$3\cdot2 \times 10^{-6}$	400
Mg^{2+}	$3\cdot2 \times 10^{-6}$	400
Ni^{2+}	$4\cdot8 \times 10^{-7}$	60
Mn^{2+}	$1\cdot2 \times 10^{-6}$	150

$[Co^{2+}] = 0\cdot8 \times 10^{-8}M$; $[H_2O_2] = 0\cdot176M$; phosphate buffer, pH 11·0.

Extraction procedures involving cobalt-complexing species such as Aliquat-336 or α-nitroso-β-naphthol have the disadvantage that in order to prevent interference from the complexing agent the extract must be fumed with acid before the determination. The procedure can be shortened if an ion-exchange separation is used. It was found that by passing the cobalt sample in 8–10M hydrochloric acid[16] through an anion-exchange resin (Amberlite CG400) interferences due to large amounts of Ca^{2+} and Mg^{2+} could be removed, the cobalt being retained on the resin. The cobalt was eluted with water (50 ml) and the solution used for the catalytic determination, after evaporation to a volume of about 15 ml. A linear calibration graph was obtained over a large range of concentrations. It is important to calibrate the method by passing standard solutions through the resin, since there is some reduction in rate, due most probably to the increased salt concentration of the solution caused by neutralization of hydrochloric acid eluted from the resin.

Precision and limits of detection

The determination of cobalt by the peroxide-catalysed oxidation of Alizarin Red S has a relative standard deviation of 7% for a cobalt concentration of 10^{-4} μg/ml, and 20% for concentrations of 5×10^{-5} μg/ml and 10^{-3} μg/ml, these latter concentrations representing conditions where the reaction is respectively very slow and very fast. The detection limit beyond which errors in rate measurement become excessively large is 5×10^{-5} μg of cobalt/ml.

By the ion-exchange separation method, the lower limit of detection is 10^{-4} μg of cobalt/ml. The relative standard deviation is 11% for 10^{-3} μg/ml and 20% for 10^{-4} μg/ml and 5×10^{-3} μg/ml, calculated from six determinations in each case.

Zusammenfassung—Die Metall-Verunreinigungen in den Kühlwasserkreisläufen von Reaktoren mussen moglichst gering gehlaten werden. Ein Verfahren zur Bestimmung von Spurenmengen Kobalt in Wasserproben wird beschrieben, das auf der Katalyse der Oxidation von Alizarinrot S mit Wasserstoffperoxid beruht. Die Bestimmung wird bei pH 11.0 in Phosphatpuffer unter Bedingungen ausgeführt, unter denen die Reaktionsgeschwindigkeit maximal ist. Störende Verunreinigungen werden durch Ionenaustausch entfernt. Das Verfahren erlaubt die Bestimmung von Kobalt in Wasserproben bis hinunter zu 10^{-1} ng/ml oder $5 \cdot 10^{-2}$ ng/ml in Proben, wo keine Ionenaustausch-Abtrennung notwendig ist.

Résumé—Les impuretés métalliques dans les circuits de refroidissement par eau des réacteurs doivant être maintenues à une valeur minimale. On décrit une méthode pour la détermination de traces de cobalt dans des échantillons d'eau, basée sur la catalyse de l'oxydation par l'eau oxygénée du Rouge d'Alizarine S. La détermination est menée à pH 11,0 dans un tampon phosphate dans des conditions où la vitesse de réaction est à un maximum. Les impuretés gênantes sont éliminées par une séparation par échange d'ions. La méthode rend possible la détermination du cobalt dans des échantillons d'eau jusqu'à 10^{-4} μg/ml, ou 5×10^{-5} μg/ml dans les échantillons pour lesquels une séparation par échange d'ions n'est pas nécessaire.

REFERENCES

1. K. B. Yatsimirskii, *Kinetic Methods of Analysis*, pp. 83–102. Pergamon, Oxford, 1966.
2. N. V. Parkhomenko, G. A. Prik and K. B. Yatsimirskii, *Zh. Analit. Khim.*, 1961, **16**, 599.
3. J. Laszlovsky, *Mikrochim. Acta*, 1961, 289.
4. *Idem, ibid.*, 1962, 441.
5. J. Bognar, *ibid.*, 1961, 90.
6. V. M. Peshkova, I. F. Dolmanova and N. M. Semonova, *Zh. Analit. Khim.*, 1963, **18**, 1228.
7. G. Popa and D. Costache, *Rev. Roum. Chim.*, 1967, **12**, 963.
8. *Idem, ibid.*, 1968, **13**, 573.
9. H. B. Mark, Jr. and G. A. Rechnitz, *Kinetics in Analytical Chemistry*, Interscience, New York, 1968.
10. H. L. Pardue, *Advan. Anal. Chem. Instr.*, 1968, **7**, 141.
11. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, p. 186. Wiley, New York, 1962.
12. T. M. Florence, Y. J. Farrar and H. E. Zittel, *Aust. J. Chem.*, 1969, **22**, 2321.
13. G. M. Nabar, V. A. Shenai and A. J. Mehta, *Indian J. Technol.*, 1966, **4**, 239.
14. J. Bognar, *Acta Chem. Acad. Sci. Hung.*, 1961, **28**, 319.
15. T. J. Janjić, G. A. Milovanović and M. B. Celap, *Anal. Chem.*, 1970, **42**, 27.
16. K. A. Kraus and F. Nelson, *1st Intern. Conf. Peaceful Uses At. Energy*, Paper 837 (1955).

Talanta, 1971, Vol. 18, pp. 1233 to 1235. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

On the distribution coefficient of nickel dimethylglyoximate between an aqueous solution and organic solvents

(*Received* 6 *July* 1971. *Accepted* 1 *August* 1971)

SUCCESSFUL applications of the regular-solution theory to the distribution coefficients of chelating reagents such as β-diketones and oxine and their metal chelates have been made.[1-4]

In the present work, the theory is applied to the distribution of nickel dimethylglyoximate.

EXPERIMENTAL

Reagents

The reagents and the solvents used were all of guaranteed reagent grade and were used without further purification.

A ^{63}Ni radiotracer of 99·9% purity was used.

Distribution measurements of nickel–dimethylglyoxime chelate

A (6-ml) volume of aqueous phase and an equal volume of an organic solvent were equilibrated by shaking in a glass-stoppered vial for 30 min. The aqueous phase contained nickel perchlorate labelled with ^{63}Ni ($2{\cdot}0 \times 10^{-5}M$) and dimethylglyoxime (DG) ($2{\cdot}8 \times 10^{-3}M$). Its pH was maintained at about 10 with sodium hydroxide and its ionic strength was adjusted to be 0·1 with sodium perchlorate. The mixture was then centrifuged for 5 min. An aliquot (0·1 or 1 ml) of the organic phase was transferred to a stainless-steel planchet, heated at 300° to remove excess of DG and counted on a 2π gas-flow counter.

Part of the aqueous phase (2 ml) was transferred to another vial and the nickel in the solution was extracted into an equal volume of chloroform. The radioactivity of the organic extract, which was measured as described above, was taken as that of the aqueous phase.

The distribution coefficients were obtained as the average of three independent runs. The experiments were all carried out in a temperature-controlled room at 20°.

RESULTS AND DISCUSSION

The distribution ratio of nickel, D_M, in terms of molarity is given by:

$$D_M = \frac{D_c{}^0[A^-]^2}{1 + \beta_1[A^-] + \beta_2[A^-]^2} \tag{1}$$

where $D_c{}^0$, β_n and $[A^-]$ represent the distribution coefficient of the nickel–DG chelate, the *n*th overall stability constant of the chelate and the concentration of the anion of DG, respectively. The preliminary experiments showed that the concentration of nickel (10^{-6}–$10^{-4}M$) did not affect the distribution ratio of nickel. The distribution ratio of nickel can be equated to the distribution coefficient of the chelate at pH 7–12 under the experimental conditions,[5] and the pH of the aqueous phase was adjusted to about 10 for experimental convenience.

The distribution coefficients of nickel–DG chelate for 6 inert solvents are given in Table I. The distribution coefficients of the chelate in terms of the mole fraction, $P_c{}^0$, are calculated from $D_c{}^0$ by multiplying by the ratio of the molar volume of an organic solvent to that of water at 20°.

The following formal relationship[1] is given by the regular-solution theory:

$$\log P_c{}^0 = \frac{V_c}{2{\cdot}30RT}(\delta_{aq} + \delta_{org} - 2\delta_c)(\delta_{aq} - \delta_{org}) \tag{2}$$

where V_c is the molar volume of the chelate, δ is the solubility parameter, and the subscripts aq, org and c refer to the aqueous phase, the organic phase and the chelate, respectively.

The distribution data in Table I are successfully interpreted by equation (2). The numerical values obtained by the method of least squares are $V_c = 182$ ml/mole, $\delta_{aq} = 18{\cdot}6$ and $\delta_c = 12{\cdot}9$. In this calculation, the δ values for organic solvents at 25° were used, because the difference of the solubility parameters between 25° and 20° is so small as to be below 0·1 δ unit,[6] and the datum for chloroform was excluded, because the distribution coefficient of the chelate for chloroform was found to be much higher than that expected from the solubility parameter of chloroform. The empirical solubility parameter for an aqueous phase, δ_{aq}, determined in this work is a little larger than those reported elsewhere.[1,3] A study of the factors affecting the empirical solubility parameter for an aqueous phase is under way.

TABLE I.—DISTRIBUTION COEFFICIENTS OF Ni-DG CHELATE FOR INERT ORGANIC SOLVENTS

No.	Solvent	δ^{6}_{org}	log D_c^0 found	log D_c^0 calcd.	log P_c^0 found
1	Chloroform	9·3	2·58	1·92	3·23
2	Methylene chloride	9·7	2·53	2·39	3·08
3	*o*-Dichlorobenzene	10·0	2·27	2·39	3·07
4	Benzene	9·2	1·85	1·78	2·54
5	Carbon tetrachloride	8·6	0·96	1·08	1·69
6	n-Hexane	7·3	−0·79	−0·81	0·07

The distribution coefficients of the chelate, calculated from equation (2) with the three values obtained above, are also given in Table I. These are seen to agree well with the observed values except in the case of chloroform.

In a plot of log $P_c^0/(\delta_{aq} - \delta_{org})$ against δ_{org} practically all the experimental points fall on a single straight line, which is independent of the organic solvents used, as expected from equation (2). In the case of chloroform, a considerable deviation is observed, and a similar trend has also been found in β-diketone[1] and oxine[3] systems with inert solvents. These facts suggest that chloroform has some specific interactions with these solutes and cannot be treated as a simple inert solvent.

S. OKI

Faculty of Engineering
Shizuoka University
Hamamatsu, Japan

Summary—The distribution coefficients of nickel dimethylglyoximate between an aqueous solution and 6 inert solvents were determined at 20°. The distribution coefficients of the nickel chelate were quantitatively interpreted in terms of solubility parameters. The solubility parameter for the nickel chelate was evaluated to be 12·9, that for the aqueous solution to be 18·6, and the molar volume of the chelate to be 182 ml/mol.

Zusammenfassung—Die Verteilungskoeffizienten von Nickeldimethylglyoximat zwischen einer wäßrigen Lösung und 6 inerten Lösungsmiteln wurden bei 20° bestimmt. Die Verteilungskoeffizienten des Nickelchelats wurden quantitativ an Hand von Löslichkeitsparametern interpretiert. Der Löslichkeitsparameter des Nickelchelats beträgt 12·9, der der wäßrigen Lösung 18·6, das Molvolumen des Chelats 182 ml/mol.

Résumé—On a déterminé les coefficients de partage à 20° du diméthylglyoximate de nickel entre une solution aqueuse et 6 solvants inertes. On a interprété quantitativement les coefficients de partage du chélate du nickel en fonction de paramètres de solubilité. Le paramètre de solubilité pour le chélate de nickel a été évalué à 12,9, celui de la solution aqueuse à 18,6, et le volume molaire du chélate à 182 ml/mol.

REFERENCES

1. T. Wakabayashi, S. Oki, T. Omori and N. Suzuki, *J. Inorg. Nucl. Chem.*, 1964, **26**, 2255.
2. T. Omori, T. Wakabayashi, S. Oki and N. Suzuki, *ibid.*, 1964, **26**, 2265.
3. T. Wakabayashi, *Bull. Chem. Soc. Japan*, 1967, **40**, 2836.
4. N. Suzuki, K. Akiba and H. Asano, *Anal. Chim. Acta*, 1970, **52**, 115, for reference.
5. D. Dyrssen, F. Krasovec and L. G. Sillén, *Acta Chem. Scand.*, 1959, **13**, 50.
6. J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes*, 3rd Ed., Dover, New York, 1964.

Talanta, 1971, Vol. 18, pp. 1235 to 1236. Pergamon Press. Printed in Northern Ireland

Cation-exchange separation and determination of silver in admixture with mercury(II)

ACCORDING to Scott and Furman[1] volumetric determination of silver by Volhard's method cannot be carried out when mercury or highly coloured salts of copper, nickel and cobalt constitute more than 60% of the sample. Iodometric,[2,3] complexometric[4] and colorimetric[5] procedures cannot be used under these conditions.

Khopkar *et al.*[6] have reported the separation of silver from a wide range of other metals, using different ion-exchange techniques, but were unable to separate it from mercury. Ion-exchange separation of silver from mercury(II) based on the differences in the stability constants of the complexes formed by these elements with EDTA has not been reported previously in the literature.

