An International Journal of Analytical Chemistry

ταλαντα

talanta

PERGAMON PRESS
OXFORD • LONDON • NEW YORK • PARIS

1970 VOLUME 17, NO. 10 OCTOBER

Books for Analytical Chemists

ANALYTICAL CHEMISTRY

Progress in Nuclear Energy Series IX,
Volume 10, Parts 1 and 2

Edited by **D. C. Stewart,** *Argonne National Laboratory, USA, and* **H. A. Elion,** *G.C.A. Corporation, USA*

Partial Contents: Part 1: Remote Analysis of Radioactive Materials—*Myron T. Kelley;* Thermogravimetric Analysis—*H. F. Green and K. V. Steed;* Remote Pipetting—*W. L. Maddox;* Sampling, Sample Dissolution, Evaporation and Combustion—*Calvin E. Lamb.* **Part 2:** Fission Gas Collection and Trace Gas Analysis—*W. Jennison;* Spectrographic Analysis in Containment Facilities—*R. H. Gaddy.*

Part 1 232 pages
Part 2 248 pages £10 set of two volumes

PROGRESS IN NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY, Volume 5

Edited by **J. W. Emsley,** *The University of Southampton,* **J. Feeney,** *Varian A.G., Zurich, and* **L. H. Sutcliffe,** *The University, Liverpool*

Contents: The INDOR Technique in High-resolution Nuclear Magnetic Resonance—*V. J. Kowalewski;* Magnetic Non-equivalence related to Symmetry Considerations and Restricted Molecular Motion—*T. H. Sidall and W. E. Stewart;* Applications of ^{1}H Nuclear Magnetic Resonance Spectroscopy to the Conformational Analysis of Cyclic Compounds—*Harold Booth.*

496 pages £7 hard cover

TIME-OF-FLIGHT MASS SPECTROMETRY

Edited by **D. Price,** *University of Salford, and* **J. E. Williams,** *Fieldtech Limited, London*

Partial Contents: Flash photolysis reactions—*R. T. Meyer and D. Price;* Shock wave reactions—*P. A. Robinson;* Fast recording techniques for time resolved mass spectrometry—*R. T. Meyer;* Detection of the NH_2 free radical and other ammoniacal complexes in the electrical discharge decomposition of ammonia gas—*K. O. Dyson.*

310 pages £5 hard cover

ENZYMATIC METHODS OF ANALYSIS

George G. Guilbault, *Louisiana State University, USA*

A stimulating and informative book which reviews all aspects of modern enzymatic analysis and acquaints chemists, biochemists and biologists with the possible uses of enzyme as analytical reagents.

Contents: General considerations; Methods of assay; Determination of Enzymes; Determination of Substrates; Determination of Activators and Coenzymes; Determination of Inhibitors; The Immobilized Enzyme; Use of Automation in Enzymic Analysis.

368 pages 75s hard cover
International Series of Monographs in Analytical Chemistry, Volume 34

THE DETERMINATION OF EPOXIDE GROUPS

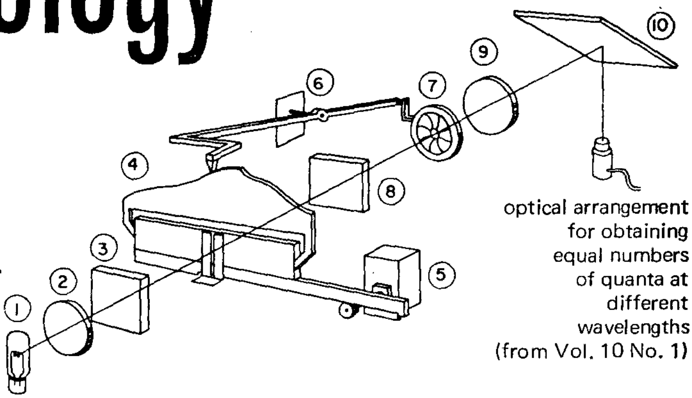
Edited by **B. Dobinson, W. Hoffman, and B. P. Stark**

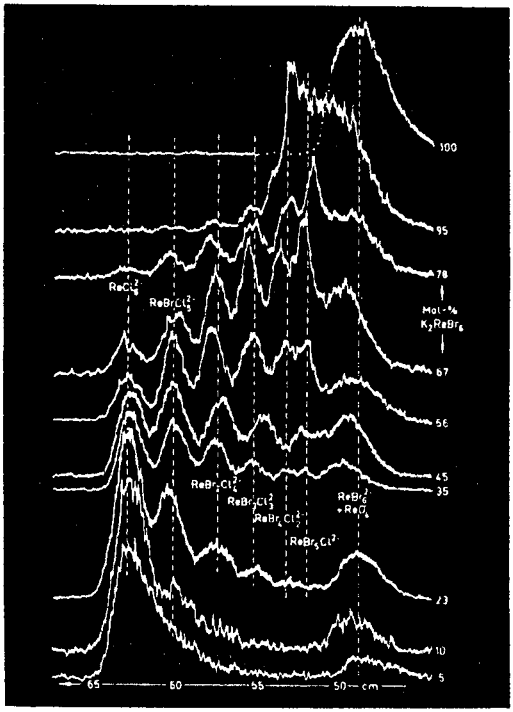
'This book combines a very thorough survey of the literature with the specialist knowledge of the authors. It will, of necessity, appeal to a limited readership, but for anyone in the least interested in this field, and the number of such people is growing, this book will prove a valuable acquisition; its publication should certainly fulfil the authors' hope that it will stimulate further work and so lead to improved methods in the future." *The Analyst*

86 pages 42s hard cover
Monographs in Organic Functional Group Analysis, Volume 1

Pergamon

T217


1
2
3
4
5
6
7
8
9
10

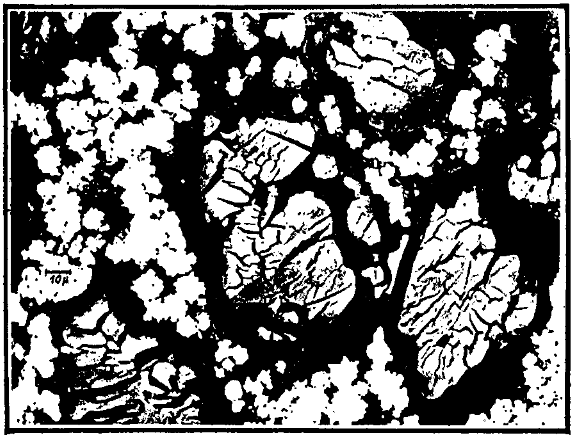


$ReCl_6^{2-}$
$ReBrCl_5^{2-}$
$ReBr_2Cl_4^{2-}$
$ReBr_3Cl_3^{2-}$
$ReBr_4Cl_2^{2-}$
$ReBr_5Cl^{2-}$
$ReBr_6^{2-}$ + $ReCl_6$
100
95
78
Mol-% K_2ReBr_6
67
56
45
35
23
10
5
65
60
55
50 cm

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.

The following papers appear in Volume 14 Number 10 of Electrochimica Acta:
H B URBACH and R J BOWEN:
Behaviour of the oxygen-peroxide couple on platinum
I FRIED and E SHAMIR:
A unified mathematical treatment of diffusion-controlled voltammetric processes
A WINSEL:
Flow rate and pressure drop of gas mixtures and electrolyte in gas-diffusion electrodes
C WAGNER:
Current yield during electrolysis of metal salt solutions with cations in different valency states
R D COWLING and A C RIDDIFORD:
The anodic behaviour of cobalt in alkaline solutions
T IWASITA and M C GIORDANO:
Kinetics of the bromine-tribromide-bromide redox processes on platinum electrodes in acetonitrile solutions

Published monthly

Please write now for full details of subscription rates, a free inspection copy and information on other related Pergamon publications.

Pergamon Press
OXFORD · NEW YORK · LONDON · PARIS · SYDNEY

1966

11/69

Residue Reviews

Residues of Pesticides and Other Foreign Chemicals in Foods and Feeds

Rückstands-Berichte
Rückstände von Pesticiden und anderen Fremdstoffen in Nahrungs- und Futtermitteln

Edited by
Francis A. Gunther
Riverside, California

Volume 26: Contents

Pesticide regulations and residue problems in Japan, K. Fukunaga and Y. Tsukano
Determination of organophosphorus pesticides in water, G. Zweig and J. M. Devine
Toxicity and hazards to man, domestic animals, and wildlife from some commonly used auxin herbicides, J. M. Way
A specific gas chromatographic method for residues of organic nitrogen pesticides, C. C. Cassil, R. P. Stanovick, and R. F. Cook
Significance of organochlorine insecticide residues in fresh plants as possible contaminants of milk and beef products, J. G. Saha
Potential interferences in certain pesticide residue analyses from organochlorine compounds occurring naturally in plants, J. W. Hylin, R. E. Spenger, and F. A. Gunther

With 14 figures. VII, 142 pages. 1969. Cloth DM 40,–; US $ 10.00

Volume 27: Contents

The regulation of pesticides in Italy, P. de Pietri-Tonelli
Polycyclic aromatic hydrocarbons (polynuclears) in smoked foods, D. J. Tilgner and H. Daun
On the problem of the harmful effect of DDT and its mechanism of action, Yu. S. Kagan, S. I. Fudel-Ossipova, B. J. Khaikina, U. A. Kuzminskaya, and S. D. Kovtun
The metabolism of diene-organochlorine (cyclodiene) insecticides, G. T. Brooks

With 6 figures. VII, 143 pages. 1969. Cloth DM 38,–; US $ 9.50

Volume 28: Contents

Insecticide residues in California citrus fruits and products, F. A. Gunther

With 38 figures. VII, 127 pages. 1969. Cloth DM 38,–; US $ 9.50

Volumen 29: Special Volume – Symposium on Decontamination of Pesticide Residues in the Environment
Atlantic City Meetings of the American Chemical Society, September 1968
Contents:

Introduction to the symposium: Decontamination of pesticide residues in the environment, G. K. Kohn
Attenuation of pesticidal residues on seeds, G. K. Kohn
The decontamination of animal feeds, T. E. Archer and D. G. Crosby
Reduction of parathion residue on celery, N. P. Thompson
Accelerated removal of pesticides from domestic animals, B. J. Liska and W. J. Stadelman
Effects of processing on pesticides in foods, B. J. Liska and W. J. Stadelman
Canning operations that reduce insecticide levels in prepared foods and in solid food wastes, R. P. Farrow, E. R. Elkins, W. W. Rose, F. C. Lamb, J. W. Ralls, and W. A. Mercer
Chemical and thermal methods for disposal of pesticides, M. V. Kennedy, B. J. Stojanovic, and F. L. Shuman, Jr.
Some research approaches toward minimizing herbicidal residues in the environment, C. L. Foy and S. W. Bingham
Decontamination of pesticides in soils, P. C. Kearney, E. A. Woolson, J. R. Plimmer, and A. R. Isensee
Interaction of diquat and paraquat with clay minerals and carbon in aqueous solutions, S. D. Faust and A. Zarins
Kinetics of hydrolysis of diazinon and diazoxon, H. M. Gomaa, I. H. Suffet, and S. D. Faust
Biodegradation kinetics of 2,4-dichlorophenoxyacetic acid by aquatic microorganisms, R. B. Hemmett, Jr. and S. D. Faust

With 46 figures. VIII, 213 pages. 1969. Cloth DM 54,–; US $ 13.50

Volume 30: Contents

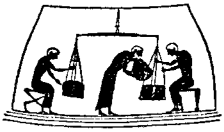
Distribution of pesticides in immiscible binary solvent systems for cleanup and identification and its application in the extraction of pesticides from milk, M. Beroza, M. N. Inscoe and M. C. Bowman
Factors affecting the extraction of organochlorine insecticides from soil, M. Chiba
Cumulative table of subjects covered, volumes 21–30
Comprehensive and cumulative subject-matter index, volumes 21–30
Cumulative author index, volumes 21–30
Cumulative list of volumes 1–30
List of promised forthcoming papers by short titles

With 11 figures. X, 169 pages. 1970. Cloth DM 58,–; US $ 14.50

Springer-Verlag
Berlin
Heidelberg
New York

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.Marr, 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(£3.10.)—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 $15(£5.5.) 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 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 © 1970 Pergamon Press Ltd.

ห้องสมุด กรมวิทยาศาสตร์

Advisory Board

Chairman: Professor R.Belcher, University of Birmingham, England

Professor G.Ackermann, School of Mines, Freiberg, German Democratic Republic
Dr.D.M.W.Anderson, University of Edinburgh, Scotland
Professor F.E.Beamish, University of Toronto, Ontario, Canada
Professor E.Cerrai, C.I.S.E., Milan, Italy
Mr.M.L.Dimbat, Shell Development Company, Emeryville, U.S.A.
Professor Fritz Feigl, Ministry of Agriculture, Rio de Janeiro, Brazil
Professor H.Flaschka, Georgia Institute of Technology, Atlanta, U.S.A.
Mr.J.K.Foreman, Laboratory of the Government Chemist, London, England
Professor H.Freiser, University of Arizona, Tucson, U.S.A.
Professor T.Fujinaga, University of Kyoto, Japan
Professor G.Gottschalk, Technical University, Berlin, German Federal Republic
Mr.S.Greenfield, Albright & Wilson (Mfg.) Ltd., Birmingham, England
Dr.T.P.Hadjiioannou, University of Athens, Greece
Professor K.Issleib, Martin Luther University Halle Wittenburg, German Democratic Republic
Professor K.J.Karrman, University of Lund, Sweden
Dr.D.H.Klein, Scripps Institution of Oceanography, La Jolla, California, U.S.A.
Dr.R.Levy, C.N.R.S., Paris, France
Professor H.Malissa, Technical University, Vienna, Austria
Professor L.Meites, Clarkson College of Technology, Potsdam, New York, U.S.A.
Dr.L.C.Pasztor, Jones & Laughlin Steel Corporation, Pittsburg, Pennsylvania, U.S.A.
Professor W.F.Pickering, University of Newcastle, New South Wales, Australia
Professor G.A.Rechnitz, State University of New York, Buffalo, U.S.A.
Dr.James E.Rein, Los Alamos Scientific Laboratory, New Mexico, U.S.A.
Dr.E.Sawicki, Taft Sanitary Engineering Centre, Cincinnati, U.S.A.
Dr.R.E.Sievers, Wright-Patterson Air Force Base, Dayton, Ohio, U.S.A.
Professor W.Simon, Eidg. Technische Hochschule, Zürich, Switzerland
Dr.A.A.Smales, A.E.R.E., Harwell, England
Professor G.Frederick Smith, University of Illinois, Urbana, U.S.A.
Professor E.Stahl, University of Saarland, Saarbrücken, German Federal Republic
Dr. G.Svehla, Queen's University, Belfast, Northern Ireland
Dr.G.Tölg, Max Planck Institute, Stuttgart, Germany
Dr.E.Wänninen, Åbo Academy, Finland
Professor T.S.West, Imperial College, University of London, England
Dr.Yu.A.Zolotov, Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, U.S.S.R.

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
Society of Cosmetic Chemists Journal
Spectrochimica Acta, Part A: Molecular Spectroscopy
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 of these leaflets which interest you.

Talanta, 1970, Vol. 17, pp. 895 to 906. Pergamon Press. Printed in Northern Ireland

TALANTA REVIEW*

QUANTITATIVE ANALYSIS IN PHARMACY AND PHARMACEUTICAL CHEMISTRY BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

D. M. Rackham
Analytical Department, Lilly Research Centre Ltd., Erl Wood Manor,
Windlesham, Surrey

(*Received* 16 *March* 1970. *Accepted* 17 *April* 1970)

Summary—The applications of n.m.r. to the quantitative analysis of pharmaceutical formulations and products of interest to the pharmacist and pharmaceutical analyst are reviewed. Special attention is paid to the accuracy of the method, the coefficients of variation being quoted (or calculated from data in the original paper) where possible. An elementary knowledge of n.m.r. is assumed.

SINCE the discovery of nuclear magnetic resonance (n.m.r.) spectroscopy in 1945[1,2] this spectroscopic technique has so gained in importance that, excluding those which quote n.m.r. data only as support to structural assignments, more than 250 papers a month are now appearing on the subject. Most of them, however, have not been concerned with the use of n.m.r. as a quantitative analytical tool. This may partly have been due to the relatively large quantity of sample required as compared with such analytical techniques as ultraviolet spectroscopy and gas-liquid chromatography (g.l.c.) and to the lack of n.m.r. facilities in less well equipped laboratories.

Recent advances in instrumentation have now made available cheaper n.m.r. spectrometers and time-averaging computer accessories which extend the scope of n.m.r. to microgram quantities. Thus it seems an opportune time for a comprehensive review on the work related to pharmaceutical chemistry. The basic principles of n.m.r. are described in elementary texts on physical chemistry but the needs of the pharmacist and pharmaceutical analyst are best served by current brief summaries.[3–5]

The use of n.m.r. depends on the measurement and interpretation of three parameters. These are signal position (the chemical shift or "δ" value), the splitting of that signal (the spin-spin coupling constants, J values, which reflect the number and nature of adjacent protons) and the signal intensity (expressed as a peak area or peak height). It is the signal intensity parameter which provides the quantitative measure of material in solution. A conventional proton n.m.r. experiment consists of a preliminary field sweep which establishes the proton δ and J values. For the assignment of unknown peaks in new compounds, several extensive compilations[6,7] can be consulted, and workers specially interested in nitrogen heterocyclics, alkaloids *etc*, will find of value the collected[8] proton n.m.r. shifts of 2306 proton groupings influenced

---

* For reprints of this Review see Publisher's announcement near end of issue.

by a nitrogen atom in the molecule. Once a peak, or group of peaks, in the n.m.r. spectrum has been related to structural features in the compounds examined, the peak areas can be accurately measured with the electronic integrator which is built in as standard equipment on all commercially-available analytical spectrometers. Provided that the compounds are chemically stable (and that suitably rapid sweep times and non-saturating observing field parameters are selected[9]) the integrated *peak areas* are directly proportional to the number of protons causing those peaks. For absolute quantitative measurements these peak areas can then be related to that of a standard solution of a single component in the same solvent and under the same instrumental conditions or against that of a quite separate standard entity which is added to the solution under test as an internal reference. In less common analytical practice, information is obtained from the ratio of spectral peak heights. In the absence of these standard reference techniques, the n.m.r. integration method yields only *relative* quantities of components from their relative peak areas.

The armoury of the n.m.r. spectroscopist is augmented by time-averaging computers (CATS) and glass micro-cells which permit the analysis of sub-milligram quantities, *e.g.*, for the determination of 0·1 mg of barbiturate mixtures and for the analysis of 0·05-mg g.l.c. fractions from a commercial terpene fraction.[10] Spectra may often be simplified by removing interfering OH and NH proton signals through addition of a few drops of heavy water (D_2O) or gaseous acid vapour. Certain n.m.r. spectrometers can be modified to operate on nuclei other than hydrogen (*e.g.*, boron-11, carbon-13, fluorine-19, and phosphorus-31). Although much employed elsewhere[6] this has found only one application pertinent to the present review. Other techniques generally available include spectrum simplification by irradiation of the samples with a second radiofrequency (a spin-decoupling experiment) and variation of the ambient probe temperature, but these methods have not been applied in the quantitative analysis of pharmaceutical products.

The most important considerations for the purpose of quantitative analysis by n.m.r. are the precision and accuracy of integration. Several authors[9,11,12] have discussed these with regard to instrument settings of field stability and strength, integral amplitude, time of scan and the concentration of the solution. Alexander[11] concludes that the measured integral is within 1% of the theoretical value if 3–4 mequiv of protons are available (*i.e.*, about 60 mg for a compound having a molecular weight of 200 with 10 protons per molecule). Spectrum integration against a suitable reference is also used[9] for the measurement of the amount of hydrogen in organic compounds and can be at least as accurate as combustion analysis. It is disturbing to find, therefore, serious discrepancies noted[13] in an inter-laboratory collaborative n.m.r. study carried out on samples of caffeine, with hexamethylcyclotrisiloxane as internal reference standard. Six collaborators quantitatively analysed sealed aliquots supplied by an associate referee. Hence the variation in their results did not depend on initial sample preparation but only on instrumental and operator errors, and on sample stability. A relative standard deviation as high as 9·7% was recorded for the caffeine content, but there were indications that decomposition or reaction between the components had occurred. A solution of rubbing alcohol was also studied by the collaborators. In this case the stability of the sample was not in question and the results proved satisfactory, *e.g.*, for the alcohol (61·2%) and water (34·6%) contents, coefficients of variation of 0·6–1·7% were found.

ANALYSIS USING, AS REFERENCE, STANDARD SOLUTIONS OF ONE COMPONENT

In these examples the standard chosen is a solution containing a known weight of a single component from the mixture. The procedure is to calculate the integral response of the n.m.r. instrument to this standard solution and then to draw a calibration curve of integrated peak areas over the range of concentration which will be encountered in the unknown solutions.

N.M.R. has proved[14,15] a useful criterion for qualitative identification of eighteen barbiturates, deuterochloroform ($CDCl_3$) or trifluoroacetic acid (TFA) being used as solvents. Rücker[16] has used a CAT and a 0·2-ml microcell for the quantitative analysis of only 0·1–1·5 mg of six barbiturates, with a quoted coefficient of variation of 10%. The CAT operates by dividing the spectral information into 1024 sections and feeding the signal amplitude data for each section into a memory channel of the computer. The effect of repetitive scanning is to augment weak signals, from small amounts of material, at the expense of interfering noise (the improvement factor in the ratio of signal to noise height being $\sqrt{n}$ after n accumulated scans). To obtain a satisfactory spectrum from such small quantities of barbiturates Rücker found that the necessary condition was that the product of the number of protons integrated as the unknown and of the number of accumulated scans must exceed 600. As an example we can consider the analysis of a mixture of 5-ethyl-5-phenylbarbituric acid (A) and 5,5-diethylbarbituric acid (B). The peaks integrated are those due to the phenyl protons of A and the methylene protons of B as shown in Fig. 1.

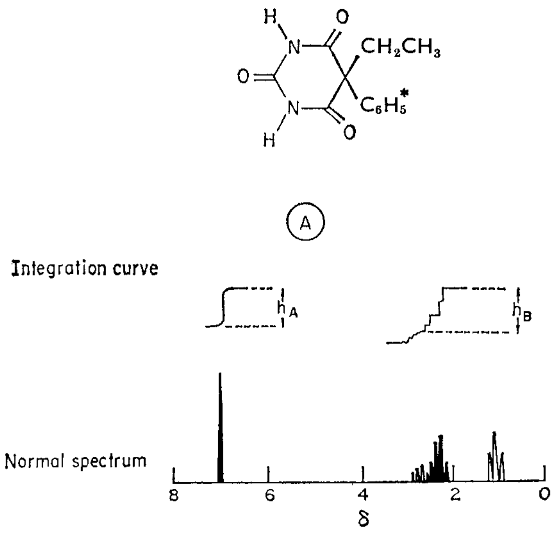


FIG. 1.—Accumulated spectrum of barbituric acids A and B. (Redrawn from *Z. Anal. Chem.*, 1967, **229**, 340 and printed by permission of the copyright holders.)

First, each component (10 mg) is dissolved in 2 ml of solvent and the spectrum of 0·2 ml of this solution accumulated 120–150 times until sufficient for integration. A constant (k) for the component and the instrument parameters is found from the equation:

$$k = \frac{h}{c.n.a.} \tag{1}$$

where h = integration height, c = concentration, n = number of protons causing the integrated peak(s) and a = number of spectra accumulated.

Quantitative analysis of a mixture (0·2 mg/ml) of A and B follows simply from integration of a 250-scan accumulated spectrum (Fig. 1) and substitution in equation (1) of the integral heights for A and B (h_A and h_B) so obtained.

Nine sedatives and hypnotics (including meclozine, methaqualone, glutethimide and ethinamate) give well defined n.m.r. spectra[17] and two ternary mixtures (containing a minimum of 3 % of each component) can be analysed with a coefficient of variation of 4 %. A microcell (without CAT) was used in this work and analyses were made on 10–15 mg quantities of the mixtures. To calibrate the integrator, each component was first made up as a solution (30–1500 mg/ml in $CDCl_3$) and the spectrum integrated to yield the relevant k values. These were then substituted into equation (1) for the calculation of mixture compositions. The author points out the advantages over other spectroscopic and chromatographic techniques, the n.m.r. method providing more specific qualitative identification and comparable quantitative accuracy.

Historically, the first application of n.m.r. to pharmaceutical formulations was the analysis[18] of aspirin, phenacetin and caffeine (APC) tablets. The analysis is based on integration of the peaks given in Table I.

TABLE I.—APC TABLET ANALYSIS

Component	Peaks integrated	Coefficient of variation, %
Aspirin	$-OCOCH_3^*$	3·5
Phenacetin	$-OCH_2^*CH_3$	4·9
Caffeine	$—N—CH_3^*$	4·5

One analysis requires 60 mg of material with deuterochloroform (or ethanol-free chloroform) as solvent. Allowance is made in this procedure for overlap of phenacetin and caffeine peaks and for an interfering carbon-13 satellite band. Binders (starch or lactose) do not dissolve in the solvent and hence do not interfere. The integration calibration is carried out with a 50 mg/ml caffeine solution and all areas are referred to this standard measurement. The merits of this method over the United States National Formulary methods have been discussed.[18,19] Two major advantages of the n.m.r. assay procedure are simplicity of sample preparation and rapid turnover (3 samples/hr).

ANALYSIS BY *IN SITU* ADDITION OF AN INTERNAL STANDARD

Addition of a reference standard directly to the solution being analysed is a procedure preferred to that described in the previous section because it eliminates possible variations of integral amplitude with a change in temperature, tube size or instrument behaviour between measurements made on standard and unknown. It is most important, however, that there should be no adverse interactions between components in the sample and the reference. These could lead to chemical degradation or to a physical change in the peak positions, thus causing overlap of areas otherwise sufficiently separated for integration.

For qualitative analysis by n.m.r., a standard very frequently used is tetramethylsilane (TMS, $\delta = 0{\cdot}00$) which is a chemically inert material having a sharp, single n.m.r. peak well separated from "normal" C—H, O—H, S—H and N—H proton positions. The low boiling point of TMS (27°) militates against its use as a reference standard for quantitative studies and structurally similar and inert (but less volatile) materials have been investigated. Barcza[20] has calculated molecular weights accurate to within 3% by n.m.r. integration of peaks from the unknown and relation of this to the integration of the single peak of the reference material hexamethylcyclotrisiloxane ($\delta = 0{\cdot}15$, m.p. 64·5°). The recently introduced[21] cyclosilane-d_{18} ($\delta = -0{\cdot}33$, b.p. 208°) also seems very suitable as a non-volatile, inert standard.

Tranquillizers and analgesics have been studied by n.m.r. methods. Neville[22] reported the identification of the salts of procaine, larocaine and lidocaine. Turczan and Kram[23] have presented simple, rapid and specific quantitative analyses of meprobamate tablets and of carisoprodol and mebutamate. Meprobamate (80 mg/ml) is measured by comparing the integration of the carbamate methylene group (H_2N—CO—O—CH_2*—) at 3·8δ with the methylene signal ($\delta = 3{\cdot}3$) of malonic acid, the standard added (80 mg/ml). Acetone (which need not be deuterated) is the solvent of choice. For seven synthetic meprobamate preparations a coefficient of variation of 1·3% was found and the authors report no interference from other active ingredients which may be present in various meprobamate formulations (*e.g.*, amphetamine salts, dexamethasone or aspirin).

The fast analysis (30 min) of hypoglycaemic agents by n.m.r.[24] compares well in accuracy with classical acidimetric and bromometric methods, without the necessity of preliminary, time-consuming separation. Glycodiazine (C), carbutamide (D) and tolbutamide (E) have easily interpreted n.m.r. spectra in trifluoroacetic acid; maleic acid ($\delta = 6{\cdot}62$) serves as the reference standard for all of these. The spectra in the 6–10δ region are given in Fig. 2 together with the coefficients of variation for five measurements on 500-mg samples. The protons used for integration are those indicated as c, d, d^1, e and e^1 and the vinylic protons of maleic acid.

It is also possible[24] to analyse a mixture of the three components by integration of the signals for the protons shown in Fig. 2 together with the aromatic methyl proton signal ($\delta = 2{\cdot}50$) of compound E. Twenty-one measurements made on synthetically prepared ternary mixtures of C, D and E with maleic acid gave coefficients of variation of 1·2% (C) and 1·7% (D and E).

A similar method[25] can be applied to the methylxanthine stimulants theophylline (F), theobromine (G) and caffeine (H) in mixtures with sodium benzoate (I) and sodium salicylate (J). *p*-t-Butylbenzoic acid is a satisfactory reference compound, with a single, very intense absorption ($\delta = 1{\cdot}40$) for the nine protons of the t-butyl group. Each component in the mixture is detectable down to 3%. N.M.R. integration has been carried out on twenty-seven synthetic mixtures (60–100 mg) of the five components and the standard (10–15 mg) in trifluoroacetic acid (0·4–0·6 ml). Coefficients of variation for the methylxanthines and the sodium salts were 1·5% (F), 2·9% (G), 3·3% (H), 1·1% (I) and 1·0% (J). Thus the n.m.r. method "brings one step nearer the goal of complete complex tablet analysis in one working process."[25]

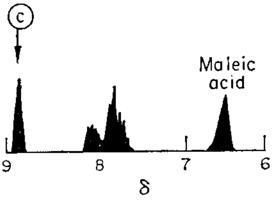
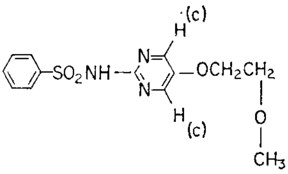
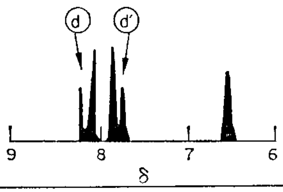
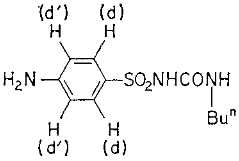
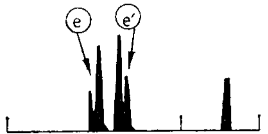
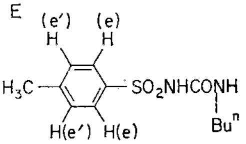
Spectrum	Compound	Coefficient of variation
	C 	1%
	D 	2%
	E 	2%

FIG. 2.—N.M.R. spectra of hypoglycaemic preparations. (Redrawn from *Z. Anal. Chem.*, 1969, **246**, 22 and printed by permission of the copyright holders.)

A contaminant sometimes found in human and veterinary preparations is dimethylsulphoxide (DMSO) which can be quantitatively assayed[26] in the range 20·0–0·05% by use of the sharp single peak in the n.m.r. spectrum. Integration of the spectrum is satisfactory for 20·0–2·0% concentration but below this level (*i.e.*, 2·0–0·05%) the integrator is insufficiently sensitive and a measurement of peak heights is made. The reference compound chosen is methanol and the method allows the use of non-deuterated water or chloroform as solvent; their n.m.r. peaks do not interfere in the region of importance. If measurements are made at room temperature (23·3°) and equal volumes of solution and methanol standard are used, the calculation of DMSO content reduces to the simple expression

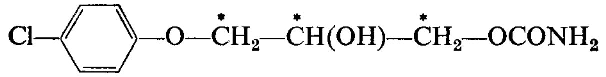
$$\%\,\text{DMSO (v/v)} = 87{\cdot}83 \times \frac{\text{DMSO area at } 2{\cdot}7\delta}{\text{methanol area at } 3{\cdot}3\delta}\,.$$

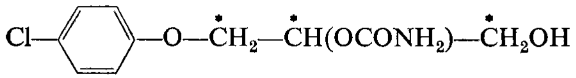
Coefficients of variation are not available for the integration method but the relative error quoted lies between 0·1 and 1·2%.

ANALYSIS BY PEAK HEIGHT OR PEAK POSITION MEASUREMENTS

In cases where a satisfactory separation of peaks (or a sufficiently high concentration) for an accurate integration of peak areas cannot be achieved, it may be advantageous to work on the measurement of the peak heights (of readily assigned signals from each component but it should be noted that this is valid only when the line widths, and multiplicities, are identical) or of peak positions (when a rapid proton exchange process occurs between the components, causing coalescence of their signals).

During the manufacture of the muscle relaxant maolate, a second isomer is formed in low yield

Maolate 

Secondary isomer 

Slomp *et al.*[27] have tested n.m.r. as a quantitative analytical method for this binary mixture. Considerable simplification can be brought about by moving —OH and —NH type protons from positions in which they will interfere with the integration of the remainder of the spectrum. This is accomplished by purging the solution (10% in hexadeuteroacetone) with hydrochloric acid vapour, which causes a rapid exchange of the OH and NH protons and a shift in their δ values. Unfortunately a small, broad interfering absorption due to OH or NH protons still remains and this has a highly unfavourable effect on the integral areas. The problem has been resolved by measurement of relative peak heights at $\delta = 3{\cdot}75$ (mainly secondary isomer) and $\delta = 4{\cdot}08$ (wholly maolate) in the region where the starred protons of the two isomers absorb, the very broad NH or OH proton residue having little effect on peak height. Data from the n.m.r. spectra were processed by an IBM 1620 which computed composition and standard deviation thus saving 80% of operator calculating time. The method of assay is considered significant to a few tenths of 1% and the coefficient of variation for 15 assays is 1–2%.

Antihistamines can be analysed qualitatively by n.m.r.[28] Koch *et al.*[29] have used n.m.r. quantitatively to estimate the ratio of salt to free base in chloroform extracts of these amines from aqueous acidic solutions. Analyses were made by measuring the time-averaged n.m.r. shift of an *N*-methyl group in base/salt mixture and comparing

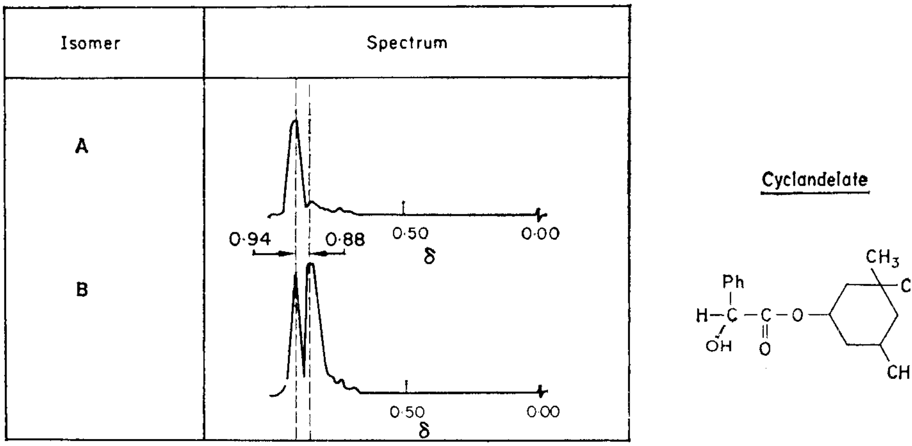


FIG. 3.—Spectra of isomers of cyclandelate. (Redrawn from *Pharm. Weekblad*, 1966, **101**, 93 and printed by permission of the copyright holders.)

this with its position in the pure free amine and amine salt components alone. The maximum shifts obtained between —N—CH_3 and $—\overset{+}{N}—CH_3$ were 10–100 Hz (*e.g.*, 36·6 Hz for diphenhydramine). Linear calibration curves were constructed for known mixtures by a least-squares analysis, with a standard deviation of 0·05–0·13 Hz. The n.m.r. technique is faster and requires less material than the alternative method of ultraviolet spectrometry followed by silver nitrate titration.

The vasodilator cyclandelate consists of a mixture of 4 isomeric esters which can be separated into two diastereoisomeric pairs of optical antipodes. The ratio of these pairs determines the final properties of the commercial material and this can be measured[30] with a coefficient of variation of 3% by n.m.r. from the peak heights. The spectra of the diastereoisomeric pairs (A, m.p. 84° and B, m.p. 55·5°) differ slightly (in their methyl proton regions only). They cannot be analysed by integration but quantitative determination of the isomeric ratio is possible from the relative peak heights of the methyl signals at 0·88 and 0·94δ (Fig. 3). A calibration graph for peak heights is first established for mixtures of known composition in deuterochloroform.

As a final example in this section we refer to the problem of dimethylsulphoxide assay.[26] When the quantities of DMSO are too small for accurate integration to be carried out (<2%), peak height measurements are made. In this case the coefficient of variation (1·4–5·4%) is greater than the relative error stated for the integration method (0·1–1·2%). A simple expedient would seem to be to use a CAT for spectrum accumulation until the peaks are of sufficient amplitude for normal integration processing.

ANALYSIS WITHOUT A REFERENCE STANDARD

When information from peak areas or peak heights is not referred to a standard compound in the manner previously described, only a *relative* measure of quantities in solution is obtained.

The opium alkaloid thebaine is naturally accompanied by small quantities of cryptopine, and Rüll[31,32] has estimated the relative proportions of these by n.m.r., down to 2% of cryptopine. This small quantity is not revealed by paper chromatography, infrared or visible spectrophotometry or by electrophoresis. Rüll found that the methoxyl signals in mixtures of the two alkaloids are not always sufficiently resolved but that an accurate integration could be achieved by considering the aromatic, olefinic, methylenedioxy and methine protons in the region 4·8–7·15δ (Table II). No coefficient of variation is available but a precision of 0·5% is stated for the cryptopine content.

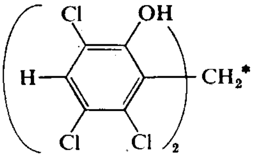
TABLE II.—OPIUM ALKALOIDS

Compound	Protons at 4·8–5·75δ	Protons at 5·75–7·15δ
Thebaine	3	2
Cryptopine	0	6

Dietrich[33] has pointed out the deficiencies of colorimetry and ultraviolet spectrophotometry in the qualitative identification and quantitation of binary mixtures of six commercial soap and detergent bacteriostats. The requirements for quantitative analysis are met by an n.m.r. method[33] based on the spectral integration of 10%

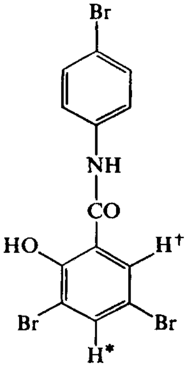
solutions of the materials (50 mg) in dimethylsulphoxide. For a mixture of hexachlorophene (K) and 3,4′,5-tribromosalicylanilide (L), the peaks integrated are those due to the methylene protons of K and the aryl protons of L (shown starred below).