Preliminary investigations showed that mercury(II) forms a stable anionic complex with EDTA at pH 4–5. This passes through a cation-exchange column unchanged. The silver–EDTA complex is not stable and is dissociated on the column, resulting in the retention of silver on the resin bed.

EXPERIMENTAL

Reagents

Ion-exchange column. A column 10 × 150 mm, containing the air-dried strongly acid cation-exchange resin Dowex 50W–X8 in the sodium form (50–100 mesh) was prepared.

Standard solutions. All metal solutions were prepared from the pure nitrates by dissolving them in about 25 ml of water containing 2 ml of concentrated nitric acid. These solutions were diluted to 250 ml to give 0·05*M* solutions.

EDTA solution 0·05*M*.

Eluent. Nitric acid 16% (v/v).

Acetate buffer pH 4·6. Glacial acetic acid (60 ml) was added to sodium acetate trihydrate (13·70 g) and the mixture was diluted to 100 ml with distilled water.

Procedure

The solution containing silver and mercury(II) as nitrates was diluted to about 30 ml. About 6–7 ml of the acetate buffer solution were added and the pH was adjusted to 4·6. To this solution a slight excess of the EDTA solution was added, and it was passed through the cation-exchange column at the rate of 5–6 ml/min. The column was thoroughly washed with 300 ml of distilled water to remove EDTA and the mercury complex. The eluate was collected from the beginning of the sorption step. An aliquot of the effluent and the washings was analysed[7] for its mercury content, by titrating the excess of EDTA.

Silver was eluted by passing 250 ml of 16% nitric acid at the rate of 4 ml/min through the column. The eluate was boiled for a few minutes, cooled and titrated with standard ammonium thiocyanate solution, with iron(III) nitrate as indicator.[8]

TABLE I.—VOLUMETRIC DETERMINATION OF SILVER IN SILVER–MERCURY MIXTURES

Ion %	Calculated amount of silver present, *mg*	Silver found, *mg*	Error, %
Hg(II) 47·98	43·16	43·09	−0·2
Hg(II) 78·82	21·58	21·58	0·0
Hg(II) 87·23	21·58	21·51	−0·4
Hg(II) 95·92	10·79	10·79	0·0
Cu(II) 80·09	21·58	21·58	0·0
Co(II) 75·44	21·58	21·58	0·0
Ni(II) 75·12	21·58	21·58	0·0
Zn(II) 80·51	21·58	21·65	+0·4

RESULTS AND DISCUSSION

Separation studies by the proposed method were conducted with solutions containing the two ions in various proportions and the results were compared with the calculated amounts of silver and mercury(II).

It can be seen from the results in Table I that the error is no greater than ±0·5% in any instance, which establishes the efficiency of the separation. In addition, copper(II), cobalt(II), nickel and zinc are also eliminated as their anionic complexes along with the mercury complex.

Department of Chemistry
Government Science College
Gwalior, India

R. L. SHRIMAL

Summary—Cation-exchange separation of silver from mercury(II), copper(II), cobalt(II), nickel and zinc, based on the differences in the stability constants of the complexes formed by these elements with EDTA at pH 4·6, is described. Silver is eluted with 16% nitric acid and is determined by Volhard's method.

Zusammenfassung—Es wird beschrieben, wie Silber von Quecksilber(II), Kupfer(II), Kobalt(II), Nickel und Zink durch Kationenaustausch getrennt werden kann. Die Abtrennung beruht auf den Unterschieden in den Stabilitätskonstanten der Komplexe dieser Elemente mit EDTA bei pH 4.6. Silber wird mit 16% Salpetersäure eluiert und nach Volhard bestimmt.

Résumé—On décrit une séparation par échange de cations de l'argent des mercure(II), cuivre(II), cobalt(II), nickel et zinc, basée sur les différences constantes de stabilité des complexes formés par ces éléments avec l'EDTA à pH 4,6. On élue l'argent par l'acide nitrique à 16% et le détermine par la méthode de Volhard.

REFERENCES

1. W. W. Scott and N. H. Furman, *Standard Methods of Chemical Analysis*, Vol. I, p. 824. Van Nostrand, New York, 1950.
2. K. Tabushi, M. Otama, Y. Matsuhashi and F. Kudot, *Sci. Repts. Hirosaki Univ.* 1957, **4**, 11.
3. S. V. Suryanarayan and H. N. Das Gupta, *Indian J. Appl. Chem.*, 1960, **23**, 209.
4. F. J. Welcher, *The Analytical Uses of Ethylenediaminetetra-acetic Acid*, p. 250. Van Nostrand, New York, 1958.
5. K. Kodama, *Methods of Quantitative Inorganic Analysis*, p. 147. Wiley, London, 1963.
6. S. M. Khopkar and A. V. Rangnekar, *Mikrochim. Acta*, 1965, 642.
7. F. J. Welcher, *The Analytical Uses of Ethylenediaminetetra-acetic Acid*, p. 164. Van Nostrand, New York, 1958.
8. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, p. 265. Longmans, London, 1961.

Talanta, 1971, Vol. 18, pp. 1237 to 1241. Pergamon Press. Printed in Northern Ireland

Dosage quantitatif des substances tensioactives par électroadsorption

(*Reçu le* 2 *avril* 1971. *Accepté le* 24 *juin* 1971)

LE DOSAGE quantitatif des substances tensioactives, et en particulier les non-ioniques, présente un sérieux problème analytique car même dans le cas où elles sont applicables aucune des méthodes usuelles n'est totalement satisfaisante du fait soit de leurs erreurs inhérentes, soit de leur complexité qui les rend impropres à être utilisées pour des analyses de routine.[1]

Il est bien connu que la présence en solution d'une substance adsorbable sur une électrode de travail influence la cinétique de décharge des espèces électroréductibles. Weber *et al.*[2] ont montré que si l'on tient compte de certaines hypothèses, la constante de vitesse du transfert d'électrons peut être donnée par l'équation suivante:

$$k_{\text{eff}} = k_0(1 - \theta) + k_1\theta$$

où θ est le taux de recouvrement de l'électrode ($0 \leqslant \theta \leqslant 1$), k_0, la constante de vitesse à $\theta = 0$ et k_1 celle de $\theta = 1$.

Le courant dû à la décharge de la substance électroréductible dépend donc de la substance tensioactive en solution. Il peut même être supprimé complètement lorsque $\theta = 1$ et si $k_1 = 0$. Le temps τ nécessaire pour que le recouvrement soit total est donné par les équations de Fick[3] en supposant que la diffusion de l'espèce adsorbable est le facteur déterminant de la cinétique d'adsorption. On trouve ainsi que:

$$\tau = \frac{K}{C_A{}^2}. \tag{1}$$

où K est une constante et C_A la concentration de substance tensioactive.

Si maintenant on agite suffisamment la solution pour détruire la couche de diffusion, Phillips a montré,[4] pour une électrode stationnaire, que:

$$\tau = \frac{K'}{C_A} \tag{2}$$

En comparant ces équations on constate que pour une même valeur de τ on a besoin d'une plus grande concentration de substance adsorbable dans la solution agitée que lorsque le recouvrement est contrôlé par la diffusion; d'où une amélioration de la sensibilité.

PARTIE EXPERIMENTALE

Appareillage

Il est constitué par un polarographe Tacussel à trois électrodes du type PRG-3 muni d'un potentiostat à réponse très rapide PRT 30-01, d'un enregistreur potentiométrique EPL-2 avec tiroir préamplificateur TV 11 GD et d'un générateur de signaux triangulaires et rectangulaires GSTP 2.

Cellule

Dans les premières expériences, on a utilisé comme électrode de travail une électrode de Kemula. Celle-ci présentait certains inconvénients et surtout la chute de la goutte due à la forte agitation et au brusque changement du potentiel appliqué; de plus, l'agitation latérale s'avérait souvent insuffisante pour arriver à l'élimination totale de la couche de diffusion.

L'électrode finalement utiliséee est constituée par un tube de verre de borosilicate (5 mm), d'environ 180 mm de long, coudé en angle droit à 30 mm de l'extrémité ouverte. A 10 mm de l'extrémité fermée, il existe une petite dépression au fond de laquelle est soudé un fil de platine qui assure le contact entre la goutte de mercure que l'on dépose dans la dépression et le mercure contenu dans le tube, qui à son tour permet le contact électrique avec le polarographe.

La cellule (Fig. 1) a une capacité de 100 ml, avec un bouchon en Plexiglass à cinq entrées qui permettent de loger les électrodes de référence et auxiliaire, l'arrivée d'azote, la baguette de l'agitateur et le capillaire à gouttes de mercure au moyen duquel on dépose un nombre déterminé de gouttes dans la dépression de l'électrode de travail. L'entrée latérale de la cuve permet de la placer aisément au-dessus de la baguette de l'agitateur. L'agitation est assurée par un moteur synchrone Radiometer M-22 tournant à 2500 tpm et entraînant une baguette de verre au bout aplati de 10 mm de diamètre.

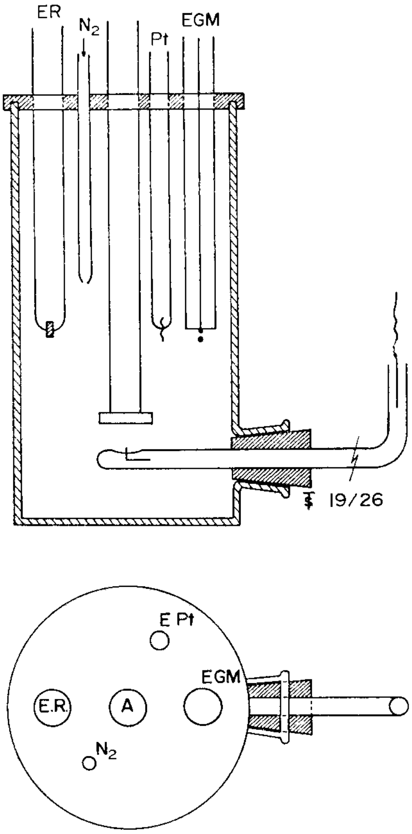


FIG. 1.—Cellule de dosage.

Produits

Tous les produits minéraux sont de qualité pur pour analyses. Les substances tensioactives ont l'origine suivante: Triton X-100 et laurylsulfonate de sodium (Touzart et Matignon), polyvinylpyrrolidones K-25 et K-40 (Fluka *purum*), Emkalix Pluronic L61R (Ugine Kuhlmann) et le tetrabutylammonium hydroxide (BDH).

L'eau est bidistillée, la deuxième fois dans un appareil en quartz à chauffage par infrarouge.

Choix du potentiel de départ. Il est fait d'après les courbes tensamétriques des produits tensioactifs en solutions 0,1M $HClO_4$ ou 0,1N H_2SO_4 comme électrolytes de base, de façon à n'avoir aucune adsorption entre le moment où on place la goutte de mercure sur l'électrode de travail et celui où on applique le potentiel de travail. Ce potentiel a été choisi égal à + 0,25 V (par rapport à une électrode à calomel KCl, saturé) pour toutes les expériences.

Choix du potentiel de travail. Au préalable, on étudie l'effet de la présence des substances tensioactives sur les courbes voltamétriques obtenus pour les solutions fortement agitées des ions électroréductibles, le potentiel de travail pour les courbes *i–t* étant choisi de façon à avoir une influence maximale de la substance tensioactive (Fig. 2).

Dépolarisants. On a étudié différents systèmes électroréductibles par voltamétrie, en solution fortement agitée, parmi lesquels Cu^{2+} et Cd^{2+} $4 \, . \, 10^{-3}M$ en solution 0,1M $HClO_4$, Cu^{2+}/EDTA pH = 3,5 et pH = 7, VO^{2+} $6 \, . \, 10^{-3}M$/0,1N H_2SO_4, Co^{2+}/KNO_3. A partir de ces données voltamétriques (Fig. 3), confirmées par l'enregistrement des courbes *i–t* correspondantes, on a choisi les systèmes $Cd^{2+}/HClO_4$ et VO^{2+}/H_2SO_4 qui présentent les plus grands avantages (différence maximale entre les courants observés pour $\theta = 0$ et $\theta = \theta_{max}$).

Enregistrement des courbes courant temps (i–t)

Un volume déterminé de la solution de substance tensioactive à étudier est ajoutée à la cellule qui contient 75 ml de la solution du dépolarisant, le tout est soigneusement débarrassé d'oxygène avant

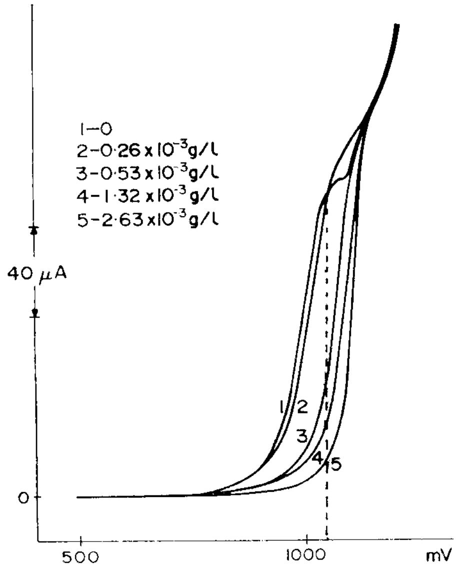


FIG. 2.—Voltamétrie en solution fortement agitée de VO^{2+}/H_2SO_4 en présence de Triton X-100. La ligne en pointillés indique la valeur du potentiel de travail.

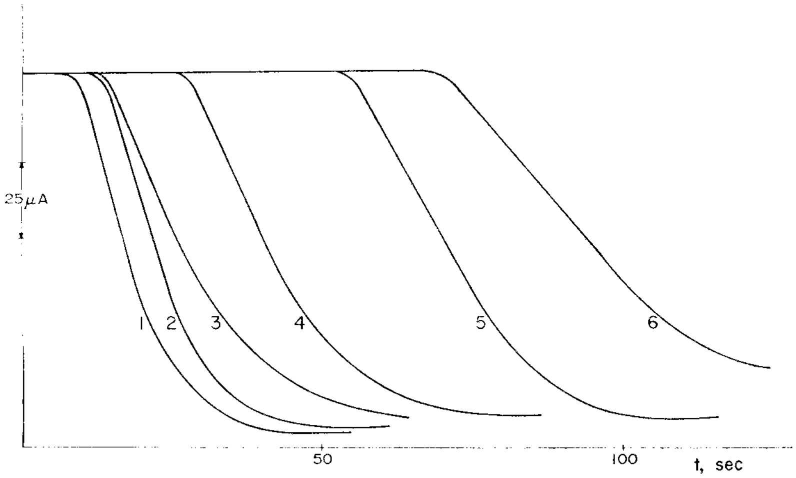


FIG. 3.—Courbes *i–t* de solutions de VO^{2+}/H_2SO_4 en présence de concentrations croissantes de $(C_4H_9)_4NOH$. 1—3,34 mg/l.; 2—2,33 mg/l.; 3—1,73 mg/l.; 4—1,39 mg/l.; 5—0,86 mg/l.; 6—0,61 mg/l.

chaque expérience par un barbotage d'azote R saturé d'eau, par un passage préalable à travers une solution identique à celle dans la cellule.

Un nombre déterminé de gouttes de mercure est placé dans la dépression de l'électrode de travail qui est déjà soumis au potentiel initial (+250 mV). On place l'électrode au-dessous de la baguette de l'agitateur et on commence l'agitation.

La courbe est enregistrée depuis l'instant où l'on applique le potentiel de travail jusqu'à celui où le courant faradaique atteint une valeur minimum stable.

Le générateur GSTP 2 permet d'effectuer le saut de potentiel en quelques microsecondes.

RESULTATS ET DISCUSSION

Des courbes typiques courant–temps ainsi obtenues sont représentées dans la Fig. 3. Les valeurs correspondantes de τ sont mesurées par extrapolation à courant zéro de la partie décroissante de la courbe. Cette extrapolation ne présente aucune difficulté majeure dans le domaine étudié, si ce n'est dans le cas des plus faibles concentrations.

Les résultats pour des temps de recouvrement correspondant à différentes substances tensioactive cationiques et non-ioniques étudiées sont indiqués aux Tableaux I et II et dans la Fig. 4. L'équation (2) est donc parfaitement applicable dans ces conditions.

La valeur du courant sur les courbes expérimentales et pendant la première partie de l'électrolyse

TABLE I.—DÉTERMINATION DE L'HYDROXYDE DE TÉTRABUTYLAMMONIUM AVEC $Cd^{2+}/HClO_4$ COMME ÉLECTROLYTE ÉLECTRORÉDUCTIBLE

C, *M*	1/*C*	*t*, *sec* (*)	*t* . *C*
$5{,}33 \cdot 10^{-6}$	$0{,}188 \cdot 10^{6}$	38,7	$206{,}3 \cdot 10^{-6}$
6,00	0,166	34,0	204,0
6,66	0,150	31,3	208,5
8,00	0,125	28,0	224,0
9,33	0,107	23,7	221,1
10,00	0,100	22,5	225,0
10,66	0,094	20,3	216,4
11,33	0,088	19,2	217,5
			$215{,}4 \cdot 10^{-6}$

(*) Moyenne de six déterminations.

TABLE II

Composé	Limite de concentration étudié *mg/ml*	Erreur, % (maximum)	Écart type, %
	(VO^{2+}/H_2SO_4)		
Triton X-100	1,05/5, 25	12	2,5
Polyvinyl K-25	4,00/13,33	4	2,0
Polyvinyl K-30	2,66/13,33	5	2,0
L 61 R	0,17/0,4%	4	2,5
$(C_4H_9)_4NOH$	0,33/3,34	7	2,0
	$(Cd^{2+}/HClO_4)$		
$(C_4H_9)_4NOH$	1,38/2,93	10	2,0

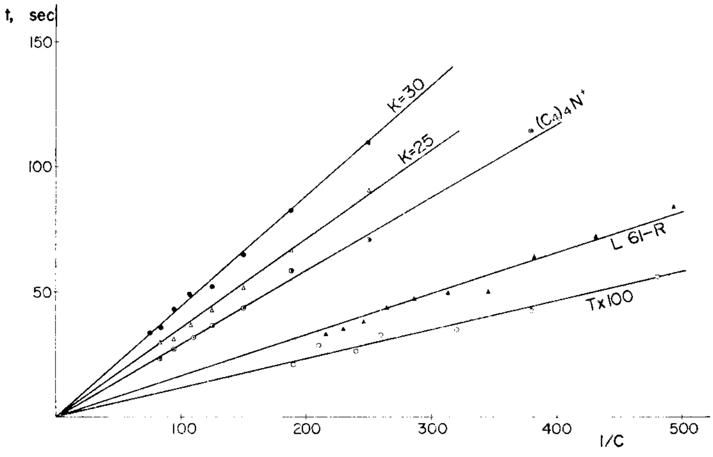


FIG. 4.—Dosage des différentes subtances tensioactives étudiées.

oscille de ±10 μA, autour d'une valeur moyenne, mais cette oscillation disparaît dès que se manifeste l'adsorption c'est-à-dire quand le courant commence à décroîre. Cette stabilité subsiste lorsqu'on atteint les valeurs minimales finales du courant faradaique, indiquant l'existence d'une adsorption.

Parmi les substances électroréductibles étudiées, le VO^{2+}/H_2SO_4 et le $Cd^{2+}/HClO_4$ donnent les meilleurs résultats du fait d'une plus grande inhibition du processus d'électrode pour une même concentration de substance tensioactive en solution. Pour les substances tensioactives non-ioniques et à l'exception du Triton X-100 (tableau II), la plus grande précision est obtenue, dans les conditions expérimentales utilisées, avec l'ion vanadyle en solution d'acide sulfurique. Pour le Triton X-100 ce manque de précision peut s'expliquer par l'existence de polymères qui empêche de connaître exactement la concentration. Néanmoins, dans tous les autres cas étudiés les déviations standard que l'on obtient montrent la bonne précision de la méthode.

La limite supérieure de ces dosages pourrait être augmentée si l'on substituait à l'enregistreur potentiométrique utilisé un oscillographe convenablement standardisé. Ceci permettrait l'enregistrement des courbes pour de plus fortes concentrations de substances tensioactive avec des temps de recouvrement très petits.

Dans le cas de la substance tensioactive anionique étudiée, le laurylsulfonate de sodium, il n'est pas possible d'effectuer une bonne extrapolation à partir des courbes obtenues. Aussi cette méthode ne peut pas être utilisée pour un dosage quantitatif car il est impossible de déterminer le temps de recouvrement avec une précision quelconque. Cependant pour des mélanges laurylsulfonate–autres substances tensioactives étudiées, on observe des temps de recouvrement inférieurs à ceux que l'on attendait. Ces résultats permettent de supposer que malgré tout, les substances anioniques sont partiellement adsorbées en présence des composés cationiques et non-ioniques.

CONCLUSION

La méthode mise au point pour le dosage de substance tensioactive donne des résultats très satisfaisants pour des composés cationiques et non-ioniques et à des concentrations de l'ordre de $10^{-6}M$. Si cette technique n'est pas spécifique elle présente néanmoins un intérêt considérable et particulièrement dans le cas des composés non-ioniques pour lesquels il existe peu de méthodes de dosage adéquates.

Equipe polarographique n° 61
Faculté des Sciences
34 Montpellier
France

E. Verdier
J. Piro

Catedra de quimica Analitica
Escuela de Ingenieria Technica-Industrial
Las Palmas de Gran Canaria
Espagne

F. Garcia Montelongo*

Résumé—Une méthode de dosage de composés tensioactifs cationiques et non-ioniques, basée sur leur effet inhibiteur de certaines réactions électrochimiques, a été mise au point. Cette technique permet de doser ces substances avec une précision de 2–3% à des concentrations de l'ordre de $10^{-6}M$.

Summary—A method for the quantitative determination of cationic and non-ionic surfactants which is based on their inhibiting effect on certain electrochemical reactions has been developed. This technique enables one to determine, with a precision of 2–3%, these substances at concentrations of the order of $10^{-6}M$.

Zusammenfassung—Wir haben eine Methode eingestelt, um oberflächenaktiven kationischen und nicht ionischen Substanzen zu dosieren. Diese Methode ist auf ihren Inhibitoreffekt gewissen elektrochemischen Reaktionen gegenüber gegründet. So ist es möglich, diesen Substanzen mit einer guten Genauigkeit (2–3%) bei Konzentrationen von ungefähr $10^{-6}M$ zu dosieren.

BIBLIOGRAPHIE

1. M. J. Rosen et H. A. Goldsmith, *Systematic Analysis of Surface-Active Agents*, Interscience, New York, 1960.
2. J. Weber, J. Koutecký et J. Koryta, *Z. Elektrochem.*, 1959, **63**, 583.
3. J. Koryta, *Collection Czech. Chem. Commun.*, 1953, **18**, 206.
4. S. L. Phillips, *Anal. Chem.*, 1966, **38**, 343.

* Stagiaire du Ministère des Affaires Etrangères, France.

Talanta, 1971, Vol. 18, pp. 1242 to 1245. Pergamon Press. Printed in Northern Ireland

Determination of thoria in thorium ores by an emission spectrographic method

(*Received* 19 *May* 1971. *Accepted* 21 *August* 1971)

LITTLE attention has been paid to the spectrographic analysis of refractory ores, though it offers a quick and accurate determination of refractory elements; an investigation was therefore undertaken to apply it to determination of thoria in thorium ores, particularly monazite sand.

EXPERIMENTAL

Equipment

A 3-m grating spectrograph (600 lines/mm) was used. The dispersion remained constant at about 0·56 nm/mm. A 30–40 V d.c. arc source was run at 3–12 A to excite the sample (electrode spacing 4 mm). Only 60% and 30% transmission filters were used. A 50-μm slit was used with fishtail masking. The spectra were recorded on Eastman Kodak Spectrum Analysis No. 2 plates, developed in the usual manner. The transmission was measured on a comparator-densitometer.

Preparation of standard samples

The most persistent thorium lines are at 269·24 and 311·18 nm, with an arc sensitivity rating of 20 (compared with a rating of 40 for the 424·18 nm uranium line and 5000 for the persistent copper lines). Thorium generally occurs in ores as thoria (thorium oxide) which is refractory and hence difficult to volatilize. This difficulty was avoided by using the internal standard and carrier distillation methods.

Thorium nitrate was selected for preparation of standards because of its availability and easy convertibility into thorium oxide. Since 99% of the matrix in natural thorium ores consists of silica and ferrous sulphide, a similar proportion of silica and iron was added in the standards. Silica sand and ferrous sulphide were ground to −200 mesh in a pulverizer. Thorium nitrate, ground to −200 mesh, was added to the prepared matrix of 50% silica and 50% iron sulphide to give 0·1–10% of thorium nitrate; these standards were weighed and mixed thoroughly in a blender.

Additives and carriers

Thorium oxide requires high temperatures for volatilization. Since halides are more volatile than most other species, addition of halide (*e.g.* fluoride) improves the volatilization rate of refractory materials. It also improves the electric conductivity and provides carriers of atoms or ions of the element to be determined. Addition of spectrographic graphite to refractory ore materials produces smoother burning of the sample and prevents the formation of a glassy bead at the bottom of the electrode. The glassy bead causes the arc to strike the electrode with the result that the electrode crater burns away and the bead is lost.[1–3]

Various halides were mixed with the 0·1% thorium nitrate standard and excited at different currents. The effect of different additives is shown in Table I.

AgCl, MoO_3 and $LaCO_3$ were the best additives, especially when mixed with graphite.

TABLE I.—EFFECT OF DIFFERENT ADDITIVES ON THORIUM NITRATE (CURRENT 6 A)

Additive	Relative density of line	Effect in electrode crater
$AgNO_3$	Not detectable	Sample lost
NaF	Weak	Sample lost
AgCl	Strong	Bubbling, sample lost
NH_4HF	Strong	Spattering
$LiCO_3$	Weak	Spattering
Sm_2O_3	Strong	Bubbling, sample lost
$La_2(CO_3)_3$	Strong	Spattering
NaCl	Weak	Spattering
MoO_3	Strong	Spattering
$KNbF_6$	Not detectable	Sample lost
V_2O_5	Not detectable	Sample lost
NH_4Cl	Weak	Spattering
Cr_2O_3	Not detectable	Sample lost
C	Good	Smooth burning

Selection of spectral line

A 30-sec preburn and 30-sec exposure, at a current of 6 A, with the 50-μm slit and a neutral 60% transmission filter gave a good density for all lines. When the current was increased, the sample was lost. At the low current thorium was not excited and the sample was not completely burnt. Most of the thorium lines were masked by the iron lines, and only the lines at 269·24 and 311·18 nm were free from iron interference, showed good sensitivity, and had densities that increased with thorium concentration.