Hexachlorophene (K)



*4·38δ

3,4′,5-Tribromo-
salicylanilide (L)



*8·00δ
†8·27δ

All possible binary mixtures can be measured by n.m.r. integration. Coefficients of variation are not given but the authors estimate a precision and error of about 3%. It is suggested that the method can also be extended to certain three-component systems. Other detergent chemicals have been studied by n.m.r. There are reports[34,35,36] of the quantitative analysis of ionic and non-ionic detergents (*e.g.*, ethylene oxide/alkylphenol condensates). In these, n.m.r. has yielded unique information regarding olefin distributions, *ortho–para* substitution ratios and average alkyl chain lengths and molecular weights.

Very recently the n.m.r. method has been used in the analysis of pesticides. Organophosphorus materials frequently have simple spectra permitting facile qualitative analysis.[37,38] The use of an n.m.r. spectrometer operating at high magnetic fields and frequencies (100 or 220 MHz instead of 60 MHz) often simplifies complex spectra. Keith *et al.* revise some of the assignments made[38] at 60 MHz for these pesticides, on the basis of a 100 MHz study.[39] A further 26 DDT-like pesticides are the subject of a paper[40] which includes the quantitative analysis of a technical DDT preparation (a mixture of the 2,4′ and 4,4′ isomers). The benzylic protons of these are well separated for integration. Typical results showed a fourfold excess of the 4,4′ isomer.

The systemic insecticide Systox consists of two isomers (M and N—see Fig. 4), in approximately equal quantities together with a small amount (1–5%) of a dithionopyrophosphate (Q). Since they differ in toxicity a method was required which would yield the quantities of M and N (in the presence of Q). A combination of g.l.c. and n.m.r.[41] is rapid, low in material requirement (100 mg) and non-degradative.

Samples of Systox are made up as 20% solutions in carbon tetrachloride. The protons of M, N and Q fall conveniently into three regions (Fig. 4) according to the adjacent C, S or O atom and the integration is measured at 1·1–1·5, 2·3–3·1 and

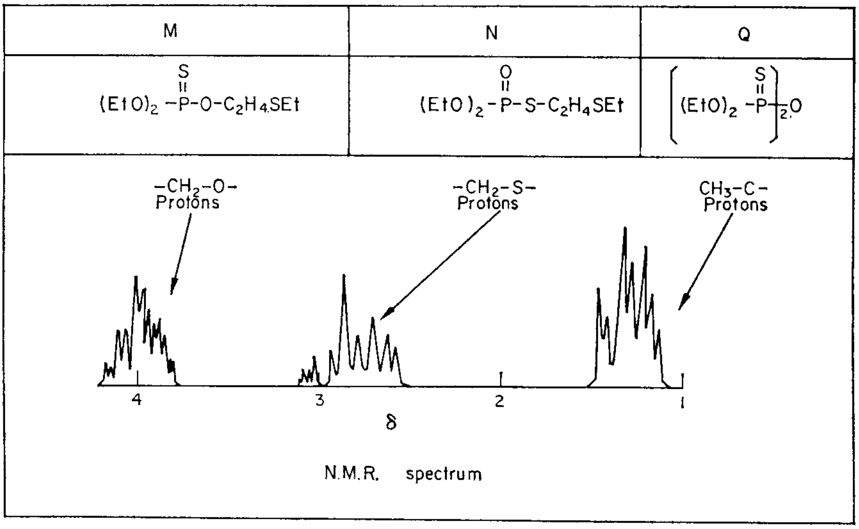


FIG. 4.—Constituents and n.m.r. spectrum of Systox. (Redrawn from *Anal. Chim. Acta*, 1968, **40**, 387 and printed by permission of the copyright holders.)

3·8–4·3δ. The weight of material taken and the ratio of the integrated areas give a relative measure of the composition. An independent determination of the Q content is made by the known g.l.c. method[42] and this leads directly to the weight of isomers M and N in technical Systox. Insufficient data are given in the paper for a calculation of the coefficient of variation but the authors quote an error of 1·5%.

Muller[43] previously employed phosphorus-31 magnetic resonance for investigating the rate law for the isomerism of M and N in Systox free from component Q. Although absorption peaks in phosphorus-31 resonance are much broader than in proton resonance, chemical shifts are frequently an order of magnitude greater. For M and N the phosphorus chemical shifts are 41·8 ppm apart and thus ideally separated for integration (contrast 1–2 ppm for the —CH_2—O— and —CH_2—S— proton chemical shifts). Unfortunately, the dearth of phosphorus-31 n.m.r. equipment means that this attractive alternative nucleus is unlikely to find wide application in quantitative pharmaceutical analysis for many years.

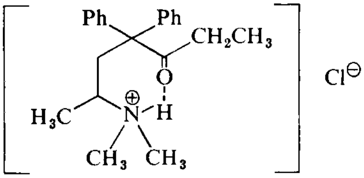
When the spectra are sufficiently resolved, the relative composition of certain stereoisomeric mixtures may be quantitatively analysed by integration of their n.m.r. spectra. Casy has found this method applicable for determining the *cis/trans* ratio of some piperidinols[44] and for the mixture of α- and β-propoxyphene carbinols.[45] In the latter a clear separation of peaks is noted for the secondary methyl doublets of the α- and β-isomers (16 Hz for the free bases and 22 Hz for their hydrochlorides).

ISOMERISM AND COMPLEXATION

In the final section brief mention will be made of some of the potentialities of n.m.r. for the identification and analysis of certain isomers and of interactions difficult to study by other physical methods. It is hoped that the analyst will thus be encouraged to consider how n.m.r. may be of assistance in problems beyond the range of those discussed so far.

Mention has already been made of the quantitative analysis of diastereoisomeric pairs of optical isomers by n.m.r. and peak height measurement. In very fortuitous examples, it is also possible to resolve the peaks due to the *optical isomers* themselves. Burlingame[46] found that the asymmetric carbinol $PhCH(OH)CF_3$ gives the expected doublet for the hydroxyl group proton in normal solvents but that this is split into a pair of doublets when an optically active naphthylethylamine is used as the solvent. This splitting is attributed to the (+) and (—) carbinols and was measured as 1·6 Hz at 60 MHz. A similar splitting (of 5 Hz) has also been noted[47] for propanol esters derived from R-*O*-methylmandelic acid.

Many examples can be found in which separate n.m.r. signals are obtained from *conformational isomers.* These need not necessarily be ring structures, *e.g.*, the straight-chain analgesic methadone hydrochloride shows two singlets in the n.m.r.[48] for its *N*,*N*-diethylamino group. This has been explained by hydrogen bonding between the ketonic group and the basic centre which can cause two different quasi-ring conformations.



Apart from pharmaceutical analysis the n.m.r. method has also found extensive use for the identification of *geometrical isomers* about an olefinic double bond (*e.g.*, in the carotenoids[49]) and in the quantitative measure of *keto–enol tautomerism* (as in acetylacetone[50]). To the pharmacologist n.m.r. has become an attractive tool for examination of the sites of complexation between drugs and protein materials. Jardetzky has shown that n.m.r. line-broadening[51] and signal decay time[52] parameters offer otherwise unobtainable information about the sites of bonding of sulphonamides to egg albumin and of NAD to enzymes.

There is no doubt that the types of n.m.r. approach described in this and previous sections will find increasing application in quantitative pharmaceutical practice when a single-step, rapid, accurate and non-destructive assay procedure is needed.

Acknowledgement—I wish to thank Dr. A. F. Cockerill and Dr. N. C. Franklin for their valuable advice in the preparation of this manuscript.

Zusammenfassung—Die Anwendungen von N.M.R. auf die quantitative Analyse von pharmazeutischen Formulierungen und Produkten, die für den Pharmazeuten und pharmazeutischen Analytiker von Interesse sind, werden besprochen. Besondere Aufmerksamkeit wird der Richtigkeit der Methode gewidmet; die Koefizienten der Variation, die zitiert (oder von Daten im ursprünglichen Referat kalkuliert) werden, waren möglich. Elementare N.M.R.-Kenntnisse werden vorausgesetzt.

Résumé—On passe en revue les applications de la RMN à l'analyse quantitative de formulations pharmaceutiques et de produits intéressant le pharmacien et l'analyste en pharmacie. On porte une attention particulière à l'exactitude de la méthode, les coefficients de variation étant fournis (ou calculés des données du mémoire original) lorsque cela est possible. On admet une connaissance élémentaire de la RMN.

REFERENCES

1. F. Bloch, W. W. Hansen and M. Packard, *Phys. Rev.*, 1946, **69**, 127.
2. E. M. Purcell, H. C. Torrey and R. V. Pound, *ibid.*, 1946, **69**, 37.
3. T. G. Alexander and S. A. Koch, *J. Assoc. Offic. Agr. Chemists*, 1965, **48**, 618.
4. R. T. Parfitt, *Pharm. J.*, 1969, 300, 320.
5. N. C. Franklin, *Pharma International*, in press.
6. J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Vols. 1 and 2, Pergamon, Oxford, 1965–1966.
7. W. Brügel, *NMR Spectra and Chemical Structure*, Vol. 1, Academic Press, New York, 1967.
8. G. Slomp and J. G. Lindberg, *Anal. Chem.*, 1967, **39**, 60.
9. W. B. Smith, *J. Chem. Educ.*, 1964, **41**, 97.
10. R. E. Lundin, R. H. Elsken, R. H. Flath, N. Henderson, T. R. Mon and R. Teranshi, *Anal. Chem.*, 1966, **38**, 291.
11. T. G. Alexander and S. A. Koch, *Appl. Spectry*, 1967, **21**, 181.
12. J. L. Jungnickel and J. W. Forbes, *Anal. Chem.*, 1963, **35**, 938.
13. T. G. Alexander and S. A. Koch, *J. Assoc. Offic. Anal. Chemists*, 1967, **50**, 676.
14. W. D. V. Philipsborn, *Arch. Pharm (Mitt.)*, 1964, **34**, 58.
15. G. Rücker, *Arch. Pharm.*, 1966, **299**, 688.
16. *Idem*, *Z. Anal. Chem.*, 1967, **229**, 340.
17. G. Rücker and P. N. Natarajan, *Arch. Pharm.*, 1967, **300**, 276.
18. D. P. Hollis, *Anal. Chem.*, 1963, **35**, 1682.
19. J. Levine, *ibid.*, 1964, **36**, 1683.
20. S. Barcza, *J. Org. Chem.*, 1963, **28**, 1914.
21. L. Pohl and M. Eckle, *Angew. Chem. (Int. Ed.)*, 1969, **8**, 380.
22. G. A. Neville, *Can. Spectr.*, 1969, **14**, 44.
23. J. W. Turczan and T. C. Kram, *J. Pharm. Sci.*, 1967, **56**, 1643.
24. K. Rehse, *Z. Anal. Chem.*, 1969, **246**, 22.
25. *Idem*, *Deut. Apotheker-Z.*, 1967, **107**, 1530.
26. T. C. Kram and J. W. Turczan, *J. Pharm. Sci.*, 1968, **57**, 651.
27. G. Slomp, R. H. Baker and F. A. MacKellar, *Anal. Chem.*, 1964, **36**, 375.
28. J. Reisch, H. Alfes and H. Möllman, *Z. Anal. Chem.*, 1968, **238**, 29.
29. S. A. Koch and T. D. Doyle, *Anal. Chem.*, 1967, **39**, 1273.
30. C. van der Vlies, G. A. Bakker and R. F. Rekker, *Pharm. Weekblad*, 1966, **101**, 93.
31. T. Rüll, *Bull. Soc. Chim. France*, 1963, 1897.
32. *Idem*, *ibid.*, 1963, 586.
33. M. W. Dietrich and R. E. Keller, *J. Am. Oil Chemists Soc.*, 1967, **44**, 491.
34. M. M. Crutchfield, R. R. Irani and J. T. Joder, *ibid.*, 1964, **41**, 129.
35. P. W. Flanagan, R. A. Greff and H. F. Smith, *ibid.*, 1963, **40**, 118.
36. P. W. Flanagan, R. A. Greff and H. F. Smith, *Anal. Chem.*, 1963, **35**, 1283.
37. H. Babad, W. Herbert and M. C. Goldberg, *Anal. Chim. Acta*, 1968, **41**, 259.
38. L. H. Keith, A. W. Garrison and A. L. Alford, *J. Assoc. Offic. Anal. Chemists*, 1968, **51**, 1063.
39. L. H. Keith and A. L. Alford, *Anal. Chim. Acta*, 1969, **44**, 447.
40. L. H. Keith, A. L. Alford and A. W. Garrison, *J. Assoc. Offic. Anal. Chemists*, 1969, **52**, 1074.
41. H. Babad, T. N. Taylor and M. C. Goldberg, *Anal. Chim. Acta*, 1968, **40**, 387.
42. W. R. Betker, C. J. Cohen, N. J. Beaker and D. M. Wasleski, *J. Agr. Food Chem.*, 1966, **14**, 318.
43. N. Muller and J. Goldensen, *J. Am. Chem. Soc.*, 1956, **78**, 5182.
44. A. F. Casy, M. A. Iorio and P. Pocha, *J. Chem. Soc. (C)*, 1967, 942.
45. A. F. Casy, *J. Pharm. Sci.*, 1967, **56**, 1049.
46. T. G. Burlingame and W. H. Pirkle, *J. Am. Chem. Soc.*, 1966, **88**, 4294.
47. M. Raban and K. Mislow, *Tetrahedron Letters*, 1966, 3961.
48. L. L. Smith, *J. Pharm. Sci.*, 1966, **55**, 101.
49. M. S. Barber, A. Hardisson, L. M. Jackman and B. C. L. Weedon, *J. Chem. Soc.*, 1961, 1625.
50. L. W. Reeves, *Can. J. Chem.*, 1957, **35**, 1351.
51. O. Jardetzky, *Naturwiss.*, 1967, **54**, 149.
52. O. Jardetzky and N. G. Wade-Jardetzky, *Mol. Pharmacol.*, 1965, **1**, 214.

Talanta, 1970, Vol. 17 pp. 907 to 914. Pergamon Press. Printed in Northern Ireland

THERMOMETRIC TITRATION STUDIES OF MIXED LIGAND COMPLEXES OF THORIUM

G. C. KUGLER and G. H. CAREY*
U.S. Army Materials and Mechanics Research Center, Watertown, Mass., U.S.A.

(*Received* 3 *December* 1969. *Accepted* 16 *March* 1970)

Summary—Mixed-ligand chelates consisting of two different multidentate ligands linked to a central thorium(IV) ion have been prepared in aqueous solution and their heats of formation studied thermometrically. Pyrocatechol, tiron, chromotropic acid, potassium hydrogen phthalate, 8-hydroxyquinoline-5-sulphonic acid, iminodiacetic acid, 5-sulphosalicylic acid and salicylic acid were used as the secondary ligands, while ethylenediaminetetra-acetate and 1,2-diaminocyclohexane-N,N,N',N'-tetra-acetate were used as primary ligands. ΔH values for the overall reactions are given, and where possible, the ΔH and ΔS values for the specific secondary ligand addition were calculated. The overall stability of the mixed-ligand chelates and the enhanced stability of EDTA mixed chelates relative to the analogous DCTA chelates were found to be due to entropy rather than enthalpy effects.

MIXED-LIGAND chelates of thorium(IV) were first prepared in solution and studied potentiometrically by Carey, Bogucki and Martell.[1] These bi-ligand chelates are formed by the reaction of various bidentate secondary ligands with thorium(IV) chelates of multidentate primary ligands such as EDTA and DCTA (1,2-diaminocyclohexane-N,N,N',N'-tetra-acetic acid). Since thorium(IV) has a co-ordination number of eight[2] and EDTA is hexadentate, the metal ion in the simple 1:1 Th-EDTA chelate has two unused co-ordinating sites available for hydrolysis, olation or polymerization reactions. Filling these two vacant sites by the addition of a bidentate secondary ligand results in the formation of a 1:1:1 mixed-ligand chelate which is found to be quite stable and more resistant towards hydrolysis than the simple EDTA chelate. Previously,[1] only free energy (log K) values were reported for such secondary ligand addition reactions. These data, though important, were of limited usefulness in explaining why mixed-ligand chelate formation occurs. The present paper provides ΔH and ΔS values for these systems in order to supply information concerning the energetics of mixed-ligand chelate formation.

Usefulness of thermometric titration techniques as an easy, rapid and accurate method to obtain enthalpy values for metal chelate systems has been amply demonstrated in the literature.[3-7] Jordan[3] has described the theory and instrumentation of thermometric titrations. Using this method Jordan and Alleman[4] have obtained heats of formation for a number of transition metal–EDTA chelates by titration of EDTA with metal ions at constant pH. Raffa *et al.*[5] determined ΔH for the dissociation of ephedrinium and pseudoephedrinium ions by titration of the ligand with sodium hydroxide or hydrochloric acid, and Freeburg[6] obtained heats of formation for bivalent metal–nitrilotriacetate chelates. Zenchelsky[7] has reviewed the field of thermometric titrations.

---

* Present addresses: George H. Carey—Dept. of Chemistry, Stonehill College, No. Easton, Mass. 02356. George C. Kugler—ESB Research Center, 19 W. College Ave., Yardley, Pa. 19068.

EXPERIMENTAL

Reagents

Fischer "certified" thorium nitrate was used. Solutions were standardized gravimetrically by evaporation and ignition to thorium dioxide. Tiron (disodium 1,2-dihydroxybenzene-3,5-disulphonate) was obtained from the La Motte Chemical Products Co., Chestertown, Md., and was used without further purification after the establishment of its purity and standardization of an aqueous solution by potentiometric titration. "Baker Analyzed" samples of the disodium salt of EDTA were used. The 5-sulphosalicylic acid (SSA), salicylic acid (SA), chromotropic acid salt (1,8-dihydroxynaphthalene-3,6-disodium sulphonate) (CS), pyrocatechol (1,2-dihydroxybenzene) (PY), and 8-hydroxyquinoline-5-sulphonic acid (HQS) were purchased from the Eastman Kodak Co.; the iminodiacetic acid (IMDA) and DCTA were obtained through the courtesy of the Dow Chemical Co. The DCTA was converted into its disodium salt before use. The potassium hydrogen phthalate (KHP) was Fischer "certified."

Instrumentation

The pH measurements and titrations were made with a Beckman Research pH Meter Model 1019, and recorded on a Sargent multi-range precision recorder. The pH meter was calibrated with various standard buffers.