Electrodes

The lower electrode, 4·8-mm diameter and 50 mm long, was cut 6 mm from one end to give a base 1·6 mm in diameter; the cavity was 4·8 mm deep and easily held the 15-mg sample (Fig. 1). The upper electrode, 4·8-mm diameter and 50 mm long, was sharpened at one end to give a point contact. A current of 6 A gave enough heat to excite the thorium.

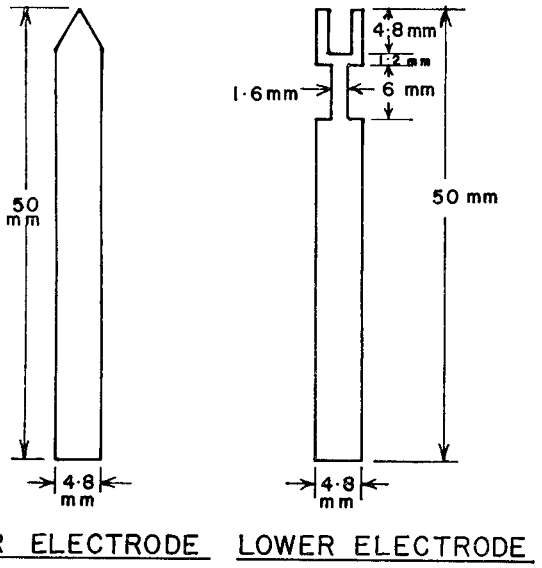


FIG. 1.—Design of electrodes.

The standards were divided into two sets, one set covering the range 0·1–1·0% thorium nitrate, and the other 1·0–10·0%. Each sample was run three times to determine the overall reproducibility. Both sets were arced under identical conditions.

The transmission of the 269·24 nm line relative to the transmission of the background is given in Table II.

TABLE II.—DATA FOR WORKING CURVE

ThO_2, %	Transmission of 269·24 nm line, %	Transmission of background, %	$\frac{\%T\ (Th)}{\%T\ (background)}$
0·055	12·0	13·0	0·93
0·110	10·5	13·5	0·78
0·220	8·0	13·0	0·62
0·330	6·5	11·6	0·56
0·440	6·3	12·3	0·51
0·550	6·1	12·0	0·49
0·880	5·2	11·0	0·47
1·100	5·0	10·9	0·46
4·400	3·2	8·3	0·38

The emulsion was calibrated with the 282·44 nm copper line, obtained from brass electrodes (4-mm gap, 5 A d.c.). A 6-step rotating sector was used to control the relative intensity of the line. The grating was masked. A 20-sec exposure was used.

MoO_3 was selected as internal standard because its 267·28 nm line had a similar arc intensity and gave good constant density in all the samples. A 10-mg sample was mixed thoroughly with 5 mg of spectrographic carbon SP-1 and 1 mg of MoO_3 and placed in the electrode crater as described above. The electrodes were installed with a 4-mm gap and given a preburn time of 30 sec at 6 A (d.c.), followed by a 30-sec exposure for recording of the first-order 225·0–360·0 nm range on Spectrum Analysis No. 2 plates, each standard being run twice. Two complete series of eight standards were run. The transmissions of the Th 269·24 nm line, the Mo 267·28 nm line and their backgrounds were measured. The transmission values were corrected to relative intensities by means of the emulsion calibration curve. The ratio of the relative exposure values of the thorium and molybdenum lines gave a linear log–log plot.

Analysis of samples

Twelve samples of thorium ore were analysed for thoria under the same conditions as those used for the standards. All samples were ground to −200 mesh. Six samples were each run five times, and the other six were run three times each. The results are tabulated in Table III.

TABLE III.—QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF THORIUM ORES FOR ThO_2 CONTENT

Sample No.	ThO_2 (wet analysis), %	No. of runs	Spectrographic method ThO_2, %	 ThO_2, average %
1	2·0	5	1·96–1·99	1·97
2	0·095	5	0·093–0·096	0·094
3	4·5	5	4·22–4·39	4·28
4	4·6	5	4·32–4·47	4·40
5	3·0	5	2·81–2·96	2·88
6	2·25	5	2·09–2·20	2·17
7	4·6	3	4·28–4·31	4·30
8	3·0	3	2·67–2·83	2·77
9	2·25	3	1·95–1·99	1·97
10	3·1	3	2·81–3·00	2·93
11	2·0	3	1·90–2·02	1·97
12	1·5	3	1·41–1·50	1·47

All the samples except Nos. 3 and 6 were prepared synthetically from Government standard ore samples; Nos. 3 and 6 were monazite sand samples. Ferrous sulphide was used as the matrix in the synthetic preparation. They were all analysed by a chemical method[4,5] for comparison. The results obtained by the spectrochemical method compare well with the chemical analysis. For samples containing 2% or less ThO_2, the spectrochemical analysis is as accurate as the chemical analysis. The spectrographic analysis gave slightly lower ThO_2 content when this exceeded 2%. This might be due to weighing error, change in the electrodes and spacing during excitation, unsteady arc current, or sample loss due to spattering and bubbling; alternatively, the chemical method might give positively based errors.

Acknowledgement—The author wishes to thank Professor D. H. Trollope for providing facilities.

Department of Engineering
James Cook University of North Queensland
Townsville, Queensland
Australia

N. C. KOTHARI

Summary—The emission spectrograph is used to determine thoria in monazite sand. A sample of only 15 mg is required and yields rapid and accurate results for 2% thoria or less. Of various additives tested as carriers, carbon and MoO_3 were found to be best. A current of 6 A gave a proper rate of volatilization without excessive spattering. The 267·28 nm Mo line was used as internal standard and the 269·24 nm Th line for analysis. Silica and iron sulphide were used as matrix in synthetic samples. Results compared well with those obtained by wet-analysis.

Zusammenfassung—Zur Bestimmung von Thoriumdioxid in Monazitsand wird ein Emissions spektrograph verwendet. Eine Probe von nur 15 mg wird verwendet; man erhält rasch genaue Ergebnisse für 2% Thoriumdioxid oder weniger. Unter verschiedenen als Träger ausprobierten Ausätzen erwiesen sich Kohlenstoff und MoO_3 als die besten. Ein Strom von 6 A ergab eine ausreichende Verflüchtigung ohne übermäßige Zerstäubung. Die Mo-Linie bei 267·28 nm wurde als innerer Standard benutzt, die Th-Linie bei 269·24 nm zur Analyse. In synthetischen Proben wurden Kieselsäure und Eisensulfid als Matrix verwendet. Die Ergebnisse stimmten gut mit denen der Naßanalyse überein.

Résumé—On utilise le spectrographe d'émission pour doser la thorine dans le sable de monazite. Un échantillon de 15 mg seulement est nécessaire et donne des résultats rapides et précis pour 2% de thorine ou moins. Des divers additifs qui ont été essayés comme porteurs, on a trouvé que le carbone et MoO_3 sont les meilleurs. Un courant de 6 A donne une vitesse de volatilisation convenable sans projections excessives. On a utilisé la raie 267,28 nm du Mo comme étalon interne et la raie 269 24 nm de Th pour l'analyse. On a utilisé la silice et le sulfure de fer comme matrice dans les échantillons synthétiques. Les résultats sont bien comparables à ceux obtenus par l'analyse par voie humide.

REFERENCES

1. G. W. Marks and B. M. Jones, *U.S. Bur. Mines Rept.* 3965, November 1946.
2. *Idem*, *U.S. Bur. Mines Rept.* 4363, November 1948.
3. G. W. Marks and E. V. Potter, *U.S. Bur. Mines Rept.* 4377, December, 1948.
4. E. S. Pilkington and A. W. Wylie, *J. Soc. Chem. Ind.*, 1947, **66**, 387.
5. R. W. Urie, *ibid.*, 1947, **66**, 437.

Talanta, 1971, Vol. 18, pp. 1245 to 1249. Pergamon Press. Printed in Northern Ireland

Spectrophotometric determination of ruthenium with diphenylthiovioluric acid

(*Received* 29 *December* 1970. *Accepted* 21 *May* 1971)

DURING investigations on the chromogenic properties of diphenylthiovioluric acid (DPHTVA) it was observed that it yields a pink-red precipitate with ruthenium(III), which is soluble in chloroform. In the present communication, the chloroform-soluble complex of ruthenium(III) has been employed for spectrophotometric determination of the metal at pH 5·5. The reaction is unaffected by the presence of many foreign ions. This method offers the advantage of high sensitivity and reasonable selectivity.

EXPERIMENTAL

Reagents

DPHTVA solution. DPHTVA was synthesized and purified by the method of Dass and Dutt.[1] Its solution (0·2%) was prepared in acetone of analytical reagent quality.

Ruthenium solution. A stock solution of ruthenium was prepared by dissolving ruthenium(III) chloride in doubly distilled water containing sufficient hydrochloric acid to give a concentration of $1M$. The ruthenium content was determined gravimetrically by precipitating ruthenium as the hydrated oxide, followed by careful ignition in air and then reducing in hydrogen and cooling in an atmosphere of carbon dioxide.

Buffer solution. It was found that 5 ml of buffer prepared from $0·5M$ sodium acetate and $0·5M$ acetic acid, in 25 ml of aqueous phase is sufficient for the requisite pH (5·5). With use of up to 10 ml of buffer, absorbances did not change, but use of larger quantities of buffer gave lower absorbance values.

General procedure for extraction of ruthenium(III) complex

A suitable aliquot of dilute ruthenium chloride solution was mixed with 2·0 ml of buffer solution of pH 5·5 and then diluted to 10 ml with water. The reagent solution in acetone was added to it. For pH studies, sodium acetate–acetic acid buffers of pH 3·5–6·0 were used and below and above this pH range, dilute solutions of hydrochloric acid and sodium hydroxide were employed. The mixture was heated on a bath of boiling water for ~ 40 min for complete complex formation, and then cooled. Ten ml of chloroform were added and the complex extracted. The phases were separated by centrifugation and the absorbance of the organic phase was measured at 520 nm against a reagent blank, prepared under similar conditions. For studies of the effect of other ions, the solution containing the ion was added before the buffer solution.

RESULTS

Absorption spectrum

The absorption spectrum of the pink-red ruthenium-DPHTVA complex (Fig. 1) has an absorption maximum at 520 nm. The yellow solution of the ligand, however, exhibits appreciable absorption around 400 nm, which sharply decreases and becomes insignificant from 440 nm onwards. All absorbance measurements were, therefore, made at 520 nm against reagent blanks.

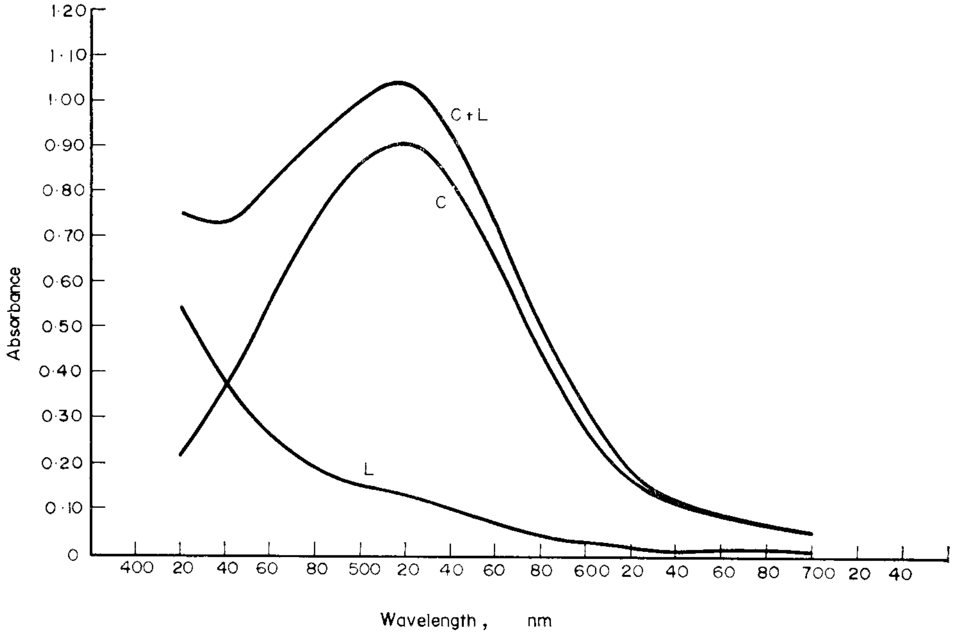


FIG. 1.—Absorption spectra of diphenylthiovioluric acid (DPHVA) and its ruthenium (III) complex
C + L—DPHTVA plus ruthenium *vs.* chloroform
C—Ruthenium complex *vs.* DPHTVA
L—DPHTVA *vs.* chloroform

Effect of pH

The effect of pH on stability of the complex was determined by preparing a series of solutions varying in pH from 2·80 to 8·50 and the absorbance was found to be maximal and to remain unchanged between pH 4·95 and 6·70. Further studies were made at pH 5·5.

Effect of concentration of reagent

The concentration of DPHTVA was varied up to 100-fold molar excess, other factors being kept constant. The results of this study indicated that nearly 40-fold molar excess of the reagent is required for complete complexation (Fig. 2); 50–60-fold molar excess was, however, used during further studies.

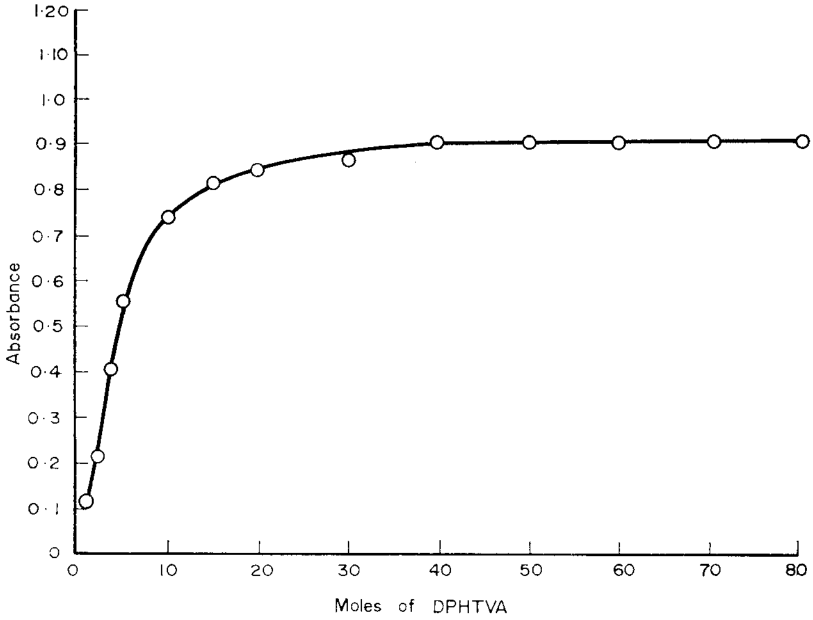


FIG. 2.—Effect of DPHTVA concentration on ruthenium(III)-DPHTVA complex: final concentration of ruthenium(III) = $4 \times 10^{-5}M$

Effect of heating time and stability of colour

For maximum colour development, heating for at least 30 min on a bath of boiling water was found to be necessary. The mixtures were, therefore, heated for about 40 min in subsequent studies to ensure complete complexation. As regards the stability of colour, it has been found that absorbance of the complex remains constant for at least 96 hr.

Calibration graph, range, sensitivity and precision

The ruthenium-DPHTVA system has been found to obey Beer's law up to 5·60 ppm of metal ion. The optimum range for determination of ruthenium, as evaluated by Ringbom plot, is 1·20–3·63 ppm of ruthenium. The molar absorptivity is $2{\cdot}23 \times 10^4$ $l.mole^{-1}.mm^{-1}$. The absorbance of six solutions containing 2·02 ppm of ruthenium had a maximum relative deviation of 1·55% and an average relative deviation of 0·48%.

Molar composition of the complex

To determine the molar composition of the complex formed, Job's method of continuous variations,[2] and the mole-ratio method[3] were employed. In Job's method the maximum in the curve clearly indicates the formation of a ruthenium complex in which the metal: ligand ratio is 1:2. The mole-ratio method was inconclusive and its results were interpreted by the logarithmic method of Bent and French[4] and the Asmus method.[5] The results obtained are in agreement with those obtained by the use of Job's method.

Effect of diverse ions

For this study, synthetic solutions containing known amounts of ruthenium and varying amounts of diverse ions were prepared and ruthenium was determined in their presence. With 2·02 ppm of ruthenium, the following amounts of foreign ions (in ppm) did not cause the absorbance to deviate by more than 3% from that expected: Ca 500, Ba 500, Sr 500, Mn(II) 250, Mg 20, Cd 120, Pb 40, Bi 50, Mo(VI) 20, Ce(IV) 30, Ti(IV) 20, Sn(II) 20, Ag 40, Tl(I) 500, Zn 140, Al 50, V(V) 60, Sb(III) 50, Th 100, Os(VIII) 10, Ir(III) 19, Rh(III) 2, Ge 20, As(III) 50, Be 50, W(VI) 50, UO_2(II) 1250. Ni, Fe(III), Co(II), Cu(II) and Pt(IV) interfere seriously.

As regards the anions, the amounts shown in parentheses (in ppm) did not cause any interference: chloride (1000), bromide (1000), iodide (1000), fluoride (400), phosphate (500), pyrophosphate (500), borate (300), sulphite (500), thiourea (600), oxalate (800), nitrate (400), nitrite (400) and thiocyanate (400). Thiosulphate, citrate, tartrate and EDTA were found to interfere seriously.

Interference due to palladium could be removed by precipitating it at pH 1·0 and extracting into chloroform. The aqueous phase was separated and ruthenium was determined. In this way, 10 ppm of palladium could be tolerated. Thiourea was found to mask 10 ppm of copper(II) while 10 ppm of platinum(IV) were masked with excess of iodate. Interference of Fe(II and III), up to 10 ppm, was obviated by the use of pyrophosphate as masking agent. However, attempts to mask cobalt were unsuccessful.

CONCLUSION

Among the many available reagents, thiourea[6] has proved to be satisfactory for the determination of about 2–15 ppm of ruthenium. Though the tolerance for iridium, rhodium, platinum and nickel offers some advantages, the sensitivity is low and palladium interferes. In the case of the *p*-nitrosodimethylaniline method[7] perhaps the most objectionable feature is the narrow acidity range for colour development, as this is also the pH required for precipitation of the hydrated oxide of ruthenium.

TABLE I.—COMPARISON OF SENSITIVITY OF VARIOUS METHODS FOR RUTHENIUM

Reagent	Sandell's sensitivity	Reference
Thiourea	0·025/650 nm	6
1,10-Phenanthroline	0·0055/448 nm	6
p-Nitrosodimethylaniline	0·0028/610 nm	7
Dithio-oxamide	0·020/630 nm	6
	0·010/650 nm	
	0·024/620 nm	
Anthranilic acid	0·024/620 nm	8
Thiocyanate/CCl_4	0·007/590 nm	6
Oximidobenzotetronic acid	0·35/520 nm	9
2,3-Diaminopyridine	0·0084/572 nm	12
Thiosalicylamide	0·016/385 nm	10
DPHTVA	0·0044/520 nm	present reagent

1,10-Phenanthroline[6] and 4,7-diphenyl-1,10-phenanthroline[6] give sensitive reactions but the intensity of the colour depends upon several factors that require control to produce precise results. Considerable interference is caused by other metals and a time-consuming prior separation of ruthenium by distillation is necessary. Determination of ruthenium with anthranilic acid[8] and 5-hydroxyquinoline-8-carboxylic acid[6] has been carried out but these reagents offer no special advantage over the use of other methods. The major advantage of 5-hydroxyquinoline-8-carboxylic acid is that water is used as blank. Recently, oximidobenzotetronic acid,[9] thiosalicylamide[10] and 8-quinolinol[11] have been used for the determination of ruthenium. Oximidobenzotetronic acid, which has been used over a wide pH range (1–12) is selective, but its sensitivity is very poor. Palladium *etc* interfere in the case of thiosalicylamide. In the 8-quinolinol method, cobalt, chromium, molybdenum, palladium and rhodium interfere and the method is lengthy and not very sensitive.

In the case of DPHTVA, the method has been made quite selective by the use of masking agents. In the presence of small quantities of Group VIII metals and much larger quantities of uranium, determination of ruthenium has been found possible, which is a distinct advantage in addition to its sensitivity as compared to other well known methods. Osmium is most frequently associated with ruthenium and is tolerated up to 10 ppm, which is another major advantage as compared to some other methods.

Comparison of some of the important reagents with DPHTVA is made in Table I, which shows that DPHTVA ranks amongst the most sensitive reagents for ruthenium.

Acknowledgement—The authors (RSC and KCT) are thankful to the Council of Scientific and Industrial Research (India) and University Grants Commission (N. Delhi) for financial assistance.

Department of Chemistry
University of Delhi, Delhi-7
A.R.S.D. College, New Delhi, India

R. S. CHAWLA
R. P. SINGH
K. C. TRIKHA

Summary—Diphenylthiovioluric acid (DPHTVA) reacts with ruthenium(III) to form a complex which has an absorbance maximum at 520 nm. Effects of pH, heating time, buffer and reagent have been studied. DPHTVA has been found to be a sensitive reagent for ruthenium(III) (sensitivity = 0.0044 μg Ru/cm^2 for log I_0/I = 0.001), and has been made selective by the use of masking agents. The composition of the complex as revealed by different methods is 1:2 (ruthenium : DPHTVA).

Résumé—L'acide diphénylthioviolurique (DPHTVA) réagit avec le ruthénium(III) pour former un complexe qui a un maximum d'absorption à 520 nm. On a étudié les influences des pH, temps de chauffage, tampon et réactif. On a trouvé que le DPHTVA est un réactif sensible pour le ruthénium(III) (sensibilité = 0,0044 μg Ru/cm^2 pour log I_0/I = 0,001), et on l'a rendu sélectif par l'emploi d'agents de dissimulation. La composition du complexe, ainsi qu'elle a été révélée par différentes méthodes, est 1:2 (ruthénium: DPHTVA).

Zusammenfassung—Diphenylthioviolursäure (DPHTVA) reagiert mit Ruthenium(III) zu einem Komplex mit einem Absorptions-maximum bei 520 nm. Die Einflüsse von pH, Erhitzungsdauer, Puffer und Reagens wurden untersucht. DPHTVA ist ein empfindliches Reagens auf Ruthenium(III) (Empfindlichkeit 0.0044 μg Ru/cm^2 für log I_0/I = 0.001) und wurde mit Hilfe von Maskierungsmitteln selektiv gemacht. Die mit verschiedenen Methoden ermittelte Zusammensetzung des Komplexes ist 1:2 (Ruthenium : DPHTVA).

REFERENCES

1. I. N. D. Dass and S. Dutt, *Proc. Ind. Acad. Sci.*, 1938, **8**, 145.
2. P. Job, *Ann. Chim.*, 1928, **9**, 113.
3. J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 111.
4. H. E. Bent and C. L. French, *J. Am. Chem. Soc.*, 1941, **63**, 568.
5. E. Asmus, *Z. Anal. Chem.*, 1960, **178**, 104; 1961, **183**, 321, 401.
6. F. E. Beamish, *Analytical Chemistry of Platinum Metals.* p. 366. Pergamon, London, 1966.
7. C. V. Banks, and J. W. O'Laughlin, *Anal. Chem.*, 1957, **29**, 1412.
8. A. K. Majumdar and J. G. Sengupta, *Z. Anal. Chem.*, 1961, **178**, 401.
9. G. S. Manku, A. N. Bhat and B. D. Jain, *Talanta*, 1967, **14**, 1229.
10. K. Sur and S. C. Shome, *Anal. Chim. Acta*, 1969, **48**, 145.
11. H. Hashitani, K. Katsuyama and K. Motojima, *Talanta*, 1969, **16**, 1553.
12. G. H. Ayres and T. Eastes, *Anal. Chim. Acta*, 1969, **44**, 67.

Talanta, 1971, Vol. 18, pp. 1251 to 1252. Pergamon Press. Printed in Northern Ireland

LETTER TO THE EDITOR

Selectivity ratios/coefficients of selective ion-sensitive electrodes

SIR,

This communication concerns the ambiguities in presenting the selectivity ratios or coefficients of selective ion-sensitive electrodes.

The selectivity ratio (coefficient), K_{ij}, for an electrode responding selectively to, say a cation

TABLE I.—SOME MANUFACTURERS' SELECTIVITY LISTINGS OF SELECTIVE ION-SENSITIVE MEMBRANE ELECTRODES AND CORRESPONDING SELECTIVITY RATIOS, K_{ij}.