Procedure

Thermometric measurements were made by recording the temperature changes in the reaction system, contained in an adiabatic reaction vessel (Dewar flask fitted with a cork stopper), using a thermistor sensing device which served as one arm of a Wheatstone bridge. The Dewar flask contained 100 ml of a $4{\cdot}0 \times 10^{-3}M$ solution of ligand and/or metal ion, with ionic strength kept constant at 0·10 by the addition of potassium nitrate. The solution was stirred by a constant speed magnetic stirrer, and a nitrogen atmosphere was maintained over the solution in order to exclude carbon dioxide and to avoid aerial oxidation. Sodium hydroxide solution, $0{\cdot}5M$, was supplied through a finely drawn capillary at the rate of 1 ml/min by a Sargent Automatic Constant Flow Rate Buret, Model C. All titrations were carried out at a nominal temperature of 25° in a constant temperature room, after the solutions had achieved thermal equilibrium with their surroundings. A diagram of the apparatus is shown in Fig. 1. The titrant concentration was about 100 times that of the titrand, so that the reaction was complete on addition of about 1 ml, and thus the volume change and consequent heat capacity change were kept to a minimum.

Figure 2 shows a typical titration curve for a two-step titration. Portion ABC represents the temperature change of the system, due to two consecutive exothermic reactions. Portion CD represents the effect of excess of titrant, and the slope of this line is due to any non-isothermality

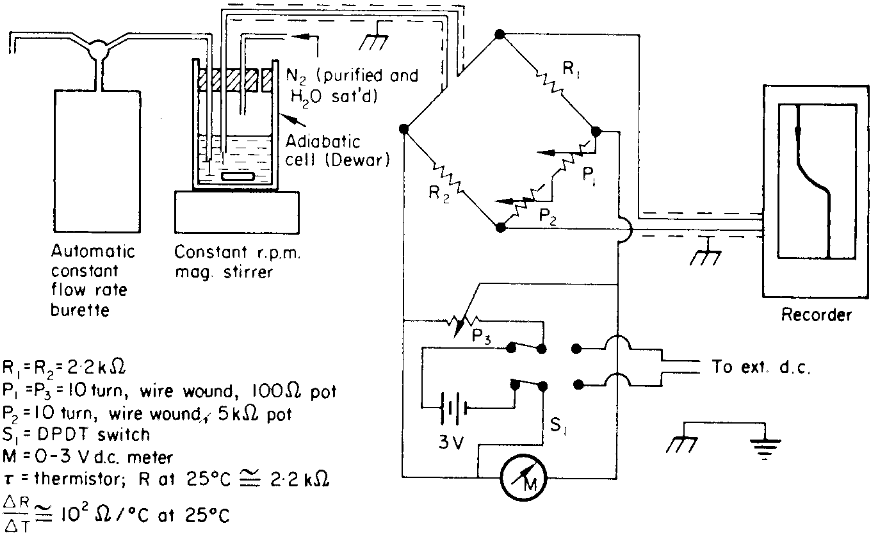


FIG. 1.—Thermometric titration apparatus.

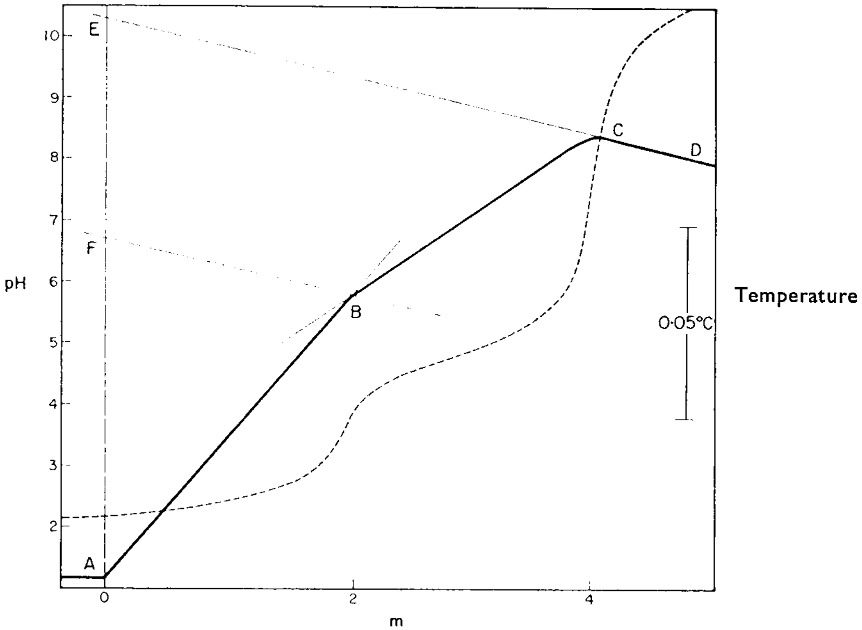


FIG. 2.—Potentiometric titration (broken line) and thermometric titration of a 1:1:1 Th(IV)-DCTA-CS mixed-ligand chelate system 4·0 × $10^{-3}M$ in Th(IV), DCTA, and CS. μ = 0·10, T = 25°C, and m = number of moles of base added per mole of metal ion.

between the titrant and titrand, heats of dilution, heats of stirring, heat loss from the system to the surroundings, and any other constant thermal interchange exclusive of the heat of reaction. Extrapolation of this line back to the start of the titration cancels out these effects, provided the line is straight and of relatively small slope. A line parallel to this extrapolation is drawn through the first break-point of the titration curve, B, located if necessary at the intersection of the extrapolated lines AB and BC. The two parallel extrapolations are carried back to intersect with a vertical line at the point corresponding to the start of the titration. The vertical distances EF and FA then correspond to the temperature increase resulting from the second and first titration steps, respectively, and after correction for the small volume change can be translated into enthalpy changes by means of a calibration curve for a standard system.

The thermometric apparatus was standardized by utilizing a system of known enthalpy change (titration of hydrochloric acid *vs.* sodium hydroxide), and constructing a calibration curve of corrected enthalpogram step height *vs.* joules liberated. A value of −56·51 kJ/mole for the heat of neutralization of hydrochloric acid by sodium hydroxide at 25° and μ = 0·10 was obtained by extrapolating the data of Hale *et al.*[8] The enthalpogram step heights were plotted *vs.* the calculated amount of heat liberated. This procedure yielded points exactly collinear, with a slope of $3{\cdot}04_4$ mm/J The calibration curve was checked periodically and was found not to vary over a period of six months. Substitution of a 0·1*M* potassium chloride medium for the 0·10*M* potassium nitrate medium was found to have no effect on the calibration curve.

For the mixed-ligand chelate experiments, 100 ml of 4·0 × $10^{-3}M$ thorium, containing primary ligand and secondary ligand, was placed in the adiabatic titration vessel after the ionic strength had been adjusted with potassium nitrate. Time was allowed for thermal equilibrium to be attained, and the solution was titrated with a concentrated solution of sodium hydroxide.

RESULTS AND CALCULATIONS

Determination of ΔH for the deprotonation of the secondary ligands

Before the ΔH due to the actual coupling of the secondary ligand onto the simple metal–primary ligand chelate (ΔH_{MLA}) could be calculated, values of ΔH for the various deprotonation steps of the secondary ligand species ($\Delta H_{\mathrm{H}_n\mathrm{A}}$) had to be known. Since the free ligands were dissolved in aqueous solution and titrated with base, the actual ΔH_{EXP} value experimentally obtained from the thermometric titration was for the reaction:

$$(a - b)\mathrm{HA} + b\mathrm{A} + b\mathrm{H}^+ + a\mathrm{OH}^- \rightarrow a\mathrm{A} + a\mathrm{H_2O} \qquad (\Delta H_{\mathrm{EXP}}). \qquad (1)$$

Consequently, in order to obtain the desired ΔH for the simple deprotonation reaction:

$$\mathrm{HA} \rightarrow \mathrm{A} + \mathrm{H}^+ \qquad (\Delta H_{\mathrm{H}_n\mathrm{A}}) \qquad (2)$$

the ΔH_{EXP} value had to be adjusted to account for the neutralization of the released hydrogen ions by the hydroxide, and also in some cases for the partial dissociation of the free ligand before the start of the titration. Hale *et al.*'s[8] value of −56·51 kJ/mole was used for the heat of neutralization. Log K values which had been potentiometrically determined[1] at 25° and $\mu = 0{\cdot}10$ were used to calculate the degree of dissociation of the free ligand.

Table I shows the thermodynamic values obtained for the free secondary ligands used in the present investigation. The inflection points in the thermometric curves are noted and the ΔH_{EXP} and $\Delta H_{\mathrm{H}_n\mathrm{A}}$ values are listed for the stepwise deprotonation of the individual ligands. In the case of some ligands (Tiron, CS, PY, and SSA), no $\Delta H_{\mathrm{H}_n\mathrm{A}}$ values are given for the loss of the second proton, since this dissociation occurs only to a small extent or not at all in aqueous solution titrations. The ΔG values for the same deprotonation reactions were calculated by using the appropriate ligand log K values and the relationship: $\Delta G = -RT \ln K$. $\Delta S_{\mathrm{H}_n\mathrm{A}}$ values were obtained from the $\Delta H_{\mathrm{H}_n\mathrm{A}}$ and the corresponding $\Delta G_{\mathrm{H}_n\mathrm{A}}$ values through use of the standard relationship $\Delta G = \Delta H - T\Delta S$.

Comparison of potentiometric and thermometric titration curves for the same mixed-ligand chelate systems

The potentiometric as well as the thermometric titration curves for the 1:1:1 Th(IV)–DCTA–CS mixed-ligand chelate system [$4{\cdot}0 \times 10^{-3}M$ in thorium(IV)] are shown in Fig. 2. An explanation for the potentiometric curve follows. The 1:1 Th–DCTA chelate is completely formed at the start of the titration, and the buffer region up to $m = 2{\cdot}00$ represents the titration of the two hydrogen ions freed from the chelated disodium salt of DCTA. The second buffer region from $m = 2$ to $m = 4$ is due to the attachment of the two hydroxyl groups on the chromotropic salt onto the 1:1 chelate to form the 1:1:1 mixed-ligand chelate. This buffer region terminates in a sharp inflection at $m = 4$ indicating that complete formation of the mixed-ligand chelate has occurred at this point.

The thermometric curve for the same system may be similarly explained. Thus, the highly exothermic constant slope region from $m = 0$ to $m = 2$ is due to the heat liberated by the neutralization of the two hydrogen ions freed from the 1:1 Th–DCTA chelate. At $m = 2$ the slope changes and we obtain another, slightly less, exothermic constant slope region from $m = 2$ to $m = 4$ due to the formation of the 1:1:1 mixed-ligand chelate. The overall heat change observed in this region is due to three factors: the heat of formation of the mixed-ligand chelate, the heat of neutralization of the two hydrogen ions freed from the chromotropic salt, and the heat of deprotonation when these two hydrogen ions are removed from the chromotropic salt. At

TABLE I.—THERMODYNAMIC DATA FOR THE DEPROTONATION OF FREE SECONDARY LIGANDS ACCORDING TO THE REACTION $HA \rightarrow A + H^+$ AT 25°C AND $\mu = 0{\cdot}1$ (KNO_3)

Ligand	Values* of inflection points	Range* over which H was calculated	pK†	ΔH_{EXP} *kJ/mole*	$\Delta H_{\mathrm{H}_n\mathrm{A}}$ *kJ/mole*	$\Delta G_{\mathrm{H}_n\mathrm{A}}$ *kJ/mole*	$\Delta S_{\mathrm{H}_n\mathrm{A}}$ *J/mole.K*
Na_2EDTA	1(w) 2(g)	0–1	6·16	−41·7	+18·2 (+18·2)§	+35·2	−57 (−56)§
		1–2	10·26	−33·1	+23·4 (+23·7)§	+58·6	−118 (−116)§
Na_2DCTA	1(w) 2(vw)	0–1	6·16	−46·3	+10·3 (+8·6)§	+35·2	−83 (−88)§
		1–2¶	12·35	−18·6	+37·9 (+27·8)§	+70·6	−109 (−142)
Tiron (H_2A)	1(g)	0–1	7·61	−35·6	+21·0	+43·5	−75
CS (H_2A)	1(g)	0–1	5·32	−43·4	+13·6	+30·4	−57
PY (H_2A)	1(g)	0–1	9·19	−31·4	+25·1	+52·5	−92
HQS (H_2A)	2(g)	0–2	3·97	−77·5	+38·5 (+35·0)‡	+70·9	−108 (−118)‡
SSA (H_3A)	2(g)	0–2	2·62	−95·5	+25·5	+15·0	+35
SA (H_2A)	1(g) 2(w)	0–1 1–2	2·89 13·6	−54·3 +1·3	+3·8 +55·2	+16·5 +77·8	−43 −75
IMDA (H_2A)	1(g) 2(g)	0–1 1–2	2·52 9·30	−53·6 −23·3	+6·8 +33·1	+14·4 +53·1	−26 −67
KHP (HA)	1(g)	0–1	5·00	−56·1	+0·3	+28·6	−95

* Moles of base added per mole of ligand (=a).

† $\mu = 0{\cdot}10$ (KNO_3), $T = 25$°C, reference 1.

§ $\mu = 0{\cdot}10$ (KNO_3), $T = 25{\cdot}3$°C, reference 9.

‡ $\mu = 0{\cdot}10$, $T = 25{\cdot}0$°C, $\Delta H_{\mathrm{H_2A}} = +18{\cdot}3$ kJ/mole, $\Delta H_{\mathrm{HA}} = +16{\cdot}7$ kJ/mole, $\Delta S_{\mathrm{H_2A}} = -13$ J/mole.K, $\Delta S_{\mathrm{HA}} = -105$ J/mole.K, reference 10.

¶ Enthalpogram is rounded between $a = 1$ and $a = 2$. At $a = 2$ there is no well defined end-point, and the curved region continues.

g—good inflection
w—weak inflection
vw—very weak inflection

$m = 4$, the curve reverts to that for addition of excess of reagent. In some instances there is a slight delay or curvature at this point, indicating minor hydrolysis.

The other mixed ligand chelate systems (not shown) in the present study exhibit the same correspondence as seen in Fig. 2, between the thermometric and potentiometric curves. The 1:1:1 Th–EDTA-secondary ligand chelate systems exhibit potentiometric curves having inflections at $m = 2$ and $m = 4$ for PY, CS Tiron and HQS; $m = 3$ and $m = 4$ for SA and IMDA: $m = 4$ and $m = 5$ for SSA; and $m = 2$ and $m = 3$ for KHP. Mixed-ligand chelate formation occurs in the regions between these inflection points.

Determination of ΔH for the formation of the mixed ligand chelates

The ΔH due to the actual coupling of the secondary ligand onto the simple metal–primary ligand chelate according to the reaction:

$$ML + A \rightarrow MLA \qquad (\Delta H_{\mathrm{MLA}}). \tag{3}$$

was sought. The actual reaction, however, has a heat output which is due, as explained earlier, to three separate factors, and is represented by the equation:

$$\mathrm{ML} + \mathrm{H}_n\mathrm{A} + n\mathrm{OH}^- \rightarrow \mathrm{MLA} + n\mathrm{H_2O} \qquad (\Delta H_{\mathrm{EXP}'}). \tag{4}$$

Thus the $\Delta H_{\mathrm{EXP}'}$ includes: (*a*) the heat of neutralization; (*b*) the heat of deprotonation; and (*c*) the heat of the actual mixed-ligand complex formation, ΔH_{MLA}. The heat of neutralization (*a*) is easily accounted for, but as stated above, not all the $\Delta H_{\mathrm{H}_n\mathrm{A}}$ values were obtainable. Thus in some cases only a value for the combination of (*b*) and (*c*) ($\Delta H_{\mathrm{MLA+H}_n\mathrm{A}}$) could be obtained. This value is the result of the reaction:

$$\mathrm{ML} + \mathrm{H}_n\mathrm{A} \rightarrow \mathrm{MLA} + n\mathrm{H}^+ \qquad (\Delta H_{\mathrm{MLA+H}_n\mathrm{A}}). \tag{5}$$

In the cases for which the $\Delta H_{\mathrm{H}_n\mathrm{A}}$ values could be obtained, ΔH_{MLA} values were calculated.

The thermodynamic results obtained from the thermometric titrations of the various mixed-ligand chelate systems are presented in Table II. The *m*-values between which mixed-ligand chelate formation occurs, and from which the thermometric data were taken, is noted for each system. The $\Delta H_{\mathrm{EXP}'}$ and $\Delta H_{\mathrm{MLA+H}_n\mathrm{A}}$ values for each secondary ligand as well as the ΔH_{MLA} values are listed. ΔG_{MLA} was calculated from the log K values reported previously[1] for mixed ligand chelates. ΔS_{MLA} for mixed ligand chelate formation was obtained from ΔH_{MLA} and ΔG_{MLA} values.

DISCUSSION

Comparison of literature values and thermometric values for secondary ligand deprotonation

Calorimetrically determined values of $\Delta H_{\mathrm{H}_n\mathrm{A}}$ and ΔS for the deprotonation of the free ligands EDTA and DCTA have been reported by Anderegg,[9] while those for HQS have been reported by Gutnikov and Freiser.[10] These values compare favourably with those obtained thermometrically (see Table I). Agreement is good for all the ligands except disodium DCTA. This discrepancy is due to a kinetically slow step, indicated by a curved region on the enthalpogram. Adjustment of the thermometric value to compensate for the slow step would yield a value close to that reported by Anderegg. Thus, to apply thermometric titrations successfully to the determination of such values, one must carefully consider the speed of reaction *vs.* titrant addition rates, heat leak rates, and subsequent reactions.

The agreement between the literature values and thermometric values for $\Delta H_{\mathrm{H}_n\mathrm{A}}$ shown in Table I demonstrates the validity of the thermometric method to obtain thermodynamic data of this type.

The energetics of mixed-ligand chelate formation

Table II reveals that the favourable ΔG for the formation of mixed ligand chelates results principally from favourable positive ΔS_{MLA} values. ΔH_{MLA} is seen to vary from favourable to unfavourable with apparently little effect upon ΔG. The large entropy value is primarily due to the release of hydrated water molecules from both

TABLE II.—THERMODYNAMIC DATA FOR THE FORMATION OF MIXED LIGAND CHELATES FROM THE ADDITION OF ONE MOLE OF SECONDARY LIGAND (H_nA) TO THE 1:1 PRIMARY LIGAND CHELATE AT 25°C AND $\mu = 0{\cdot}10$ (KNO_3)

Secondary ligand	*m* values between which mixed ligand complex occurs	Primary ligand EDTA					Primary ligand DCTA				
		ΔH_{EXP}	ΔH_{MLA+H_nA}	ΔH_{MLA}	ΔG_{MLA}	ΔS_{MLA} *J/mole.K*	ΔH_{EXP}	ΔH_{MLA+H_nA}	ΔH_{MLA}	ΔG_{MLA}	ΔS_{MLA} *J/mole.K*
		kJ/mole					*kJ/mole*				
CS	2–4	−68·2	44·8	—	−78·1	—	−65·2	47·8	—	−75·1	—
Tiron	2–4	−97·2	15·8	—	−76·6	—	−84·6	28·4	—	−72·4	—
PY	2–4	−61·8	51·1	—	−73·7	—	−59·5	53·5	—	−70·1	—
SA	3–4	−20·7	35·8	−19·4	−61·1	140	−20·5	36·0	—	—	—
SSA	4–5	−24·8	31·7	—	−53·1	—	−21·5	35·0	—	−50·7	—
HQS	2–4	−81·2	31·8	−6·8	−39·9	111	−93·0	20·0	−18·5	−38·3	66
IMDA	3–4	−13·4	43·2	+10·0	−38·3	162	−19·9	36·6	+3·5	−34·9	129
KHP	2–3	−32·7	23·8	+23·5	−17·7	138	−35·5	21·0	+20·7	−15·0	120

m = moles of base added per mole of metal ion present.
* At 25·3°C, $\mu = 0{\cdot}10$ (KNO_3), reference 11.

the free ligand and the metal ion in the simple 1:1 chelate upon mixed-ligand chelate formation.

The inability to obtain explicit ΔH_{MLA} values for certain secondary ligand systems does not prevent a meaningful comparison between the ΔH_{MLA+H_nA} values of the EDTA and DCTA mixed ligand chelates of the same secondary ligands. This is so because the heat of deprotonation for a given secondary ligand is constant during mixed-ligand formation, even though in certain cases it may be indeterminable. Thus, for any given secondary ligand the effective heats of mixed-ligand addition for the EDTA system may be compared with those for the DCTA system.

The EDTA mixed-ligand chelates were previously[1] found to be more stable than the analogous DCTA mixed-ligand chelates, as is evidenced in the comparison of the ΔG_{MLA} values for the various secondary ligand additions. The buffer region in which the mixed-ligand chelate is formed occurs at a higher pH with DCTA than with EDTA.

This enhanced stability of the EDTA system cannot be accounted for by enthalpy effects, since the ΔH values for the two systems can be seen to show no definite trend in relation to each other; the ΔH_{MLA+H_nA} values involving the secondary ligands CS, PY, Tiron and SSA are more positive for the DCTA system, while the opposite is true for the ligands HQS, IMDA and KHP. Consequently, the greater stability of the EDTA mixed-ligand chelates must depend on entropy effects, which is evidenced by the more favourable positive ΔS_{MLA} values. This effect is probably due to less saturation of the co-ordinating tendencies (less effective shielding of the charge) of the thorium(IV) ion in the simple 1:1 Th–EDTA chelate. This leads to greater hydration and subsequent release of a greater number of water molecules upon mixed-ligand chelate formation.

Zusammenfassung—Chelate mit verschiedenen Liganden, die aus zwei verschiedenen, an ein Thorium(IV)-Zentralion gebundenen mehrzähnigen Liganden bestehen, wurden in wäßriger Lösung hergestellt und ihre Bildungswärmen thermometrisch untersucht. Brenzcatechin, Tiron, Chromotropsäure, Kaliumhydrogenphthalat, 8-Hydroxychinolin-5-sulfonsäure, Iminoessigsäure, 5-Sulfosalicylsäure und Salicylsäure wurden als Zweitliganden, Äthylendiamintetraacetat und 1,2-Diaminocyclohexan-*N*, *N*, *N'*, *N'*-tetraacetat als Erstliganden eingesetzt. ΔH-Werte für die Bruttoreaktionen werden angegeben und, soweit möglich, ΔH- und ΔS-Werte speziell für den Eintritt des Zweitliganden berechnet. Die Bruttostabilität der gemischten Chelate und die erhöhte Stabilität der gemischten Chelate mit EDTA, verglichen mit den analogen DCTA-Chelaten, beruht offenbar eher auf Entropie- als auf Enthalpieeffekten.

Résumé—On a préparé en solution aqueuse des chélates de ligands mixtes consistant en deux ligands différents à multicoordination liés à un ion thorium (IV) central, et l'on a étudié thermométriquement leurs chaleurs de formation. Les pyrocatéchol, tiron, acide chromotropique, phtalate acide de potassium, acide 8-hydroxquinoléine 5-sulfonique, acide iminoacétique, acide 5-sulfosalicylique et acide salicylique ont été utilisés comme ligands secondaires, tandis que l'éthylènediaminetétracétate et le 1,2-diaminocyclohexane *N*, *N*, *N'*, *N'*-tétracétate ont été utilisés comme ligands primaires. On donne les valeurs ΔH pour les réactions globales et, lorsque c'était possible, les valeurs ΔH et ΔS pour l'addition spécifique du ligand secondaire ont été calculées. On a trouvé que la stabilité d'ensemble des chélates de ligands mixtes et la stabilité accrue des chélates mixtes d'EDTA par rapport aux chélates analogues de DCTA sont dues à des influences d'entropie plutôt que d'enthalpie.

REFERENCES

1. G. H. Carey, R. F. Bogucki and A. E. Martell, *Inorg. Chem.*, 1964, **3**, 1288.
2. J. T. Hoard and J. V. Silverton, *ibid.*, 1963, **2**, 235.
3. J. Jordan, *J. Chem. Educ.*, 1963, **40**, A5.
4. J. Jordan and T. G. Alleman, *Anal. Chem.*, 1957, **29**, 9.
5. R. J. Raffa, M. J. Stern and L. Malspeis, *ibid.*, 1968, **40**, 70.
6. F. E. Freeberg, *ibid.*, 1969, **41**, 54.
7. S. T. Zenchelsky, *ibid.*, 1960, **32**, 289R.
8. J. D. Hale, R. M. Izatt and J. J. Christensen, *J. Phys. Chem.*, 1963, **67**, 2605.
9. G. Anderegg, *Helv. Chim. Acta*, 1963, **46**, 1834.
10. G. Gutnikov and H. Freiser, *Anal. Chem.*, 1968, **40**, 39.
11. G. H. Carey and A. E. Martell, unpublished results.

Talanta, 1970, Vol. 17, pp. 915 to 924. Pergamon Press. Printed in Northern Ireland

VERWENDUNG VON ALKYLPHOSPHORSÄUREN IN DER ANALYTISCHEN CHEMIE

EXTRAKTION VON GALLIUM(III) AUS LÖSUNGEN SAUERSTOFFHALTIGER SÄUREN MIT LÖSUNGSMITTELGEMISCHEN

I. S. Levin und N. A. Balakireva
Institut für physikalisch-chemische Grundlagen der Aufarbeitung von Mineralstoffen, Novosibirsk, Derzhavina 18, U.S.S.R.

(*Eingegangen am* 14. *März* 1968. *Revidiert am* 27. *Oktober* 1969.
Angenommen am 31. *März* 1970)

Zusammenfassung—Gallium(III) kann durch kombination zweier Extraktionsmittel (M2EHPS mit TBP, oder M2EHPS mit Methylhexylketon) aus schwefel- oder bromwasserstoffsauren Lösungen von Aluminium abgetrennt werden, wobei Gallium in der organischen Phase verbleibt. Alle andere extrahierten Metallen werden mittels selektiver Waschlösungen abgetrennt.

Gallium(III) kann durch Extraktion mit Pyroalkylphosphorsäuren (PAPS) von den meisten Begleitstoffen außer Aluminium abgetrennt werden.[1] Zur Galliumbestimmung wird dann die organische Phase mit Oxalsäure extrahiert und Gallium mit Malachitgrün photometrisch bestimmt,[2] wobei Aluminium nicht stört. Bei der komplexometrischen Galliumbestimmung jedoch müssen Aluminium und Oxalsäure abwesend sein. In der folgenden Arbeit wird daher ein Verfahren zur gleichzeitigen Abtrennung des Galliums(III) von Aluminium(III) und Begleitelementen beschrieben. Als Extraktionsmittel dient Mono-2-äthylhexylphosphorsäure (M2EHPS)* sowie ein Gemisch von M2EHPS mit verschiedenen Antagonisten.

Galliumbestimmungen im Milligrammbereich wurden komplexometrisch mit dem Indikator Xylenolorange[4] und im Mikrogrammbereich photometrisch mit Malachitgrün[2] ausgeführt.

Abtrennung von Ga(III) *und* Al(III) *mit Monoalkylphosphorsäure*

Es wurde (Abb. 1–3) die Abtrennung des Ga mit M2EHPS aus mineralsauren Lösungen verschiedener Konzentration untersucht. Es zeigt sich, daß durch Änderung der Säurekonzentration in der wäßrigen Phase eine getrennte Extraktion von Ga(III) und Al(III) mittels M2EHPS unmöglich ist. Auch das Zusammenwirken von Trialkylphosphaten S, wobei S auch Alkohole oder Ketone sein können und Säuren (HX = Schwefel- oder Salpetersäure) im System Me(III)–M2EHPS–S–HX bewirkt keinen Trenneffekt (Abb. 4).

Jedoch läßt sich Gallium(III) von Alkoholen, Trialkylphosphaten und Ketonen aus Lösungen verschiedener Halogenwasserstoffkonzentration (Abb. 5) sehr gut extrahieren. In diesem System liegen die Trennfaktoren

$$\beta_{Ga/Al} = D_{Ga}/D_{Al}$$

---

* Die extraktive Galliumabtrennung mit Dialkylphosphorsäuren ist wegen zu niedriger Verteilungskoeffizienten unmöglich.[3] Monoalkylphosphorsäuren sind nach einem bereits beschriebenen Verfahren zugänglich.[5] Zur Herstellung von Galliumlösungen wurde Gallium hoher Reinheit in den entsprechenden Säuren aufgelöst.

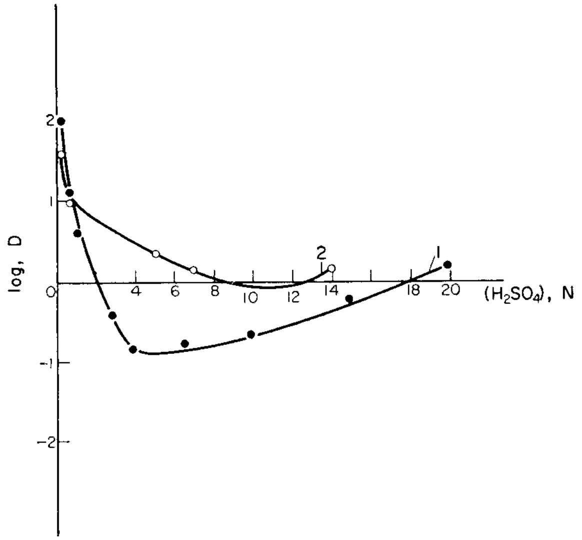


Abb. 1.—Verteilungskoeffizienten von Ga(III) und Al(III) in Abhängigkeit von der H_2SO_4-Konzentration in der wäßrigen Phase.
Organische Phase: 1,5*N* M2EHPS in Heptan
Kurve 1: Ga, 1,18 mg/ml
Kurve 2: Al, 4 mg/ml.

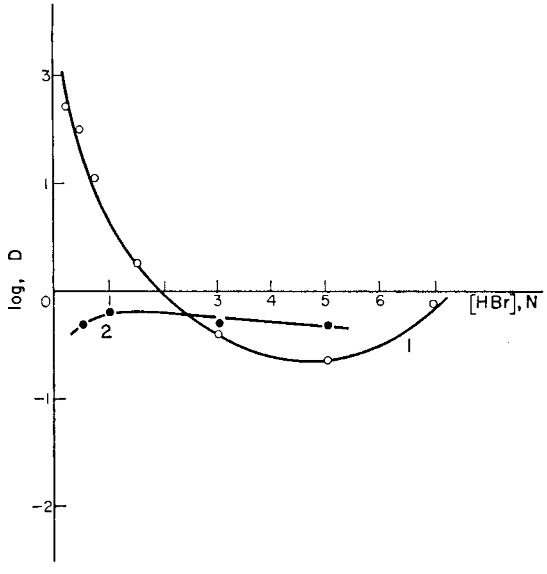


Abb. 2.—Verteilungskoeffizienten von Ga(III) und Al(III) in Abhängigkeit von der HBr-Konzentration in der wäßrigen Phase.
Organische Phase: 1,5*N* M2EHPS in Heptan
Kurve 1: Ga, 1 mg/ml
Kurve 2: Al, 3 mg/ml.

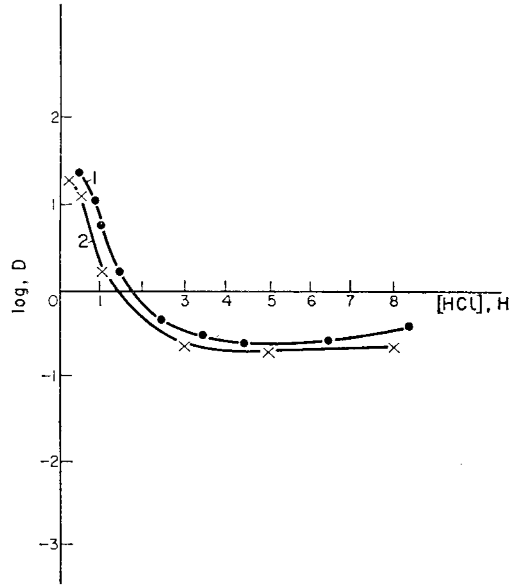


Abb. 3.—Verteilungskoeffizienten von Ga(III) und Al(III) in Abhängigkeit von der HCl-Konzentration in der wäßrigen Phase.
Organische Phase: 1,5*N* M2EHPS in Heptan
Kurve 1: Ga, 1 mg/ml
Kurve 2: Al, 3 mg/ml.

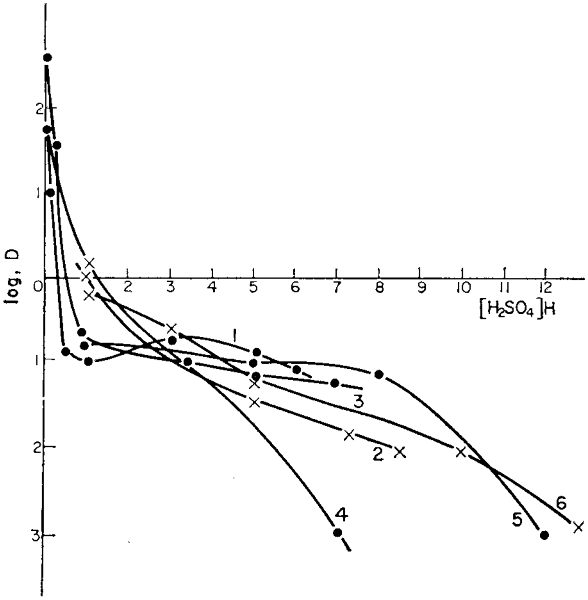


Abb. 4.—Verteilungskoeffizienten von Ga(III) und Al(III) in Abhängigkeit von der H_2SO_4-Konzentration in der wäßrigen Phase.
$c_{Ga} = 1{,}77$ mg/ml; $c_{Al} = 2{,}1$ mg/ml
I. Org. Phase: M2EHPS (0,75*N*) und TBP (1,88*N*) in Heptan
Kurve 1: Ga; Kurve 2: Al
II. Org. Phase: M2EHPS (0,75*N*) und 2EHA (3*N*) in Heptan
Kurve 3: Ga; Kurve 4: Al
III. Org. Phase: M2EHPS (0,75*N*) und MHK (3,2*N*) in Heptan
Kurve 5: Ga; Kurve 6: Al.

(D = entsprechende Verteilungskoeffizienten) bei etwa 10^2. Im System Me(III)-M2EHPS-S-HX, wobei HX = HCl oder HBr, ist die Komponente S von großer Wichtigkeit.

Untersucht wurden die Systeme

Ga(III)-M2EHPS-TBP-HBr	(TBP = Tributylphosphat)
Ga(III)-M2EHPS-2EHA-Hbr	(2EHA = 2-Ethylhexylphosphat)
Ga(III)-M2EHPS-MHK-HBr	(MHK = Methylhexylketon)

als Funktion der Bromwasserstoffsäurekonzentration (Abb. 6). Es zeigt sich, daß in diesen Systemen M2EHPS die Rolle eines Antisynergentenmittels spielt. M2EHPS allein vermag Ga(III) nur in geringem Umfang aus HBr-Lösungen zu extrahieren. Durch Erhöhung der Acidität (Zugabe von Schwefelsäure) jedoch wird D_{Ga} merklich größer (Abb. 7), während Al(III) unter diesen Bedingungen kaum extrahiert wird.

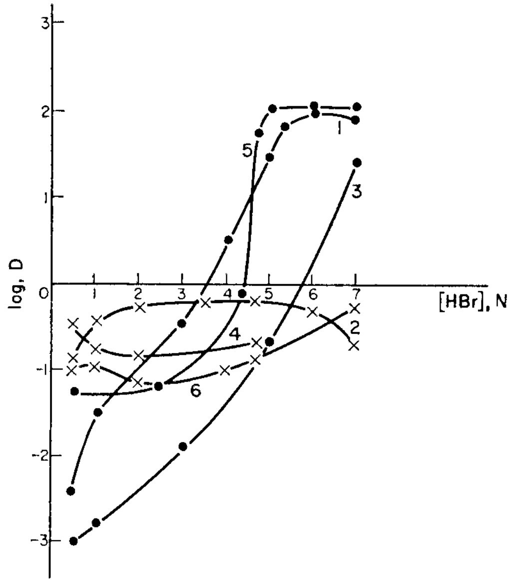


ABB. 5.—Verteilungskoeffizienten von Ga(III) und Al(III) in Abhängigkeit von der HBr-Konzentration in der wäßrigen Phase.
c_{Ga} = 1,77 mg/ml; c_{Al} = 2,1 mg/ml
I. Org. Phase: TBP (3,76N) in Heptan
Kurve 1: Ga; Kurve 2: Al
II. Org. Phase: 2EHA (6N) in Heptan
Kurve 3: Ga; Kurve 4: Al
III. Org. Phase: MHK (6,4N) in Heptan
Kurve 5: Ga; Kurve 6: Al.

Abbildung 8 zeigt den gemeinsamen Einfluß von M2EHPS und TBP auf das Extraktionsverhalten von Ga(III) und Al(III). Die Verteilungskoeffizienten ergeben für dieses System Trennfaktoren von 10^3 bis 10^5.

Bei Verwendung ein Semisch von TBP + M2EHPS wird bereits durch ein- bis zweimalige Extraktion eine Ga/Al-Trennung erreicht. Aber wie aus Tabelle I zu ersehen ist, hat die Aluminium-konzentration in der wäßrigen Phase einen Einfluß auf der Verteilungskoeffizient D_{Ga}. Diese Störung kann durch Einstellung der zu

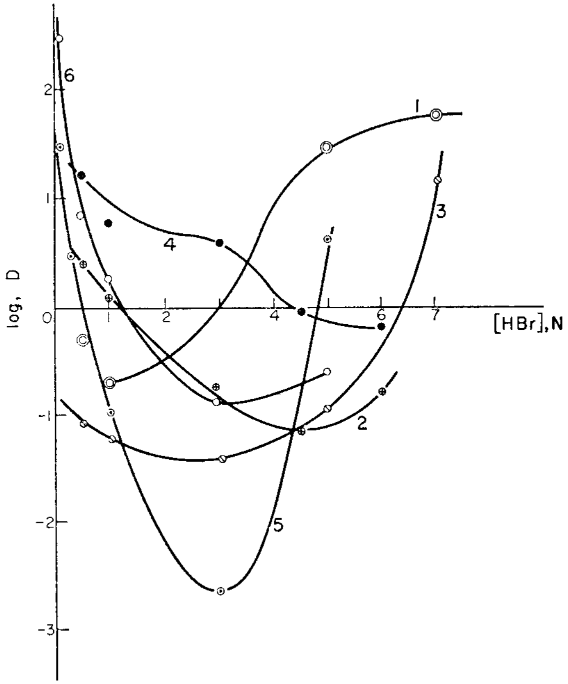


ABB. 6.—Verteilungskoeffizienten von Ga(III) und Al(III) in Abhängigkeit von der HBr-Konzentration in der wäßrigen Phase.
$c_{Ga} = 1,77$ mg/ml; $c_{Al} = 2,1$ mg/ml
I. Org. Phase: M2EHPS (0,75*N*) und TBP (1,88*N*) in Heptan
Kurve 1: Ga; Kurve 2: Al
II. Org. Phase: M2EHPS (0,75*N*) und 2EHA (3*N*) in Heptan
Kurve 3: Ga; Kurve 4: Al
III. Org. Phase: M2EHPS (0,75*N*) und MHK (3,2*N*) in Heptan.
Kurve 5: Ga; Kurve 6: Al.

extrahierenden Lösung auf pH 4–5 behoben werden, wobei der pH so gewählt wird, daß die Ausfällung von Hydroxiden unterbleibt.