Electrode and catalogue No.	Manufacturer's selectivity presentation	K_{ij}
Beckman Sodium 39278 Electrode (Bulletin 7145)	Selectivity ratio in the form	
	$\frac{Na^+}{H^+} = 2\cdot8 \times 10^{-2}$	$K_{NaH} = 36$
	$\frac{Na^+}{K^+} = 5500$	$K_{NaK} = 1\cdot8 \times 10^{-4}$
	$\frac{Na^+}{Ag^+} = 7 \times 10^{-3}$	$K_{NaAg} = 1\cdot4 \times 10^2$
Corning Calcium 476041 Electrode	Calcium ion selectivity in the form	
	100 to 1 over $\{Ba^{2+}$	$K_{CaBa} = 10^{-2}$
	Sr^{2+}	$K_{CaSr} = 10^{-2}$
	Ni^{2+}	$K_{CaNi} = 10^{-2}$
	Mg^{2+}	$K_{CaMg} = 10^{-2}$
	1000 to 1 over $\{Na^+$	$K_{CaNa} = 10^{-3}$
	K^+	$K_{CaK} = 10^{-3}$
Corning Chloride 476131 Electrode	Apparent selectivity constant in the form	
	$K_{Cl/I} = 0\cdot067$	$K_{ClI} = 15$
	$K_{Cl/ClO_4} = 0\cdot2$	$K_{ClClO_4} = 5$
	$K_{Cl/NO_3} = 0\cdot4$	$K_{ClNO_3} = 2\cdot5$
	$K_{Cl/Br} = 0\cdot4$	$K_{ClBr} = 2\cdot5$
Coleman Bromide 3-801 Electrode	Interferences in terms of K (maximum ratio of interfering ion to bromide ion):	
	$OH^- = 3 \times 10^4$	$K_{BrOH} = 3\cdot3 \times 10^{-3}$
	$Cl^- = 400$	$K_{BrCl} = 2\cdot5 \times 10^{-3}$
	$I^- = 2 \times 10^{-4}$	$K_{BrI} = 5 \times 10^3$
Orion Chloride 96-17 Electrode	Maximum allowable ratio (mole/mole) of interfering species to chloride ion:	
	$OH^- = 80$	$K_{ClOH} = 1\cdot25 \times 10^{-2}$
	$Br^- = 3 \times 10^{-3}$	$K_{ClBr} = 3\cdot33 \times 10^2$
	$I^- = 5 \times 10^{-7}$	$K_{ClI} = 2 \times 10^6$
	$CN^- = 2 \times 10^{-7}$	$K_{ClCN} = 5 \times 10^6$
Orion Calcium 92-20 Electrode	Selectivity ratios with respect to various interfering ions:	
	$H^+ = 10^5$	$K_{CaH} = 10^5$
	$Zn^{2+} = 3\cdot2$	$K_{CaZn} = 3\cdot2$
	$Fe^{2+} = 0\cdot80$	$K_{CaFe} = 0\cdot80$
	$Mg^{2+} = 0\cdot014$	$K_{CaMg} = 0\cdot014$
	$Na^+ = 10^{-4}$	$K_{CaNa} = 10^{-4}$

i^{z+} in the presence of an interfering ion, say j^{y+}, may be obtained from the electrode potential, E,

$$E = \text{Constant} + \frac{2{\cdot}303RT}{zF} \log \left[a_{i^{z+}} + K_{ij}(a_{j^{y+}})^{z/y}\right] \qquad (1)$$

where the a terms refer to activities.

Frequently, the term *selectivity constant* is used for K_{ij} but this term can be misleading on several counts. First, the value for any two cations (or, of course, anions) is dependent on the solution conditions; secondly, any actual selectivity value for the two cations [equation (1)] depends on whether potentials are taken in mixed or separate solutions of i^{z+} and j^{y+} cations as well as on the actual equation employed in the subsequent calculations; finally, they are occasionally given as reciprocals of K_{ij}, that is, as K_{ji}, or worse, listed as just K with or without a mention of the particular evaluation method.

Because of the dependence on activity, the term *selectivity ratio* or *selectivity coefficient* is to be preferred for K_{ij}. However, the primary object of this communication is not to discuss the pros and cons of the term employed for K_{ij}, nor its determination; these have been detailed for both cation[1,2] and anion-responsive electrodes.[3] It is the inconsistency in presenting selectivity data that is disconcerting, particularly in manufacturers' literature (Table I).

The variety of listings shown in Table I can only cause bewilderment. On the other hand, the universal adoption of K_{ij} for listing selectivity ratios, as in the last column of Table I, would consistently indicate an electrode that selectively responds to the primary ion, i^{z+}, over the interfering ion, j^{y+}, whenever $K_{ij} < 1$.

Even consistent presentation of the selectivity ratio in terms of K_{ij} does not make for adequate information as to the possible application of the electrode in a particular test situation. For this purpose, the conditions under which K_{ij} was determined are needed. Thus, for the mixed solution method[1–3] where potentials are measured in solutions containing a fixed initial activity, $a_{j^{y+}}$, of interferent, j^{y+}, and varying activities of that ion, i^{z+}, for which the electrode was designed, it is desirable to know $a_{j^{y+}}$. Should the level of j^{y+} in the test situation exceed this, and the expected activity level of i^{z+} be less than $K_{ij}(a_{j^{y+}})^{z/y}$ then the electrode is unlikely to be useful in such a test situation.

Finally, the unique interference behaviour of crystal membrane electrodes is interesting. Here, except for hydroxyl interference with the lanthanum fluoride electrode, interference is attributed to the electrode membrane, composed of an insoluble salt of the primary ion, i^{z+}, being covered by an insoluble salt of the interfering ion, j^{y+}, and responding in a Nernstian fashion to j^{y+}. The offending interference film can usually be easily removed by abrasion, but the pertinent point here is that the selectivity ratio K_{ij} should be constant. This follows because K_{ij} depends on the ratio of the solubility products of the salts concerned, as illustrated by thiocyanate interference with the silver bromide electrode.

$$K_{\mathrm{BrSCN}} = \frac{\text{Solubility product of AgBr}}{\text{Solubility product of AgSCN}}$$

This means that for the electrode to be functional to bromide in the presence of thiocyanate, the ratio of the interfering thiocyanate to the primary bromide activity must not exceed the ratio of solubility product of AgSCN to solubility product of AgBr. All selectivities should be quoted in terms of K_{ij} together with the particular experimental method for their determination. It is even more realistic to show an actual mixed activity–potential plot or failing this, to quote the selectivities for definite interference activities.

Chemistry Department
University of Wales Institute of Science and Technology
Cardiff, Wales
24 *May* 1971

G. J. MOODY
J. D. R. THOMAS

REFERENCES

1. G. J. Moody and J. D. R. Thomas, *Lab. Practice*, 1971, **20**, 307.
2. *Idem*, *Selective Ion Sensitive Electrodes*, Merrow Publishing Co., Watford, England, 1971.
3. K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, 1969, **41**, 1203.

Talanta, 1971, Vol. 18, pp. i to ii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Synergic solvent extraction of lanthanides with mixtures of aliphatic fluorinated β-diketones and organophosphorus donors: James W. Mitchell and Charles V. Banks. (24 *August* 1971)

Losses of iridium during heating in various atmospheres: A. Chow. (31 *August* 1971)

A simple spectrophotometric method for determination of zirconium or hafnium in selected molybdenum-base alloys: William A. Dupraw. (13 *September* 1971)

Rapid volumetric method for estimation of thallium(I): M. Chandrasekharan, V. R. S. Rao and G. Aravamudan. (23 *September* 1971)

Potentiometric determination of stepwise stability constants of zirconium and thorium chelates formed with aspartic and glutamic acids: M. K. Singh and M. N. Srivastava. (29 *September* 1971)

Quantitative separation of Al, Ga, In and Tl by cation-exchange chromatography in hydrochloric acid–acetone: F. W. E. Strelow and A. H. Victor. (30 *September* 1971)

Fast analytical König reactions: P. F. van Peborgh. (30 *September* 1971)

Developments in indicators: László Légrádi. (30 *September* 1971)

Light scattering, X-ray diffraction, elemental analysis and infrared spectrometry characterization of chitosan, a chelating polymer: Riccardo A. A. Muzzarelli, Adele Ferrero and Maria Pizzoli. (30 *September* 1971)

Titration of quinoline derivatives with sulphide and cyanide and cyanide in molten alkali thiocyanates: Paolo Cescon, Filippo Pucciarelli and Vito Bartocci. (1 *October* 1971)

Comprehensive study of isomeric butylbenzenes by gas–liquid chromatography: Sabri M. Farroha, Albertine E. Habboush and Adnan H. Tameesh. (1 *October* 1971)

Extraction of some metal phenylacetates into chloroform: Jiří Adam, Rudolf Přibil and Vladimír Veselý. (4 *October* 1971)

Formation of hydrogen peroxide upon oxidation of oxalic acid in the presence and absence of oxygen—II. Oxygen as oxidant: I. M. Kolthoff, E. J. Meehan and Masaru Kimura. (4 *October* 1971)

Semi-automated determination of aluminium with Xylenol Orange: A. Dodson and V. J. Jennings. (29 *September* 1971)

Determination of molybdenum(VI) and *o*-diphenols by high frequency titration: R. N. Soni and J. S. Nahata. (5 *October* 1971)

Oxidative decarboxylation of polyaminocarboxylic acids—VI. A study of the reaction of diethylenetriaminepenta-acetic acid (DTPA) with cerium(IV) in sulphuric acid media: Samir B. Hanna, Rita K. Hessley, William R. Carroll and William H. Webb. (5 *October* 1971)

Ion-exchange behaviour of metals on DEAE-cellulose in methanol–thiocyanate media: Rokuro Kuroda, Takaaki Kondo and Koichi Oguma. (17 *September* 1971)

Qualitative identification of alloys by energy-dispersive X-ray spectroscopy: P. E. Harrison and B. T. Kenna (23 *September* 1971)

Investigation of complexation equilibria, using the concept of effective stability constant: B. W. Budesinsky. (30 *September* 1971)

Studies on nucleation from solution applied to some analytically important metal chelates—II. Nickel dimethylglyoximate: J. D. Hanna and O. E. Hileman, Jr. (30 *September* 1971)

Precision of fragmentation patterns in high-resolution mass spectrometry: W. F. Brown and I. P. Fisher. (12 *October* 1971)

Eine Säulenchromatographische Methode der Molybdänmatrix—Abtrennung zur Bestimmung von Alkali- und Erdalkalispuren in Molybdän und Molybdänverbindungen: S. KARAJANNIS, H. M. ORTNER and H. SPITZY. (14 *October* 1971)

Reductive elution of copper(II) in cation-exchange chromatography by hydroxylamine hydrochloride solution: YASUMUSA SHIGETOMI, RYUZO ARIMOTO and TSUTOMU NAGAHATA. (14 *October* 1971)

Selective extraction of zinc dithizonate in the presence of dithiocarbaminoacetic acid as masking agent. Quantitative treatment of an extraction equilibrium: O. BUDEVSKY, E. RUSSEVA and R. STOYTCHEVA. (15 *October* 1971)

Determination of water: CLIFFORD HARRIS. (15 *October* 1971)

Electrochemical behaviour of membrane-electrodes with an applied current—I. Current–membrane potential curves for the membrane electrode impregnated with $BaSO_4$: CANDIN LITEANU and IONEL CĂTĂLIN POPESCU. (20 *October* 1971)

Talanta, 1971, Vol. 18, p. iii. Pergamon Press. Printed in Northern Ireland

ERRATA

In the paper by J. Agterdenbos and J. Vink, *Talanta*, 1971, **18**, 467, equation (7) should be corrected to read

$$b = \frac{\lambda_I{}^0 - \lambda_E{}^0}{\text{half-bandwidth of } I_\lambda{}^0 \text{ curve}} \cdot \sqrt{2} \qquad (7)$$

In the paper by M. Pryszczewska and E. Krzeszowska, *Talanta*, 1971, **18**, 638, the following corrections should be made.

In the title—for **Kupfer** read **Kupfer(I)**

On p. 641, line 2, for "pH-Gebeit" read "pH-Gebiet" and for "der Zinkionen. . . . wie in Abwesenheit der Kationen" read "der Zinkionen im ganzen Gebiet der Cu^+-Konzentrationswerte ($6{,}25 \,.\, 10^{-5}M$–$1{,}00 \,.\, 10^{-3}M$) und Konzentrationsverhältnisse bei denselben Bedingungen wie in Anwesenheit sowie Abwesenheit der kationen"

On p. 641, line 4, for "Abwesenheit" read "Anwesenheit"

On p. 641, in **Zusammenfassung** line 6, for "Te^+" read "Tl^+".

Reprints of the following reviews published in Talanta are available from Learned Journals Division, Pergamon Press Ltd., Headington Hill Hall, Oxford, England, or Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.

1 **Precipitation of Metal Chelates from Homogeneous Solution** by F. H. Firsching

2 **Recent Developments in the Ring Oven Technique** by H. Weisz

3 **Adsorption Indicators in Precipitation Titrations** by R. C. Mehrotra and K. N. Tandon

4 **Radiometric Titrations** by T. Braun and J. Tölgyessy

5 **Recent Uses of Liquid Ion Exchangers in Inorganic Analysis** by H. Green

6 **Applications of Nuclear and Electron Magnetic Resonance in Analytical Chemistry** by B. D. Flockhart and R. C. Pink

7 **A Critical Evaluation of Colorimetric Methods for Determination of Noble Metals—III: Palladium and Platinum** by F. E. Beamish

8 **A Critical Evaluation of Colorimetric Methods for Determination of Noble Metals—III: Rhodium, Iridium, Ruthenium, Osmium and Gold** by F. E. Beamish

9 **Present State of Complexometry—I: Determination of Quadrivalent and Tervalent Metals** by R. Přibil

10 **Some Recent Developments in Radioactivation Analysis: A Review of Improvements in the Analytical Technique** by F. Girardi

11 **Separation of Transplutonium Elements** by J. Starý

12 **Differential Spectrophotometry** by G. Svehla

13 **A Critical Review of Gravimetric Methods for Determination of the Noble Metals—II** by F. E. Beamish

14 **A Critical Review of Titrimetric Methods for Determination of the Noble Metals—II** by F. E. Beamish

15 **Present state of Complexometry—II: Determination of Bivalent Metals** by R. Přibil

Reprints of Talanta Reviews

As the volume of scientific literature grows, reviews provide one of the best means of keeping abreast with recent developments. Talanta has commissioned a series of comprehensive and critical reviews of topics of current interest to analytical chemists; many of these reviews will also be of value to chemists in general and to other scientists. Talanta Reviews are intended primarily to introduce the non specialist to a subject about which he previously knew little, but they may also help the specialist fill gaps in his knowledge of his own field or illuminate the subject from a new angle.