DISKUSSION

Im folgenden wird ein allgemeines Verfahren zur Abtrennung von Ga(III) aus Lösungen, die Beimengungen an Kupfer, Zink, Cadmium, Kobalt, Eisen u.a. enthalten, beschrieben.

Fe(III) wird zunächst zu Fe(II) reduziert und verbleibt bei der Extraktion mit M2EHPS in der wäßrigen Phase. Dabei geht Tl(III) in Tl(I) auch über. Die Begleitelemente, die bei der Extraktion mit M2EHPS in geringem Umfang in der organischen Phase nachzuweisen sind (Tabelle III), werden durch Waschen mit konzentrierter Perchlorsäure entfernt.

Nach Abtrennung dieser schlecht extrahierbaren Elemente mit Perchlorsäure läßt sich Aluminium durch Zugabe des Schwefelsäure-Bromwasserstoffsäure-Gemisches nur schwer wieder aus der organischen Phase extrahieren. Vermutlich verbleibt Al(III) in Form von gemischten Ga–Al-Komplexen in der organischen Phase. Für diese Annahme spricht die ungestörte Al(III)-Abtrennung aus galliumfreien Lösungen.

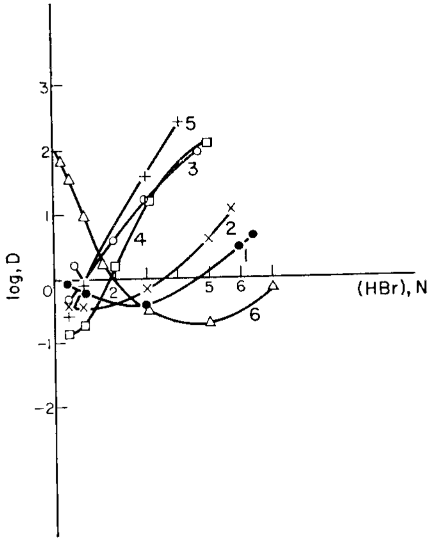


ABB. 7.—Verteilungskoeffizient von Ga(III) in Abhängigkeit von der H_2SO_4–HBr-Konzentration in der wäßrigen Phase.
Organische Phase: M2EHPS bzw. TBP in Heptan
$c_{Ga} = 1{,}77$ mg/ml; $c_{M2EHPS} = 1{,}5N$, $c_{TBP} = 3{,}76N$

Kurve 1: M2EHPS, $3N\ H_2SO_4$	Kurve 4: TBP, $3N\ H_2SO_4$
Kurve 2: M2EHPS, $7N\ H_2SO_4$	Kurve 5: TBP, $7N\ H_2SO_4$
Kurve 3: M2EHPS, $12N\ H_2SO_4$	Kurve 6: M2EHPS

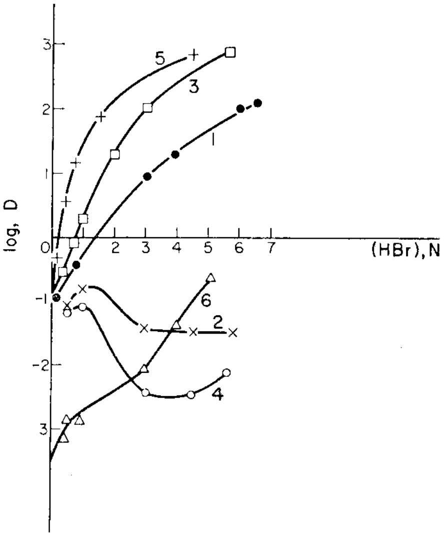


ABB. 8.—Verteilungskoeffizienten von Ga(III) und Al(III) in Abhängigkeit von der H_2SO_4–HBr-Konzentration in der wäßrigen Phase.
Organische Phase: M2EHPS + TBP in Heptan.
$c_{Ga} = 1{,}77$ mg/ml, $c_{Al} = 2{,}1$ mg/ml, $c_{M2EHPS} = 0{,}75N$ und $c_{TBP} = 1{,}88N$

Kurve 1: Ga, $3N\ H_2SO_4$	Kurve 4: Al, $7N\ H_2SO_4$
Kurve 2: Al, $3N\ H_2SO_4$	Kurve 5: Ga, $12N\ H_2SO_4$
Kurve 3: Ga, $7N\ H_2SO_4$	Kurve 6: Al, $12N\ H_2SO_4$

TABELLE I.—EINFLUSS DES ALUMINIUMS AUF DER EXTRAKTION VON GALLIUM MIT TBP UND M2EHPS

[Ga] In der wäßrigen Phase, *mg/l.*	[Al] *g/l.*	[Ga] in der wäßrigen Phase nach einer Extraktion, *mg/l.*	D_{Ga}
925	0	6	153
925	6	73	11,7
925	12	145	5,38
926	18	162	4,71
927	24	166	4,58
93	0	2	45,5
93	6	13	6,15
94	12	28,4	2,29
94	18	38,4	1,45
95	24	43	1,20

TABELLE II.—TRENNUNG DES GALLIUMS VON ALUMINIUM DURCH EXTRAKTION MIT TBP UND M2EHPS

[Al], *g/l.*	[Ga], *g/l.*	Al:Ga	Ga, gefunden im Reextrakt, *g/l.*	Al, gefunden bei Wäschen, *g/l.*
24	1,42	17	1,44	
24	0,142	170	0,142	
25,6	1,42	18	1,45	
31,4	0,142	220	0,136	
25,6	0,07	370	0,08	
0,19	6,8	0,03	6,58	0,178
0,98	5,68	0,2	5,39	0,102
2	6,8	0,3	6,71	2,11

$V_0:V_B = 1{\cdot}5:1$, [M2EHPS] = 0,75*N*, [TPB] =1,88*N*.

In Anwesenheit von Ga(III) werden 45–65% Al ausgewaschen. Yedoch, wenn man die organische Phase vorläufig mit Wasser auswascht, wird das al leicht durch Zugalee des Schwefelsäure = Bromwasser — stoffsäure = Gemisches reextrahiert.

Zusammen mit Gallium(III) befinden sich In, Tl(III), Sb(III), Bi, Sn(II), Sn(IV) U, Th, Zr, Hf, Sc, Seltene Erden, Ti u.a. in dem M2EHPS-Extrakt. Davon sind Ti, Zr, Hf, Sc nur schwer wieder aus der organischen Phase zu entfernen. Liegen in der galliumhaltigen Lösung In(III), Sb(III), Sn(II) und Bi(III) vor, dann können sie, wie Abb. 9 zeigt, durch zusätzliche Extraktion mit 2-Äthylhexanol und Salzsäure aus der organischen Phase abgetrennt werden.[6]

Isolierung von Ga(III) *aus Lösungen vorgegebener Zusammensetzung*

Der in Abb. 9 gezeigte Trennungsgang wurde an einer Lösung folgender Zusammensetzung geprüft:

Element	Konzentration (*g/l.*)
Ni	2,84
Hg	1,42

usw.

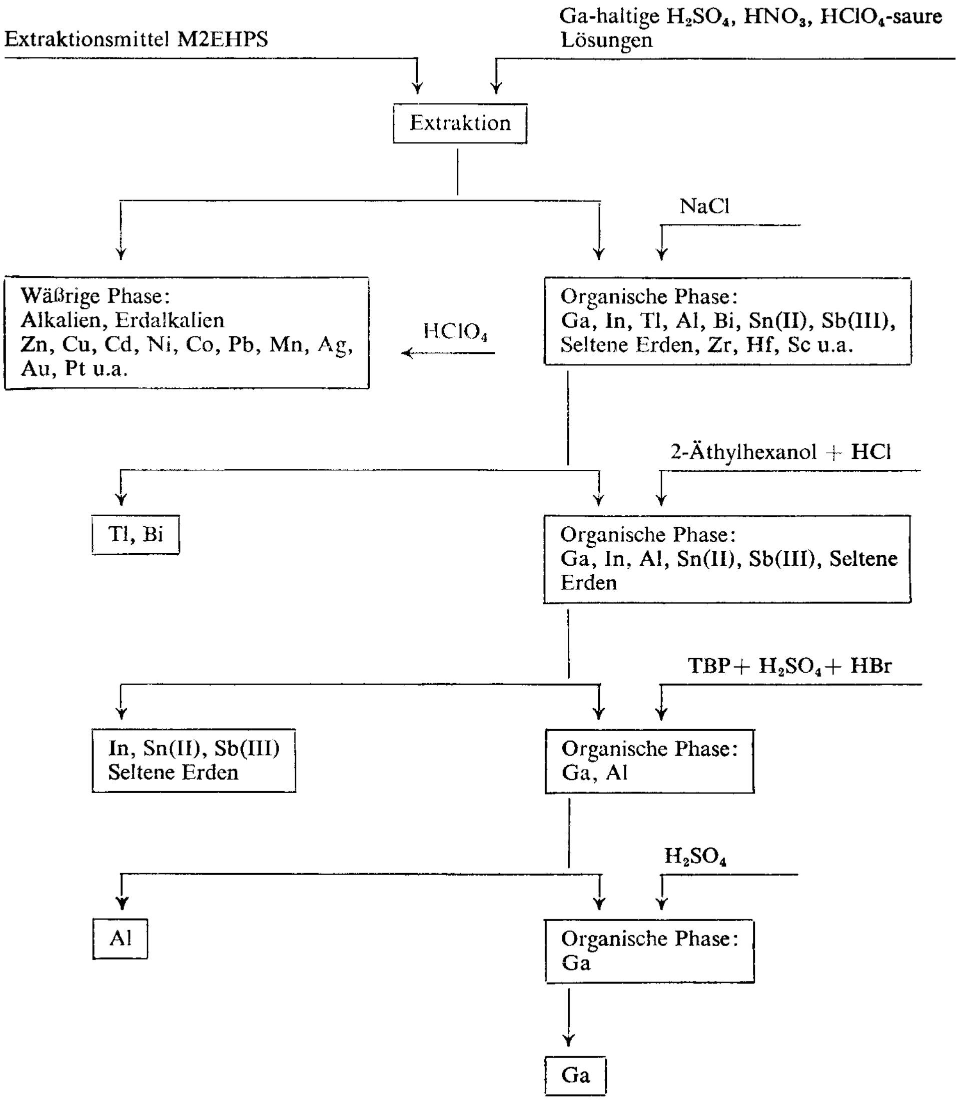


ABB. 9.—Extraktionsschema zur Isolierung von Ga.

Die Galliumkonzentration nach Ausführung des Trennungsganges betrug 1,15 g/l., die der vorgegebenen Lösung 1,18 g/l.

EXPERIMENTELLER TEIL

Galliumhaltige Zwischenprodukte aus Tonerdebetrieben werden zunächst nach den üblichen Verfahren aufgeschlossen. Dann stellt man mit Lauge in den schwach salpeter- oder perchlorsauren Lösungen einen pH-Wert zwischen 4 und 5 ein und extrahiert mit dem 1,5-fachen Volumen einer Lösung von 2*N* M2HPS* in Heptan. Sollte die ursprüngliche Lösung Fe(III) enthalten, dann wird zunächst mit fester Ascorbinsäure reduziert. Die Vollständigkeit der Reaktion wird durch das Ausbleiben der Eisen(III)-thiocyanatreaktion auf Filterpapier geprüft.

---

* M2HPS ist ein Gemisch aus 92–93% M2EHPS und 7–8% D2EHPS. Dieses Extraktionsmittel entsteht[5] bei der Einwirkung von P_2O_5 auf ROH nach $P_2O_5 + 2\,ROH \rightarrow R_2H_2P_2O_7$ und nachfolgender sechsstündiger Hydrolyse mit HCl (1:1).

TABELLE III.—ABTRENNUNG DES GALLIUMS VON SCHLECHT EXTRAHIERBAREN METALLEN

Me	[Me], *g/l.*	[Ga], *g/l.*	[Me]:[Ga]	Ga in Reextrakt, *g/l.*
Ni	40	1,42	28,2	1,39
Co	40	0,142	282	0,140
	40	1,42	28,2	1,42
	40	0,142	282	0,146
	40	1,42	28,2	1,37
Cu	40	0,142	282	0,150
	40	1,42	28,2	1,15
Cd	40	0,142	282	0,146
Mn(II)	16	1,42	11,3	1,44
	16	0,142	113	0,143
Pb	7,79	1,42	5,5	1,40
	7,79	0,142	55	0,144
Hg	20	1,42	14	1,39
	20	1,142	140	0,136
Zn	64	1,42	45	1,41
	64	0,142	450	0,146

$V_o : V_b = 1{,}5 : 1$, [M2EHPS] = 2N, Lösungsmittel Heptan.

Die Extraktion erfolgt unter Schütteln (Schütteldauer 1 Minute). Die organische Phase wird zweimal mit konzentrierter Perchlorsäure und dann einmal mit Wasser gewaschen, wobei die wäßrigen Phasen jeweils verworfen werden. Zur Abtrennung des Aluminiums wird die organische Phase mit dem gleichen Volumen TBP versetzt und Aluminium durch Ausschütteln mit demselben Volumen einer Lösung, die 7N an Schwefelsäure umd 7N an Bromwasserstoffsäure ist, entfernt. Zur Isolierung des Galliums wird die verbleibende organische Lösung zweimal mit 4N Schwefelsäure extrahiert und Gallium dann in den vereinigten Lösungen komplexometrisch bestimmt.

Dazu wird die gallliumhaltige Lösung mit Wasser auf 60–70 ml gebracht, ein Überschuß an 0,01M Komplexonlösung zugegeben, auf 70° erhitzt und dann mit Ammoniak bis zur Rotfärbung von Kongorot neutralisiert. Nach Zugabe des Acetatpuffers vom pH 5 wird die Lösung mit wenigen Tropfen Xylenolorange versetzt und mit 0,01M Zinknitratlösung bis zum Farbton rosa titriert.

Die Galliummenge errechnet sich nach

$$\mathrm{Ga} = 0{,}697(V_1 - V_2)\,\mathrm{mg}$$

wobei V_1 (ml) das zugesetzte Komplexonvolumen und V_2 (ml) der Verbrauch an Zinknitrat bedeuten.

Anwendung fand das Verfahren bei der Analyse von Zwischenprodukten, wie sie in Tonerdebetrieben vorkommen. Diese Produkte enthalten nach anderen Bestimmungsmethoden[7] ermittelte Galliumbeimengungen von 0,48%. Nach dem hier beschriebenen Verfahren wurde aus 10 Bestimmungen ein Galliumgehalt von 0,49 ± 0,02% ermittelt.

Summary—Gallium(III) can be separated from aluminium in sulphuric or hydrobromic acid medium by synergic extraction with a combination of mono(2-ethylhexyl)phosphoric acid and tributyl phosphate, or of mono(2-ethylhexyl)phosphoric acid with hexyl methyl ketone. All other metals extracted are removed by selective stripping reactions.

Résumé—Le Gallium(III) peut être séparé de l'aluminium en milieu d'acide sulphurique ou hydrobromique par extraction synergique avec une combinaison d'acide mono(2-ethylhexyl) phosphorique et de phosphate de tributyl ou avec une combinaison d'acide mono(2-ethylhexyl)phosphorique et de ketone d'hexyl methyl. Tous les autres métaux extraits sont prélevés par réactions lamellisantes sélectives.

LITERATUR

1. I. S. Levin und N. A. Balakireva, *Zh. Analit. Khim.*, 1967, **22,** 1475.
2. I. M. Dalton und W. I. S. Pringle, *Fuel*, 1962, **41,** 41.
3. I. S. Levin und N. A. Balakireva, *Zh. Neorgan. Khim.*, 1968, **13,** 857.
4. R. Přibil und M. Kopanica, *Microchim. Acta*, 1962, 29.
5. I. S. Levin und T. G. Asarenko, *Zh. Analit. Khim.*, 1965, **20,** 62.
6. I. S. Levin, A. A. Schatalova und T. G. Asarenko, *ibid.*, 1965, **20,** 452.
7. T. B. Tscherkaschina, *Zavodsk. Lab.*, 1956, **22,** 276.

Talanta, 1970, Vol. 17, pp. 925 to 935. Pergamon Press. Printed in Northern Ireland

PHOTOCHEMICAL PRECIPITATION OF THORIUM AND CERIUM AND THEIR SEPARATION FROM OTHER IONS IN AQUEOUS SOLUTION

M. DAS*, ARNO H. A. HEYN®, MORTON Z. HOFFMAN and R. P. AGARWAL†
Department of Chemistry, Boston University, Boston,
Massachusetts 02215, U.S.A.

(*Received* 16 *June* 1969. *Revised* 21 *March* 1970. *Accepted* 16 *April* 1970)

Summary—Thorium was precipitated from homogeneous solution by exposing solutions of thorium and periodate in dilute perchloric acid to 253·7 nm radiation from a low-pressure mercury lamp. Periodate is reduced photochemically to iodate which causes the formation of a dense precipitate of the basic iodate of thorium(IV). The precipitate was redissolved, the iodate reduced, the thorium precipitated first as the hydroxide, then as the oxalate and ignited to the dioxide for weighing. Thorium(IV) solutions containing 8–200 mg of ThO_2 gave quantitative results with a standard deviation (s) of 0·2 mg. Separations from 25 mg each of iron, calcium, magnesium, 50 mg of yttrium and up to 500 mg of uranium(VI) were quantitative (s = 0·25 mg). Separations from rare earths, except cerium, were accomplished by using hexamethylenetetramine rather than ammonia for the precipitation of the hydroxide. Cerium(III) was similarly precipitated and converted into CeO_2 for weighing. Quantitative results were obtained for 13–150 mg of CeO_2 with a standard deviation of 0·2 mg. Separations from 200 mg of uranium were quantitative. Other rare earths and yttrium interfered seriously. The precipitates of the basic cerium(IV) and thorium iodates obtained are more compact than those obtained by direct precipitation and can be handled easily. Attempts to duplicate Suzuki's method for separating cerium from neodymium and yttrium were not successful.

PRECIPITATION from homogeneous solution (PFHS) has been effected by a number of methods,[1] but until recently, photochemical oxidation or reduction had not been applied. Yen and Yang[2] produced non-quantitative precipitation of tantalum selenite from homogeneous solution by the photo-induced oxidation of oxalate by bromine in the presence of manganese(II) chloride. The tantalum was originally complexed by the oxalate and after oxidation of the oxalate, the tantalum precipitated as the selenite. Suzuki[3] reported a method for the photochemical separation of cerium from some other rare-earth elements by a photochemical method which involved the IO_4^-–IO_3^- system. We did not become aware of his work until after the publication of our preliminary communication.[4]

Thorium and some other elements are frequently precipitated as the iodates. Stine and Gordon[5] introduced a PFHS method for thorium, based on the reduction of periodate by 2-hydroxyethyl acetate, resulting in the precipitation of thorium iodate. In order to achieve a separation from rare earths, a 2·5–3M nitric acid solution had

---

* Present address: Department of Chemistry, University of Tabriz, Tabriz, Iran.

† Leave of absence, Roorkee University, Roorkee, India. This paper was presented in part before the Division of Analytical Chemistry, 154th and 155th National Meetings, American Chemical Society, Chicago, Ill., 1967 and San Francisco, Calif., April 1968. Work supported by a Grant-in-Aid from the Graduate School, Boston University and by the National Science Foundation Grant GP-7532, and taken in part from the Ph.D. Thesis of M. Das, Boston University, 1967.

to be used. Meyer and Speter[6] had used $7M$ nitric acid in the direct precipitation of thorium iodate, but Stine and Gordon recognized that such a high concentration of acid caused an intolerable loss of thorium which appeared to be partially compensated by co-precipitation of silica. On the other hand, too low a concentration of nitric acid allowed the co-precipitation of cerium. Inasmuch as Stine and Gordon's method does not provide for a separation from cerium, a lower acid concentration was used. Meyer and Speter had to add a very large excess of the expensive iodate in order to decrease the solubility of thorium iodate. In all these methods, the thorium iodate precipitates as a mixture of different iodates. Consequently, it is necessary to convert the thorium into a weighable form such as ThO_2. However, direct ignition of the iodate to ThO_2 does not succeed, requiring the precipitate to be dissolved and thorium precipitated as the oxalate. Special modifications were used in the separation from rare earths and from uranium to decrease interferences.

The work reported here applies the photochemical reduction of periodate to the *in situ* precipitation of thorium. Head and co-workers[7,8] have demonstrated that metaperiodate is readily reduced to iodate by the action of ultraviolet radiation. Periodate shows an absorption maximum at 220 nm ($\varepsilon = 980$ l.mole^{-1}.mm^{-1}) and an absorptivity of 180 l.mole^{-1}.mm^{-1} at 253·7 nm. Because of the high absorbance of the nitrate ion in the ultraviolet and the low absorbance of perchlorate, perchloric acid solutions have been used throughout this work. It has been found that for thorium the optimum perchloric acid concentration range is $1{\cdot}0$–$1{\cdot}8M$, the solubility of thorium iodate then being very low, requiring only a small excess of iodate.

We modified the procedure involving the *in situ* generation of iodate from the photoreduction of periodate so that it could be applied to cerium. It is known[9] that cerium(III) in perchlorate solution is photochemically oxidized to the quadrivalent form, albeit with a low quantum yield. Furthermore, in dilute acidic solutions, periodate does not oxidize cerium(III) to (IV). It was, therefore, of interest to see whether cerium(III) perchlorate solutions in the presence of periodate would undergo photochemical oxidation–reduction with the formation of insoluble ceric iodates. Inasmuch as ceric periodate is only sparingly soluble, it would be preferable to start with the more soluble cerium(III) periodate and, after irradiation, obtain the insoluble ceric iodate.

Brinton and James[10] utilized the low solubility of cerium(IV) iodate in developing a method for the precipitation of cerium in dilute nitric acid solution. Willard and Yu[11] oxidized cerium(III) to (IV) with peroxydisulphate or bromate in $0{\cdot}5M$ nitric acid in the presence of iodate and obtained a dense precipitate of ceric iodate by this PFHS method. Reprecipitation of the cerium was required, however, in order to accomplish satisfactory separations from equal amounts of rare earths.

In order to avoid the precipitation of the cerium(IV) periodate, Suzuki,[3] who started with cerium(IV), added potassium periodate in small portions during the irradiation period. By starting with cerium(III) and sodium periodate, we avoided the formation of cerium(IV) periodate, and the disadvantages of the low solubility of potassium periodate. Suzuki carried out the photochemical reduction in $0{\cdot}7$–$0{\cdot}8M$ sulphuric acid. He claimed excellent separations of cerium from neodymium and yttrium. We have made repeated attempts to duplicate his results, using his method, but have found that neodymium is co-precipitated to the extent of 5–8% and yttrium to an even greater extent.

EXPERIMENTAL

Equipment and reagents

Lamp. A helical-coil low-pressure mercury resonance lamp with a quartz envelope, Nester/Faust Co. Model NFUV-100, was used. Approximately 85–90% of the output is at 253·7 nm. An inexpensive Sylvania lamp, H 37-5 KB/RS which is used for street illumination, was modified by cutting an opening into the external glass envelope. It was used for some of the work and gave equivalent results with one-half the irradiation times. The larger heat generation from this lamp was dissipated with a slow stream of air.

Thorium perchlorate. Reagent grade $Th(NO_3)_4 \cdot 4H_2O$ was repeatedly evaporated with a small excess of 60% perchloric acid. After dilution, the solution contained approximately 0·56 g of ThO_2 and 1 g of 60% perchloric acid per 100 ml. The thorium content was determined by the modification of Vogel's method.[12] A volume of solution containing about 100 mg of ThO_2 was mixed with 225 ml of water and 5 ml of concentrated hydrochloric acid and heated to boiling. With stirring, 55 ml of hot 10% oxalic acid dihydrate solution were added slowly. The hot solution was digested for 2 hr and then allowed to stand overnight at room temperature. The solutions were filtered through a medium ashless filter paper; the precipitate was washed with 150–200 ml of wash solution, dried, ashed, and ignited at 700–800° in an electric muffle and weighed as ThO_2. The wash solution consisted of 2·5 g of oxalic acid dihydrate dissolved in 3·5 ml of concentrated hydrochloric acid diluted to 100 ml.

Cerium(III) perchlorate solution. The calculated amount of $Ce(ClO_4)_3 \cdot 6H_2O$ was dissolved in 1% perchloric acid to make a 0·025*M* solution. The solution was standardized gravimetrically by precipitating cerium(III) oxalate; 25 ml of the perchlorate solution were diluted to 75 ml, heated to boiling, and 25 ml of 10% oxalic acid solution were added slowly with constant stirring. The precipitate was allowed to stand for 2 h, filtered off on ashless paper, washed with cold 2% oxalic acid solution, dried, ashed, and ignited to CeO_2 at 900°, following the recommendations of Brinton and James.[10]

Solutions of rare earths, uranium, and yttrium. Appropriate amounts of the nitrates were dissolved and heated to fumes with a small excess of perchloric acid, or alternatively, the carbonates were treated with a small excess of dilute perchloric acid. The rare-earth and yttrium compounds were of at least 99·9% purity, and were examined spectrographically for the presence of interfering elements. The solutions were analysed by precipitation of the rare earths or yttrium as the oxalates and ignition to the oxides by the standard procedures. Reagent grade uranyl nitrate was used. Uranium was determined by the precipitation of ammonium diuranate and ignition to U_3O_8 by standard procedures.

All other reagents used were A.C.S. reagent grade.

Procedures

Photochemical precipitation of thorium. The exposures were carried out by placing the solution to be photolysed in a 100 × 50 mm crystallizing dish under the mercury lamp which was held in a horizontal position about 50 mm above the level of the solution. Aluminium foil over the top of the lamp increased the available radiation by reflection and shielded the operator from the direct radiation when the opaque fume-cupboard window was opened for inspection (protective ultraviolet-absorbing goggles must be worn).

The solution consisted of an appropriate volume of the thorium perchlorate solution, 60 ml of water, 10 ml of 60% perchloric acid and 4 g of sodium periodate. The range of thorium was equivalent to 8–210 mg of ThO_2. Photolysis times of 4 hr were found to be adequate.

After it was cooled to room temperature, the solution was decanted and the precipitate transferred to Schleicher and Schüll 589 Blue Label (high retention) filter paper. The precipitate on the filter paper and that adhering to the crystallizing dish was dissolved in 100 ml of 1*M* hydrochloric acid. The iodate was reduced to iodide by the addition of solid sodium sulphite until the tri-iodide color was discharged. The solution was heated to 60–70° and filtered ammonia solution added until there was a slight excess. The resulting thorium hydroxide was filtered off on medium ashless filter paper and washed with water until the excess of ammonia was removed. The precipitate was dissolved with 0·5*M* hydrochloric acid. After dilution to 250 ml, the thorium was determined by the oxalate method given above.

Hexamine precipitation of thorium hydroxide. The solution obtained from the dissolving of the thorium iodate was neutralized, after reduction of the iodate, with filtered ammonia solution until a slight turbidity appeared; a few drops of hydrochloric acid were then added to remove the turbidity. The solution (300 ml) was heated to 70–80° and a 10% hexamethylenetetramine solution was added dropwise with stirring until a white turbidity appeared, after which an additional 7 ml of the reagent solution were added. The mixture was digested for 1 hr at 70°, filtered, and the precipitate washed with water, then dissolved in the dilute hydrochloric acid and precipitated as the oxalate, as above.

Determination of thorium in the filtrates. In order to evaluate any thorium loss in these precipitations, the thorium in the filtrates was extracted with thenoyltrifluoroacetone in benzene in the presence of calcium nitrate at a pH of about 2. The thorium was stripped with 2*M* nitric acid, and the nitric acid removed by evaporation after the addition of a few ml of perchloric acid. Thorium was determined by adding 2 ml of concentrated hydrochloric acid and 0·1% thoron solution ([*o*-(2-hydroxy-3,6-disulpho-1-naphthyl)azo]benzene arsonic acid disodium salt) and measuring the absorbance at 545 nm. Aliquots of a standard thorium solution were similarly extracted to obtain a standard curve. The extraction was omitted in the case of the filtrate from the oxalate precipitation; instead, the oxalate was destroyed by careful evaporation with nitric acid followed by repeated evaporation with perchloric acid.

Analysis of the thorium iodate precipitates. The photochemically prepared thorium iodate was filtered off on a sintered-glass crucible, washed with alcohol and dried at 25° for 3 hr. Thorium was determined by the oxalate method after the precipitate was dissolved in concentrated hydrochloric acid. Iodate was determined by dissolving the precipitate in 2*M* sulphuric acid, adding an excess of potassium iodide and titrating the tri-iodide with standard thiosulphate. The precipitate was also analysed spectroscopically, and was shown to contain less than 0·05% sodium.

Photochemical precipitation of cerium. Samples containing an appropriate amount of cerium(III) perchlorate, 3 ml of 60% perchloric acid and 4 g of sodium periodate in 75 ml total volume were irradiated as for thorium. The precipitate of the basic cerium(IV) iodate was allowed to stand for 30 min, then the supernatant liquid was decanted through No. 589 Blue Label filter paper. The precipitate was washed 3–4 times by decantation and transferred to the filter paper with cold water, after which the filter was punctured and the precipitate in the filter transferred into a beaker. The punctured filter was added and the mixture was heated with 6 g of solid oxalic acid until no more iodine was evolved. An additional 1 g of oxalic acid was added and the mixture heated for a further 5 min. About 50 ml of hot water were added, the precipitate was allowed to settle for several hours (usually overnight) and the precipitate of cerium(III) oxalate was filtered off on No. 589 Blue Label filter paper, washed with 2% aqueous oxalic acid solution, dried, ashed and ignited to CeO_2 at 800° to constant weight. The decomposition of the iodate, conversion to cerium(III) oxalate, and ignition essentially follows the precedure in Scott's *Standard Methods*.[13]

Determination of lamp efficiency. The lamp efficiency, and therefore the appropriate exposure times, were found by irradiating a solution containing 4 g of sodium periodate and 3 ml (for cerium analysis) or 10 ml (for thorium analysis) of 60% perchloric acid and analysing it volumetrically for iodate by the method in Scott's *Standard Methods*.[14] Sufficient iodate must be formed to provide a 50% excess.

It was found that the amount of iodate produced with a 4-hr exposure sufficed for precipitating up to 240 mg of thorium or 145 mg of cerium. Such exposures were therefore used in all runs, except for those using the Sylvania lamp, in which case a 2-hr exposure was sufficient.

The quantum yield of the process was determined by irradiating uranyl oxalate solutions, using the same experimental geometry. A quantum yield of 0·37 was obtained for the periodate reduction in 0·9*M* perchloric acid solution.

RESULTS AND DISCUSSION

Results for thorium are shown in Tables I–V and for cerium in Tables VI–IX.

Thorium

Acidity. With 3·6*M* perchloric acid the thorium loss was about 5·1 mg of ThO_2 out of 147 mg, as compared to 0·0 mg in solutions which were up to 1·8*M* in perchloric acid. A maximum acidity of 1·8*M* perchloric acid was therefore chosen.

Excess of iodate. The method of Meyer and Speter[6] requires 15 g of potassium iodate in the 250 ml of solution in order to keep the solubility of the thorium iodate sufficiently low in the presence of 7*M* nitric acid. In perchloric acid, the solubility losses are low and only a small excess of iodate is required. The PFHS method of Stine and Gordon[5] uses 2·5–3*M* nitric acid but still suffers a slight solubility loss requiring the use of 14 g of sodium periodate followed by the addition of 2 g of potassium iodate after the initial reduction, in order to ensure complete precipitation. In the photochemical method, only 4 g of sodium periodate are required. This presents an appreciable economy, in view of the high cost of periodates.

Determination of thorium in the filtrates. Table I shows the weight of ThO_2 in the filtrates from the three methods (as determined by the thoron method) and also in the

TABLE I.—THORIUM IN THE FILTRATE (140·0 mg OF ThO_2 TAKEN)

Method	ThO_2 in filtrate		
	average, *mg*	No. of detns., *n*	Std. devn., *s*,
Meyer and Speter[6]	1·45	4	0·11
Stine and Gordon PFHS[5]	0·14	4	0·06
Photochemical PFHS	0·04	4	0·02
Oxalate precipitation[12]	0·13	5	0·08

filtrate of the oxalate precipitation. The photochemical PFHS method shows the lowest thorium loss. No thorium could be found in the filtrates of the thorium hydroxide precipitation, which is to be expected in view of its known very low solubility.

Composition of the precipitate. Chernikov and Uspenskaya[15] gave the composition of the precipitate obtained by the method of Meyer and Speter as $4Th(IO_3)_4{\cdot}KIO_3{\cdot}18H_2O$, giving an IO_3^-:Th mole ratio of 4·25:1; Moeller and Fritz[16] found a ratio of 4·02:1 and based a volumetric method for thorium on this value. The precipitate produced by the photochemical method has an IO_3^-:Th ratio of 2·26:1. The precipitate apparently consists mostly of basic thorium iodate, $ThO(IO_3)_2$, containing a small portion of the normal iodate. Inasmuch as the precipitation is used for separation, this non-stoichiometric composition does no harm. The composition of the precipitate is not surprising in view of the low acid concentration used.

Determination of thorium. Because of the non-stoichiometric composition of the thorium iodate precipitate, direct weighing of the precipitate was not attempted. In addition, the presence of non-volatile electrolytes made direct weighing or ignition to thorium dioxide impractical at this stage. Water-washing to remove the electrolytes would have resulted in excessive solubility losses. The precipitation as the hydroxide removes interfering electrolytes and makes the application of the oxalate precipitation possible. Although a PFHS of the oxalate could have been applied at this point, little would have been gained by doing so. Results for solutions containing known amounts of thorium in the absence of interfering ions are given in Table II. Table III shows the results obtained in the presence of possible interfering ions introduced as the perchlorate salts. It is seen that calcium, magnesium, iron, yttrium and uranium

TABLE II.—DETERMINATION OF THORIUM

ThO_2 taken, *mg*	Error in ThO_2 found,† *mg*			
8·10*	−0·1;	0·0;	+0·2;	+0·1
15·05*	+0·1;	0·0;	0·0;	+0·2
26·8*	−0·3;	−0·1;	0·0;	+0·2
39·5*	−0·1;	0·0;	0·0;	−0·1
81·1	+0·2;	0·0;	+0·2;	0·0
122·7	+0·1;	−0·4;	−0·3;	0·0
163·1		0·0;	−0·2	
164·7	−0·4;	+0·1;	−0·1;	−0·4
206·1		+0·2;	+0·4	

* 12 hr digestion used.

† S 0·20 *mg*, $n = 32$. A regression-line analysis yielded a straight line with no significant differences in the slope and intercept from the expected values of 1·000 and 0·00, respectively (95% probability).

TABLE III.—EFFECT OF FOREIGN IONS ON DETERMINATION OF THORIUM

Element added, *mg*		ThO_2, *mg* Taken	ThO_2, *mg* Found, error	
Ca	25	143·2	−0·3	$n = 10$ $s = 0{\cdot}24$ mg
Mg	25	143·2	−0·1	
Fe	7	143·2	0·0	
	14	143·2	0·0	
	28	143·2	−0·5	
Y	25	143·2	−0·3	
	50	143·2	0·0	
U	25	142·7	+0·1	
	50	142·7	+0·2	
	100	143·2	−0·1	
La	24	142·8	+0·2	$n = 11$ $s = 1{\cdot}71$ mg
Nd	25	142·7	+0·5	
	50	142·7	+1·1	
Pr	25	142·7	+0·8	
	50	142·7	+2·0	
Mixture*	87	113·7	+1·3; +0·8	
	174	113·7	+1·3; +2·0	
	261	113·7	+2·6; +2·9	

* Approximately equal amounts of Sm, Eu, Gd, Dy, Er.

do not interfere at the levels shown. The standard deviation in these cases does not differ significantly from that for the results in Table II. It is seen that some of the rare earths are apparently co-precipitated to a certain extent, giving up to 2·9 mg error for ThO_2. The rare-earth interference is expected to be more serious in the photochemical method, in accordance with the findings of Moeller and Fritz,[16] who pointed out that a high nitric acid concentration prevents such interference. In the photochemical method the concentration of free acid, as well as of iodate, was much lower than in the other methods. The increased co-precipitation of rare earths was overcome, however, by precipitating the thorium hydroxide by the hexamine procedure of Ismail and Harwood.[17] Table IV shows the results obtained by introducing this modification. It can be seen that the precision of the thorium determinations does not differ significantly whether these other metals or the rare earths are present or not.

TABLE IV.—DETERMINATION OF THORIUM, RARE EARTHS PRESENT, HEXAMINE PROCEDURE

Element added, *mg*		ThO_2, *mg* Taken	ThO_2, *mg* Found, error†
Mixture*	87	112·1	−0·4; −0·4
	174	112·1	0·0; +0·1
	261	112·1	−0·1; 0·0
	435	109·3	−0·1
	610	109·3	0·0; +0·3
	870	109·3	−0·2

* Approximately equal amounts of: Sm, Eu, Gd, Dy, Er.
† $n = 10$; $s = 0{\cdot}23$ mg.