16 **Derivatography: A Complex Method in Thermal Analysis**
by F. Paulik, J. Paulik and L. Erdey

17 **Potassium Dichromate as an Oxidimetric Reagent**
by G. Gopala Rao

18 **Newer Acylation Methods for the Determination of Organic Hydroxyl and Amino Compounds** by N. K. Mathur

19 **A Critical Review of Neutron Activation and Tracer Methods for the Determination of the Noble Metals**
by F. E. Beamish, K. S. Chung and A. Chow

20 **Process Gas Chromatography** by C. S. F. Pine

21 **Present State of Complexometry—III and IV: Determination of Univalent Metals and Determination of Rare Earths** by R. Přibil

22 **A Critical Review of Methods of Isolating and Separating the Noble Metals—II: Ion Exchange and Solvent Extraction**
by F. E. Beamish

23 **A Critical Review of Methods of Isolating and Separating the Noble Metals—III: Chromatography, Precipitation and Fire Assay** by F. E. Beamish

24 **Complexation Reactions of Dithiocarbamates**
by A. Hulanicki

25 **Polarographic Behaviour of Metal Chelates of *o,o'*-Dihydroxyazo Dyes** by G. W. Latimer, Jr.

26 **Characteristic Metal–Halogen Vibrational Frequencies of Complexes with Bivalent Metal Halides** by R. H. Nuttall

27 **Amplification Reactions** by R. Belcher

28 **Ternary Complexes in Analytical Chemistry**
by A. K. Babko

29 **Determination of Antioxidants in Polymeric Materials**
by D. A. Wheeler

30 **A Critical Review of Atomic Absorption, Spectrochemical, and X-ray Fluorescence Methods for the Determination of the Noble Metals—II**
by F. E. Beamish, C. L. Lewis and J. C. Van Loon

continued overleaf

£0.35 or $1 each

ORDER FORM Date.............

(Customers in America and Canada should return this form to the New York address)

Please send ......copy/copies of the following Talanta Reviews (please list numbers)

....

for which I enclose £................ $.................

Name...

Address.......................................

....

....

Pergamon Press

Headington Hill Hall
Oxford, England

Maxwell House,
Fairview Park, Elmsford,
New York 10523, U.S.A.

31 **Applications of Digital Computers in Analytical Chemistry—I** by C. W. Childs, P. S. Hallman and D. D. Perrin

32 **Applications of Digital Computers in Analytical Chemistry—II** by C. W. Childs, P. S. Hallman and D. D. Perrin

33 **Fluorescence Analysis in Air Pollution Research** by E. Sawicki

34 **Radioactive Kryptonates and their Uses in Chemical Analysis** by J. Tölgyessy and Š. Varga

35 **Quantitative Analysis in Pharmacy and Pharmaceutical Chemistry by Nuclear Magnetic Resonance Spectroscopy** by D. M. Rackham

36 **Recent Developments in Substoichiometric Analysis** by J. Starý and J. Růžička

37 **Analytical and Experimental Aspects of Molecular-Sieve Chromatography** by D. M. W. Anderson, I. C. M. Dea and A. Hendrie

38 **Use of Basic Dyes in the Determination of Anions, Particularly as a Means of Determining Antimony, Thallium, and Gallium** by A. G. Fogg, C. Burgess and D. Thorburn Burns

SUMMARIES FOR CARD INDEXES

Use of basic dyes in the determination of anions, particularly as a means of determining antimony, thallium and gallium: A. G. Fogg, C. Burgess and D. Thorburn Burns, *Talanta*, 1971, **18**, 1175 (Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire.)

Summary—The use of xanthene, triphenylmethane and other basic dye cations as reagents for the determination of anions is reviewed. Elements and anions determined include Sb, Tl, Ga, Au, Te, In, Zn, Ta, Hg, Re, Sn, U, Os, B, Cr, Ag, ClO_4^-, PO_4^{3-}, SO_4^{2-} and NO_3^-. Difficulties encountered in developing satisfactory procedures involving basic dyes are discussed. Procedures for the purification and analysis of basic dye samples are outlined.

A neutron-activation scheme developed for the determination of 42 elements in lunar material: A. O. Brunfelt and E. Steinnes, *Talanta*, 1971, **18**, 1197. Mineralogical-Geological Museum, University of Oslo, Oslo, Norway, and Institutt for Atomenergi, Isotope Laboratories, Kjeller, Norway.)

Summary—A neutron-activation scheme designed for the determination of 42 elements in lunar rocks and fines is described. The scheme is based on seven different irradiations, four of which are followed by direct γ-spectrometry, and three by radiochemical separation systems. The total sample consumption for duplicate analysis is about 800 mg. The scheme has been tested on basalt BCR-1, and results for this standard rock are presented. Analytical experience obtained from analyses of lunar samples and BCR-1 is discussed.

Electrochemical behaviour of aluminium(III) and beryllium(II) perchlorates in dimethylformamide: M. Galová and D. A. Pantony, *Talanta*, 1971, **18**, 1209. (Department of Analytical Chemistry, Technical University, Svermová 3, Kosice, Czechoslovakia, and Department of Metallurgy, Imperial College of Science and Technology, London, S.W.7, U.K.).

Summary—Well defined voltammetric peaks of Al(III) and Be(II) were obtained in DMF at the HMDE, and the nature of the electrochemical process in this medium was investigated. Adsorption and chemical reaction coupled with the charge transfer were observed in both cases. The optimum depolarizer concentration and scan-rate for analytical determination were established. Close similarities were found in the electrochemical behaviour of Al(III) and Be(II), and differences were in degree rather than of kind.

ИСПОЛЬЗОВАНИЕ ОСНОВНЫХ КРАСИТЕЛЕЙ ДЛЯ ОПРЕДЕЛЕНИЯ АНИОНОВ, В ЧАСТНОСТИ ДЛЯ ОПРЕДЕЛЕНИЯ СУРЬМЫ, ТАЛЛИЯ И ГАЛЛИЯ:

A. G. Fogg, C. Burgess and D. Thorburn Burns, *Talanta*, 1971, **18**, 1175.

Резюме—Приведен обзор использования катионов основных красителей ксантенового, трифенилметанового и других классов в качестве реагентов для определения анионов. Определимые элементы и анионы включают Sb, Tl, Ga, Au, Te, In, Zn, Ta, Hg, Re, Sn, U, Os, B, Cr, Ag, ClO_4^-, PO_4^{3-}, SO_4^{2-} и NO_3^-. Обсуждены проблемы разработки удовлетворительных методов основанных на использовании основных красителей. Приведены методы очистки и анализа основных красителей.

СХЕМА ОПРЕДЕЛЕНИЯ 42 ЭЛЕМЕНТОВ В ЛУНАРНЫХ МАТЕРИАЛАХ МЕТОДОМ НЕЙТРОННО-АКТИВАЦИОННОГО АНАЛИЗА:

A. O. Brunfelt and E. Steinnes, *Talanta*, 1971, **18**, 1197.

Резюме—Разработана схема нейтронно-активационного анализа для определения 42 элементов в лунарных горных породах и мелочи. Схема основана на семь различных облучениях, четыре из которых с непосредственной γ-спектрометрией, а три—использующих системы радиохимического разделения. Общее количество пробы требуемое для повторного анализа равно 800 мг. Схема испытана на базальте BCR-1 и приведены результаты полученные на этой эталонной горной породе. Обсужден опыт полученный в анализе лунарных образцев и BCR-1.

ЭЛЕКТРОХИМИЧЕСКИЕ ХАРАКТЕРИСТИКИ ПЕРХЛОРАТОВ АЛЮМИНИЯ(III) И БЕРИЛЛИЯ(III) В ДИМЕТИЛФОРМАМИДЕ:

M. Galová and D. A. Pantony, *Talanta*, 1971, **18**, 1209.

Резюме—Получены хорошо изображенные вольтамперометрические пики Al(III) и Be(III) в ДМФ на электроде в форме висячей ртутной капли и изучена природа электрохимического процесса в этой среде. Адсорбция и химическая реакция, сопряжённые с переносом заряда, обнаружены в обоих случаях. Определены оптимальная концентрация деполяризатора и оптимальная скорость перемены потенциала для аналитического определения. Электрохимические характеристики Al(III) и Be(III) весьма схожи:eони различаются только в степени, не в характере.

Interaction of cobalt(II) chloride with 2-nitroso-1-naphthol in a 96:4 benzene–ethanol solution: Vincenzo Carunchio, Alessandro Bondoli and Maria Antonia Fogaroli, *Talanta*, 1971, **18**, 1217. (Institute of Analytical Chemistry, University of Rome, Rome, Italy.)

Summary—The cobalt(II) chloride-2-nitroso-1-naphthol system has been studied spectrophotometrically in a 96:4 (v/v) benzene–ethanol solution. Two species have been found, the M:L complexation ratios of which are 1:1 and 1:2. The concentration quotients of the formation equilibria are $K_1 = 1{\cdot}2 \times 10^3$ and $K_2 = 1{\cdot}4 \times 10^4$ respectively. The first step of the reaction is accompanied by a configurational change from a tetrahedral to an octahedral structure.

A catalytic method for the determination of cobalt impurities in reactor cooling-water circuits: G. E. Batley, *Talanta*, 1971, **18**, 1225. (Australian Atomic Energy Commission, Research Establishment, Lucas Heights, N.S.W., Australia.)

Summary—Metal impurities in reactor cooling-water circuits must be kept to a minimum. A method is described for the determination of trace levels of cobalt in water samples, based on catalysis of the hydrogen peroxide oxidation of Alizarin Red S. The determination is carried out at pH 11·0 in a phosphate buffer under conditions where the reaction rate is a maximum. Interfering impurities are removed by an ion-exchange separation. The method enables cobalt to be determined in water samples down to 10^{-4} μg/ml, or 5×10^{-5} μg/ml in samples where an ion-exchange separation is not required.

On the distribution coefficient of nickel dimethylglyoximate between an aqueous solution and organic solvents: S. Oki, *Talanta*, 1971, **18**, 1233. (Faculty of Engineering, Shizuoka University, Hamamatsu, Japan.)

Summary—The distribution coefficients of nickel dimethylglyoximate between an aqueous solution and 6 inert solvents were determined at 20°. The distribution coefficients of the nickel chelate were quantitatively interpreted in terms of solubility parameters. The solubility parameter for the nickel chelate was evaluated to be 12·9, that for the aqueous solution to be 18·6, and the molar volume of the chelate to be 182 ml/mol.

Cation-exchange separation and determination of silver in admixture with mercury(II): R. L. Shrimal, *Talanta*, 1971, **18**, 1235. (Department of Chemistry, Government Science College, Gwalior, India.)

Summary—Cation-exchange separation of silver from mercury(II), copper(II), cobalt(II), nickel and zinc, based on the differences in the stability constants of the complexes formed by these elements with EDTA at pH 4·6, is described. Silver is eluted with 16% nitric acid and is determined by Volhard's method.

ВЗАИМОДЕЙСТВИЕ ХЛОРИДА КОБАЛЬТА(II) И 2-НИТРОЗО-1-НАФТОЛА В РАСТВОРЕ БЕНЗОЛА—ЭТАНОЛА 96:4:

VINCENZO CARUNCHIO, ALESSANDRO BONDOLI and MARIA ANTONIA FOGAROLI, *Talanta*, 1971, **18**, 1217.

Резюме—Система состоящаяся из хлорида кобальта(II) и 2-нитрозо-1-нафтола изучена спектрофотометрическим методом в растворе бензола—этанола 96:4 по объему. Обнаружены два комплекса, отношение М:Л которых было 1:1 и 1:2. Частные концентраций равновесного образования равны $K_1 = 1{,}2 \times 10^3$ и $K_2 = 1{,}4 \times 10^4$, соответственно. Первый шаг реакции сопровождается структурным переходом из тетраэдрической в октаэдрическую форму.

КАТАЛИТИЧЕСКИЙ МЕТОД ОПРЕДЕЛЕНИЯ ПРИМЕСЕЙ КОБАЛЬТА В ВОДЕ ИЗ ОХЛАЖДАЮЩИХ СИСТЕМ РЕАКТОРОВ:

G. E. BATLEY, *Talanta*, 1971, **18**, 1225.

Резюме—Надо сводить на минимум примеси металлов в воде охлаждающих систем реакторов. Описан метод определения следовых количеств кобальта в воде, основанный на катализе окисления ализаринового красного S перекисью водорода. Определение проводится при pH 11,0 в растворе фосфатного буффера при условиях соответсвующих минимуму скорости реакции. Мешающие примеси отстраняют ионообменным методом. Метод позволяет определять кобальт в пробах воды вплоть до 10^{-4} мкг/мл или вплоть до 5×10^{-5} мкг/мл в пробах не изыскующих ионообменное разделение.

О КОЭФФИЦИЕНТЕ РАСПРЕДЕЛЕНИЯ ДИМЕТИЛГЛИОКСИМАТА НИКЕЛЯ МЕЖДУ ВОДНЫМ РАСТВОРОМ И ОРГАНИЧЕСКИМИ РАСТВОРИТЕЛЯМИ:

S. OKI, *Talanta*, 1971, **18**, 1233.

Резюме—Определены при 20° коэффициенты распределения диметилглиоксимата никеля между водным раствором и 6 инертными растворителями. Коэффициенты распределения хелата никеля количественно протолкованы с точки зрения параметров растворимости. Рассчитан параметр растворимости хелата никеля 12,9, водного раствора —18,6, а молярный объем хелата —182 мл/моль.

ОТДЕЛЕНИЕ СЕРЕБРА ОТ РТУТИ(II) МЕТОДОМ КАТИОННОГО ОБМЕНА И ЕГО ОПРЕДЕЛЕНИЕ:

R. L. SHRIMAL, *Talanta*, 1971, **18**, 1235.

Резюме—Описано отделение серебра от ртути(II), мели(II), кобальта(II), никеля и цинка методом катионного обмена, основанном на разнице констант устойчивости комплексов, образующихся с ЭДТА при pH 4,6. Серебро елюируют 16 %тной азотной кислотой и определяют методом Вольхарда.

Dosage quantitatif des substances tensioactives par électroadsorption: E. Verdier, J. Piro and F. Garcia Montelongo, *Talanta*, 1971, **18**, 1237. (Equipe polarographique n° 61, Faculté des Sciences, 34 Montpellier, France, and Catedra de quimica analitica, Escuela de Ingenieria Technica-Industrial, Las Palmas de Gran Canaria, Espagne).

Summary—A method for the quantitative determination of cationic and non-ionic surfactants which is based on their inhibiting effect on certain electrochemical reactions has been developed. This technique enables one to determine, with a precision of 2–3%, these substances at concentrations of the order of $10^{-6}M$.

Determination of thoria in thorium ores by an emission spectrographic method: N. C. Kothari, *Talanta*, 1971, **18**, 1242. (Department of Engineering, James Cook University of North Queensland, Townsville, Queensland, Australia.)

Summary—The emission spectrograph is used to determine thoria in monazite sand. A sample of only 15 mg is required and yields rapid and accurate results for 2% thoria or less. Of various additives tested as carriers, carbon and MoO_3 were found to be best. A current of 6 A gave a proper rate of volatilization without excessive spattering. The 267·28 nm Mo line was used as internal standard and the 269·24 nm Th line for analysis. Silica and iron sulphide were used as matrix in synthetic samples. Results compared well with those obtained by wet-analysis.

Spectrophotometric determination of ruthenium with diphenylthiovioluric acid: R. S. Chawla, R. P. Singh and K. C. Trikha, *Talanta*, 1971, **18**, 1245. (Department of Chemistry, University of Delhi, Delhi-7, and A.R.S.D. College, New Delhi, India.)

Summary—Diphenylthiovioluric acid (DPHTVA) reacts with ruthenium(III) to form a complex which has an absorbance maximum at 520 nm. Effects of pH, heating time, buffer and reagent have been studied. DPHTVA has been found to be a sensitive reagent for ruthenium(III) (sensitivity = 0.0044 μg Ru/cm^2 for log $I_0/I = 0.001$), and has been made selective by the use of masking agents. The composition of the complex as revealed by different methods is 1:2 (ruthenium : DPHTVA).

КОЛИЧЕСТВЕННОЕ ОПРЕДЕЛЕНИЕ ПОВЕРХНОСТНО-АКТИВНЫХ ВЕЩЕСТВ МЕТОДОМ ЭЛЕКТРОАДСОРБЦИИ:

E. Verdier, J. Piro and F. Garcia Montelongo, *Talanta*, 1971, **18**, 1237.

Резюме—Разработан метод количественного определения катионных и неионогенных поверхностно-активных веществ, основанный на их ингибирующем действии на некоторые электрохимические реакции. Этот метод позволяет определять эти вещества при концентрациях $10^{-6}M$ с точностью 2–3%.

ОПРЕДЕЛЕНИЕ ОКИСИ ТОРИЯ В РУДАХ ТОРИЯ СПЕКТРОГРАФИЧЕСКИМ МЕТОДОМ:

N. C. Kothari, *Talanta*, 1971, **18**, 1242.

Резюме—Эмиссионный спектрограф использован для определения окиси тория в монацитном песке. Метод требует только 15 мг пробы и позволяет получать быстрые и точные результаты для меньше чем 2% окиси тория. Из испытанных носителей уголь и MoO_3 дали самые лучшие результаты. Подходящая скорость улетучивания получена током 6 *a* без чрезмерного обрызгивания. Линия спектра 267,28 нм Mo использована в качестве внутреннего эталона, а линия 269,24 нм Th—для анализа. Двуокись кремния и сульфид железа использованы в качестве матрицы в искусственных пробах. Результаты хорошо соглашаются с результатами, полученными химическим методом.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ РУТЕНИЯ ДИФЕНИЛТИОВИОЛУРОВОЙ КИСЛОТОЙ:

R. S. Chawla, R. P. Singh and K. C. Trikha, *Talanta*, 1971, **18**, 1245.

Резюме—Дифенилтиовиолуровая кислота (ДФТВК) реагирует с рутением(III) образуя комплекс, максимум светопоглощения которого лежит при 520 нм. Изучено влияние pH, продолжительности нагревания, буффера и реагента. ДФТВК представляет собой чувствительный реагент для рутения(III)—чувствительность равна 0,0044 мкг $Ru/см^2$ для G $1_0/1 = 0{,}001$; его избирательность повышается использованием маскирующих агентов. Выработанный различными методами состав комплекса 1:2 (рутений: ДФТВК).

NOTES FOR AUTHORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable. Original papers, preliminary and short communications, annotations, reviews, and letters will be published.

Because TALANTA is an international journal, contributions are expected to be of a very high standard. They should make a definite contribution to the subject. Papers submitted for publication should be new publications. The submission of a paper is held to imply that it has not previously been published in **any language,** that it is not under consideration for publication elsewhere, and that, if accepted for publication, it will not be published elsewhere without the written consent of the Editor-in-Chief. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, **but should be critical.** The Editor-in-Chief will welcome correspondence on matters of interest to analytical chemists. Annotations should be critical commentaries on some aspects of analytical chemistry and may deal with topics such as sources of error, or the scope and limitations of methods and techniques.

Original papers, short communications annotations and reviews will be refereed (see *Talanta*, 1962, **9**, 89). Referees will be encouraged to present critical and unbiased reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor-in-Chief, the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

Preliminary communications will be refereed urgently and will be accorded priority in publication. Letters to the Editor will not be refereed, but will be published at the discretion of the Editor-in-Chief. If accepted, they will also be given priority.

Fifty free reprints will be provided (regardless of the number of authors) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

2. Script Requirements

By following the Script Requirements carefully, authors will ensure more rapid publication of their papers.

General

Contributions should be submitted to the Editor-in-Chief or to a Regional Editor where appropriate (see editorial page for addresses). They may be written in English, French or German. All contributions in the French language should be submitted to Dr. M. Pesez, and those in the German language to Professor E. Blasius.

Preliminary communications should be limited to less than 1000 words in length and should not contain diagrams. If they do not fulfil these conditions they will be treated as short communications.

Scripts should be submitted in duplicate; they should be typewritten and the lines double-spaced. Where possible, papers should follow the pattern: *Introduction, Experimental, Results, Discussions, Conclusions* (or such of these headings as apply).

Because all material will be set directly in page proof, every attempt should be made to ensure that before being submitted, manuscripts are essentially in the final form desired by the authors, and that no alterations of moment will be required at the proof stage. Alterations suggested by the referee will be agreed with the authors at the manuscript stage. Authors writing in a foreign language are advised that in submitting papers they should endeavour to have the paper thoroughly corrected before submitting for publication. If the manuscript requires considerable editing, it may have to be returned to the authors for retyping. resulting in a serious delay in publication.

Summaries

The essential contents of each paper should be briefly recapitulated in a summary **placed at the beginning of a paper, or at the end of a preliminary or short communication.** This should be in the language of the paper, but for French or German papers an English version should also be provided wherever possible.

Illustrations

Illustrations should be separate from the typescript of the paper. Original line drawings should be supplied (about twice the final size required) together with one set of copies. **If the illustrations require redrawing, publication of the paper will be delayed.** The following standard symbols should be used on line drawings:

▲ △ ⊡ □ ● ○ ◬ ⊙ ⊕ ⊖ ⏀ ⊗

Photographs should be restricted to the very minimum required.

Legends for illustrations should be typed on a separate sheet.

Straight-line calibration graphs are not generally permitted; the necessary information can usually be included in the text (*e.g.* in the form of an equation).

Tables should be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarize results by an accepted method of expression (*e.g.* standard deviation). The same information should not be produced in both tables and figures.

The preferred positions for all figures and tables should be indicated in the manuscript by the authors.

References

References should be indicated in the text by consecutive superior numbers placed outside any punctuation marks; the full references should be given in a list at the end of the paper in the following form:

1. J. B. Austin and R. H. H. Pierce, *J. Am. Chem. Soc.*, 1955, **57**, 661.
2. S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*, 2nd Ed., Vol. 3, p. 214. Pergamon Press, Oxford, 1956.
3. R. J. Winterton in C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Vol. IB, p. 238. Elsevier, Amsterdam, 1960.
4. A. B. Smith, *The Effect of Radiation on Strength of Metals.* A.E.R.E., M/R 6329, 1962.
5. W. Jones, *Brit. Pat.* 654321, 1959.

Journal-name abbreviations should be those used in *Chemical Abstracts* (see *Chem. Abstr.*, 1961, *et seq.*).

Footnotes to pages and to tables, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, ¶, beginning anew on each page.

Proofs

Proofs are not set in galley form and will be sent out to authors in page form for correction. **It is emphasized that at this stage alterations to the text or failure to return the corrected proofs promptly may result in serious delay in publication, and authors will be charged for changes other than printers' errors.**

Authors are particularly requested to check the correctness of their references, which should also, at some stage, be checked against the original papers.

Miscellaneous

Because of the international character of the journal, authors should follow the recommendations of the *International Union of Pure and Applied Chemistry* as regards nomenclature and symbols. In the editing of papers for publication, English spelling will be used for all matter in the English language. Authors who wish to retain American spelling, or to adhere to other generally accepted usages, should indicate this clearly at the time of submission of the manuscript. Attention is particularly drawn to the importance of correctness of grammar and clarity of expression.

Where several authors are involved in a paper, an indication of the author to whom requests for reprints should be addressed may be given by placing the symbol ® after the name of that author.

Des exemplaires en français des Notes aux Auteurs peuvent être obtenus auprès du Rédacteur en Chef

Deutsche Abdrucke der Anmerkungen für Mitarbeiter sind beim Hauptschriftleiter zu erhalten

Оттиски правил для авторов на русском языке можно получить у главного редактора

Volume 18, 1971

January–June, Nos. 1–6

SUBJECT INDEX

PRINTED IN NORTHERN IRELAND AT THE UNIVERSITIES PRESS, BELFAST

are these important journals in your library?

Carbon
Editor-in-Chief:
DR S MROZOWSKI
Carbon Research Laboratory
State University of New York
at Buffalo
Buffalo NY 14214 USA

This Journal is devoted to the physics and chemistry, as well as to the scientific aspects of the technology of a class of materials ranging from organic crystals and polymers through chars and carbons to graphite. The interest of the Journal is limited to those organic substances which are related in some way to aromatic or tetrahedrally bonded carbonaceous solids. CARBON aims to provide a reliable source of information on the majority of original research carried out on these materials; reference to carbon research published elsewhere is included in a special literature section.
Published bi-monthly

Corrosion Science
Official Journal of the Corrosion and Protection Association (CAPA)
Editor-in-Chief:
PROF T K ROSS
Department of Chemical Engineering
University of Manchester Institute of Science & Technology
P O Box 88 Manchester M60 1QD

This Journal carries papers which make important contributions to an understanding of the phenomenon of corrosion and its control in practice, whether in the field of corrosion science or corrosion technology. The scope of corrosion is very wide and covers high-temperature oxidation, passivity, anodic oxidation, aqueous and fused salt corrosion and many other aspects of corrosion science. Papers published in English, French or German also appear in a separate Technology section which deals with corrosion from the viewpoint of industry and technology, whilst any paper of only 1000–2000 words in length appear under the title of Short Communications. All papers include abstracts in English, French and German.
Published monthly

Materials Research Bulletin
Joint Editors-in-Chief:
HEINZ K HENISCH AND
RUSTUM ROY
Materials Research Laboratory
The Pennsylvania State University
University Park Pennsylvania 16802
USA

Since its inception, this Journal has rapidly established itself as a valuable source of research information on crystal growth and materials preparation and characterization. Papers deal with the structure and properties of electronically, optically and mechanically interesting solids considered and discussed specifically as a function of the preparational parameters.
Because of the Journal's format, papers can be published within six weeks of submission to the Editors. For this reason, it has become a forum for all the latest developments in research within this field.
Published monthly

Inspection Copies
Inspection copies of all Pergamon Learned Journals are available on request from Dept. ED (t), Pergamon Press, Oxford.

Pergamon Press
Headington Hill Hall Oxford OX3 0BW
Maxwell House Fairview Park Elmsford New York 10523 USA
Pergamon House 19a Boundary Street Rushcutters Bay NSW 2011 Australia

8/70

Volume 18, No. 12 December 1971

Contents

Short Communications

Letter to the Editor

Talanta Annual Subscription Rates (including postage)

\$10 (£3·50)—*Bona fide* students

\$90 (£36)—Multiple-reader institutions

Private individuals whose departmental libraries subscribe, may obtain this journal for their personal use at a reduced rate of \$25 (£8) per annum.

Printed in Northern Ireland at The Universities Press, Belfast