Although uranium co-precipitates to a slight extent during the photochemical precipitation (Table V), the uranium remains complexed by the oxalate and thus is

TABLE V.—DETERMINATION OF THORIUM, URANIUM(VI) PRESENT

	Uranium taken, *mg*	ThO_2, *mg*		
		Taken	Found, error	
Method I	100	48·2	−0·1; −0·1	*n* = 10 *s* = 0·31 mg
	300		−0·1; +0·1	
	500		0·0; 0·0	
	750		−0·5; −0·5	
	1000		−0·4; −0·4	
	1500		−1·0; −1·1	
Method II	100	48·0	+1·1; +0·6	*n* = 9 *s* = 2·5 mg
	200		+2·3; +1·7	
	300		+2·5; +2·5	
	400		+3·0; +3·4	
	500		+3·3	

Method I: Final precipitation of thorium from oxalate solution (usual method).
Method II: Final precipitation of thorium as hydroxide; no oxalate present.

separated from thorium in the final precipitation. Owing to the absorbance of the uranyl ion, however, incomplete precipitation of thorium(IV) could result in the presence of very large amounts of uranyl ion because of the lower ultraviolet flux which would be available for the periodate reduction.

Cerium must be removed prior to the determination because cerium(IV) iodate is similarly precipitated.

No photochemical system can be truly concentration-homogeneous, as Fitzgerald[18] pointed out, because of the decrease in the intensity of radiation with thickness of the solution; absorption of the photochemically effective radiation is required in order to have a photochemical change. Yet the described method is much closer to the gradual formation of the precipitate typical for PFHS than is direct addition of a reagent.

Cerium

Acidity. The original method of precipitating cerium(IV) iodate, by Brinton and James,[10] made use of 8*M* nitric acid solution. Other rare-earth iodates are sufficiently soluble in this highly acidic solution to permit separations from cerium. Solubility errors due to the increased solubility of cerium(IV) iodate in this high concentration of nitric acid were decreased by keeping an extremely large excess of iodate in solution.

TABLE VI.—DETERMINATION OF CERIUM, SULPHITE PROCEDURE

CeO_2 taken, *mg*	Error in CeO_2 found, *mg*†
12·7	−0·3, −0·2, −0·2, −0·2
25·5	0·0, 0·0, +0·1, 0·0
43·0	+0·2, +0·2, +0·1, 0·0
66·6	0·0, −0·1, 0·0
97·6	−0·3, −0·3, −0·3, −0·4
104·6	−0·2, −0·1
133·0	+2·1, +2·2, +0·4, +1·2, +0·9
148·1*	+0·2, +0·4

* Oxalate procedure.
† *n* = 23 (excluding 133·0-mg determinations); *s* = 0·20 mg.

The method described here makes use of only dilute acid solutions (0·13–0·50*M* perchloric acid) and requires only a modest excess of the iodate. This lower acidity causes a decrease in solubility errors due to cerium(IV) iodate (Table VIII), but at the expense of separations from rare earths and yttrium (Tables VII and IX). Willard and Yu[11] found much less interference by other rare earths; nitric acid is apparently more effective in preventing the precipitation of rare earth iodates than is perchloric acid. However, because of the strong absorption of ultraviolet radiation by nitric acid, we could not use this acid.

TABLE VII.—DETERMINATION OF CERIUM, RARE EARTHS PRESENT

Rare earth added, *mg*		60% $HClO_4$, *ml*	CeO_2, *mg*	
			Taken	Found, error
Gd_2O_3	15	3	62·7	+9·1, +10·0
	30	3	62·7	+14·2, +14·8
	60	3	62·7	+22·6, +22·3
	50	1	74·2	+43·5
	100	1	74·2	+92·4
Dy_2O_3	30	3	62·7	+6·6
	50	1	74·2	+45·5
	100	1	74·2	+91·8
Pr_2O_3	30	3	62·7	+24·8, +26·0
	50	1	74·2	+47·7
	100	1	74·2	+95·0
Ho_2O_3	50	1	74·2	+42·2
	100	1	74·2	+85·3
La_2O_3	100	1	74·2	+101·4
	200	1	74·2	+200·4
Yb_2O_3	30	3	62·7	+11·3
	60	3	62·7	+15·7
Nd_2O_3	60	3	62·7	+33·3
	57·6	1	148·5	+56·3
	57·6	2	148·5	+57·6
	57·6	3	148·5	+53·0
	57·6	4	148·5	+45·5
	57·6	6	148·5	+41·7
	57·6	8	148·5	+21·9

TABLE VIII.—EFFECT OF ACIDITY ON THE RECOVERY OF CERIUM (107·1 mg OF CeO_2 TAKEN)

Perchloric acid, *M*	Error in CeO_2 found, *mg*
0·28	−0·1
0·56	−3·6
0·94	−7·4

Composition of the precipitate. The composition of the precipitate shifts progressively in favour of basic iodates as the acidity is lowered. Our analysis gave a ratio of 3·6 for the molar ratio of $CeO(IO_3)_2$:$Ce(IO_3)_4$. It is interesting to note that despite our use of perchloric acid, this composition of the precipitate corresponds exactly to that shown by Willard and Yu (Fig. 1 of Ref. 11) for 0·3*M* nitric acid. The amount of iodate found was 89% of that in normal cerium(IV) iodate. Suzuki[8] obtained a mixed iodate of cerium and potassium, but our precipitates contained no

TABLE IX.—EFFECT OF FOREIGN IONS ON DETERMINATION OF CERIUM

Foreign species present, *mg*		60% $HClO_4$, *ml*	CeO_2, *mg*	
			Taken	Found, error
Y_2O_3	100	1	74·2	44·9
	200	1	74·2	+63·9
	32	3	62·6	+7·1
	64	3	62·6	+8·3
U_3O_8 [as U(VI)]	69·6	2	148·4	+0·1
	139·2	2	148·4	0·0
	208·8	2	148·4	+0·1
MgO	356	1	74·2	0·0
	712	1	74·2	+0·6
Fe_2O_3	287	1	74·2	+1·0*
	575	1	74·2	+1·6*
CaO	342	1	74·2	+220·9
	683	1	74·2	+291·7

* Precipitates were brownish due to the contamination by Fe.

more than traces of sodium or potassium. The presence of the basic iodate does not affect the analytical result inasmuch as it is at least as insoluble as the normal iodate and, in any case, the precipitate is converted into the dioxide for weighing.

Determination of cerium. In our re-examination of the system, the cerium(IV) iodate was initially decomposed as given in our method for thorium, by adding sulphite, heating until all the iodine was volatilized, and then precipitating cerium(III) hydroxide with ammonia, followed by ignition to the dioxide. In view of the high results obtained for larger samples (Table VI) we used oxalate to decompose the cerium(IV) iodate as discussed in the experimental section above. We attempted direct ignition of cerium(IV) iodate to CeO_2, following the method of Willard and Yu,[11] but found that the loss due to sputtering was significant.

To compare the density of the precipitates obtained by the photochemical method and the direct addition method of Brinton and James,[10] precipitates were allowed to settle for 24 hrs after transfer into graduated cylinders. The precipitate from magnetically stirred photochemically reduced solution showed the least volume but even an unstirred solution gave a volume of the precipitate significantly less than that from the direct addition method. The volume ratios of precipitate were found to be approximately 1:2:4 for the same amounts of cerium precipitated by the photochemical method with stirring, without stirring, and by the direct addition method, respectively. Photomicrographs of the ceric iodate precipitates obtained by these methods showed that the particles obtained by the photochemical method were more compact and appeared less gelatinous than those obtained by the direct addition method of Brinton and James.[10] It was apparent that the more dense particles should be more easily washed than the almost gelatinous aggregates obtained by direct precipitation.

In view of the low acidity of the solution, it is not surprising that the rare earths and yttrium interfere seriously with the determination of cerium although separations from uranium (as uranyl ion) were accomplished. It was found that the initial iodate precipitate contained some uranium but that the oxalate precipitation step kept the uranyl ion in solution as the oxalato complex. Separation from much larger amounts of uranium necessitated modification of the procedure and will be reported elsewhere together with data on the separation of thorium from uranium. Further, Table IX shows that cerium can be separated essentially quantitatively from magnesium and almost quantitatively from iron(III), although the precipitate appears to retain a small amount of iron which gives a brownish colour to the precipitate and causes slightly high results. Calcium is co-precipitated to a large extent, but not quantitatively. Thorium, of course, behaves similarly to cerium and will be co-precipitated quantitatively. The results in Table VII suggest that the photochemical precipitation method should give quantitative results for neodymium and lanthanum; some preliminary results have been reported.[9]

We were never able to reproduce the exceedingly good separations which Suzuki reported in Table 6 of his paper.[3] Samples containing 71·3 mg of cerium dioxide and 15·2 and 30·4 mg of neodymium oxide were treated by Suzuki's procedure and gave recoveries which were high by 4·2 and 6·2 mg, respectively. The presence of 100 mg of yttrium oxide in the cerium gave results which were 44·5 mg too high.

The method of Willard and Yu[11] is to be preferred if separation from other rare earths is desired, and the method reported here is to be preferred if it is desired to carry out the cerium precipitation at room temperature or if uranium is present, which seriously interferes with the non-photochemical precipitation procedure.[11]

Zusammenfassung—Thorium wurde aus homogener Lösung gefällt, indem Lösungen von Thorium und Perjodat in verdünnter Überchlorsäure der 253,7 nm-Strahlung einer Niederdruck-Quecksilberlampe ausgesetzt wurden. Perjodat wird photochemisch zu Jodat reduziert; dieses führt zur Bildung eines dichten Niederschlags von basischem Thorium(IV) jodat. Der Niederschlag wurde wieder gelöst, das Jodat reduziert, das Thorium zuerst als Hydroxid, dann als Oxalat gefällt, zum Oxid verglüht und gewogen. Thorium(IV)-Lösungen mit 8–200 mg ThO_2 gaben quantitative Ergebnisse mit einer Standardabweichung (s) von 0,2 mg. Abtrennungen von je 25 mg Eisen, Calcium, Magnesium, 50 mg Yttrium und bis zu 500 mg Uran(VI) waren quantitativ (s = 0,25 mg). Abtrennungen von seltenen Erden außer Cer wurden erreicht, wenn zur Fällung des Hydroxids Hexamethylentetramin statt Ammoniak verwendet wurde. Cer(III) wurde ähnlich gefällt und zur Wägung in CeO_2 überführt. Quantitative Erebnisse wurden für 13–150 mg CeO_2 mit einer Standardabweichung von 0,2 mg erhalten. Abtrennungen von 200 mg Uran waren quantitativ. Andere seltene Erden und Yttrium störten erheblich. Die Niederschläge der basischen Jodate von Cer(IV) und Thorium sind kompakter als die, die man bei direkter Fällung erhält, und leichter zu handhaben. Versuche, das Verfahren von Suzuki zur Trennung von Cer von Neodym und Yttrium nachzuarbeiten, blieben ohne Erfolg.

Résumé—On a précipité le thorium en solution homogène en exposant des solutions de thorium et de periodate en acide perchlorique dilué à la radiation 253,7 nm d'une lampe à mercure à basse pression. Le periodate est réduit photochimiquement en iodate qui provoque la formation d'un précipité dense de l'iodate basique de thorium(IV). Le précipité est redissous, l'iodate réduit, le thorium précipité d'abord à l'état d'hydroxyde, puis d'oxalate et calciné en dioxyde pour pesée. Les solutions de thorium(IV) contenant 8–200 mg de ThO_2 ont donné des résultats quantitatifs avec un écart type (s) de 0,2 mg. Des séparations de 25 mg de chacun des métaux fer, calcium, magnésium, de 50 mg d'yttrium et jusqu'à 500 mg d'uranium(VI) ont été quantitatives (s = 0,25 mg). Les séparations de terres rares, à l'exception du cérium, ont été réalisées en utilisant l'hexaméthyléne tétramine

plutöt que l'ammoniaque pour la précipitation de l'hydroxyde. Le cérium(III) a été précipité de manière semblable et converti en CeO_2 pour la pesée. On a obtenu des résultats quantitatifs pour 13–150 mg de CeO_2 avec un écart type de 0,2 mg. Des séparations de 200 mg d'uranium ont été quantitatives. Les autres terres rares et l'yttrium interfèrent sérieusement. Les précipités d'iodates basiques de cérium (IV) et de thorium obtenus sont plus compacts que ceux obtenus par précipitation directe et peuvent être manipulés aisément. Des essais pour reproduire la méthode de Suzuki de séparation du cérium du néodyme et de l'yttrium n'ont pas réussi.

REFERENCES

1. L. Gordon, M. L. Salutsky and H. H. Willard, *Precipitation from Homogeneous Solution.* Wiley, New York, 1959.
2. J. Y. Yen and W. Yang, *Sci. Sinica (Peking)*, 1964, **13**, 343.
3. Y. Suzuki, *Kogyo Kagaku Zasshi*, 1965, **68**, 2352.
4. M. Das, A. H. A. Heyn and M. Z. Hoffman, *Talanta*, 1967, **14**, 439.
5. C. Stine and L. Gordon, *Anal. Chem.*, 1953, **25**, 1519.
6. R. J. Meyer and M. Speter, *Chemiker Z.*, 1910, **34**, 306; *Z. Anorg. Allgem. Chem.*, 1911, **71**, 65.
7. F. S. H. Head, *Nature*, 1950, **165**, 236.
8. F. S. H. Head and H. A. Standing, *J. Chem. Soc.*, 1952, 1457.
9. L. J. Heidt and A. F. McMillan, *J. Am. Chem. Soc.*, 1954, **76**, 2135.
10. P. H. Brinton and C. James, *ibid.*, 1919, **41**, 1080.
11. H. H. Willard and S. T. Yu, *Anal. Chem.*, 1953, **25**, 1754.
12. A. I. Vogel, *Textbook of Quantitative Inorganic Analysis*, 3rd Ed., p. 541. Wiley, New York, 1961.
13. N. H. Furman, ed., *Scott's Standard Methods of Chemical Adalysis*, 6th Ed., Vol. 1, p. 318. Van Nostrand, Princeton, 1962.
14. *Idem, ibid.*, p. 522.
15. Y. A. Chernikov and T. A. Uspenskaya, *Zavodsk. Lab.*, 1940, **9**, 276.
16. T. Moeller and N. D. Fritz, *Anal. Chem.*, 1948, **20**, 1055.
17. A. M. Ismail and H. F. Harwood, *Analyst*, 1937, **62**, 185. See also S. S. Berman, P. Semeniuk and D. S. Russell, *Talanta*, 1966, **13**, 837.
18. J. M. Fitzgerald, R. J. Lukasiewicz and H. D. Drew, *Anal. Letters*, 1967, **1**, 173.
19. R. P. Agarwal, A. H. A. Heyn and M. Z. Hoffman, *Anal. Letters*, 1969, **2**, 485.

Talanta, 1970, Vol. 17, pp. 937 to 944. Pergamon Press. Printed in Northern Ireland

COULOMETRIC DETERMINATION OF URANIUM WITH A PLATINUM WORKING ELECTRODE

W. DAVIES, W. GRAY* and K. C. MCLEOD
United Kingdom Atomic Energy Authority (Reactor Group),
Dounreay Experimental Reactor Establishment, Thurso, Caithness, Scotland

(*Received* 5 *February* 1970. *Accepted* 10 *April* 1970)

Summary—Experimental conditions have been established which enable uranium to be determined coulometrically by the reduction of uranium(VI) to uranium(IV) at a platinum working electrode, by controlled-potential or controlled-potential-limit techniques. The procedure has been used successfully as a subsidiary method in the routine determination of uranium in pure uranyl nitrate solutions. The platinum electrode has several important practical advantages over the well established mercury-pool electrode for the coulometric determination of uranium. The consecutive determination of iron(III) and uranium(VI), or plutonium(IV) and uranium(VI) can be carried out with the same working electrode in the same solution and the coulometric oxidation of uranium(IV) to uranium(VI) is practicable. The rate of stirring of the cell liquor is much less critical in the case of the platinum electrode. Two main problems had to be overcome before a practical procedure could be achieved; hydrogen evolution during the uranium(VI)–(IV) reduction had to be eliminated so that 100% current efficiency could be obtained for the desired reaction and electrode-surface poisoning phenomena had to be controlled so that reaction times could be kept reasonably short. It was found that selection of a hydrochloric acid base solution containing a small amount of bismuth(III) enabled hydrogen evolution to be avoided: also electrode-surface poisoning with this base solution was not particularly serious and could be maintained at a satisfactorily low level by occasionally anodizing the electrode in dilute sulphuric acid. Bismuth(III) forms a complex with chloride ions and its presence increases the hydrogen overvoltage at the working electrode: no visible deposit of bismuth metal forms on the electrode during the uranium reduction. Samples containing nitrate can be analysed provided sulphamic acid is added to this hydrochoric acid base solution.

THE DETERMINATION of uranium by controlled-potential coulometry, employing a mercury-pool working electrode at which uranium(VI) is reduced to uranium(IV), is a well established technique. Analytical procedures have been described by Booman *et al.*,[1] Goode *et al.*[2] and McColm *et al.*[3]

There are, however, two main disadvantages associated with the application of the mercury-pool electrode to coulometric analyses in general. One is that, for optimum performance, the experimental arrangements for mixing the contents of the working compartment of the coulometric cell are somewhat critical; both aqueous and mercury phases need to be efficiently stirred without producing detached droplets of one phase within the other. The other main disadvantage is that mercury dissolves under mildly oxidizing conditions: for example, it is impracticable to perform coulometric oxidations of uranium(IV), iron(II) and plutonium(III) in the usual mineral-acid base electrolytes.

These two disadvantages do not apply to the platinum-gauze working electrode,

---

* Present address is Shell Research Ltd., Woodstock Agricultural Research Centre, Sittingbourne, Kent, England.

and it appeared that a useful improvement in coulometric technique would be accomplished if the mercury pool could be replaced by a platinum electrode in the case of uranium determinations. Such a change of working electrode is not a straightforward matter, since difficulties due to hydrogen evolution and surface-poisoning effects arise at the platinum electrode at the potentials needed for the reduction of uranium(VI) to uranium(IV).

This paper describes how these difficulties were overcome and how a practical procedure for the coulometric determination of uranium at a platinum working electrode was achieved.

EXPERIMENTAL

Apparatus

Coulometer. The constant-current potential-limit coulometer described by McColm *et al.*[3] was used for this work. This instrument contains sixteen constant current sources providing currents of 512, 256, 128, 64, 32 . . . 0·16 mA. When the working electrode voltage reaches the set potential limit, the current is automatically halved until a pre-set maximum current is reached. Hence the conditions of controlled-potential coulometry are approximated to by a series of discrete controlling steps, rather than the continuous control normally used.

Cell and electrodes. Figure 1 depicts the cell employed in the later stages of the investigational work and for the final recommended procedure. The body of the cell was made from borosilicate glass. The ion-exchange membranes were sealed with picein wax into ground-in ledges made inside standard glass cone-and-socket joints. The working electrode consisted of a strip of platinum gauze about 30 mm wide and 300 mm long, formed into a cylinder two to three layers thick: it fitted loosely in the working compartment and when in position needed about 20 ml of liquid to cover it. The liquor in the working compartment was stirred by a compressed-air operated glass stirrer running in PTFE bearings. The reference electrode compartment contained an E.I.L. type RJ.23 "saturated calomel" element immersed in saturated potassium chloride solution. The dimensions and construction of the platinum auxiliary electrode were not critical. The purpose of the conducting bridge was to isolate the auxiliary electrode reaction products from the working compartment. The total resistance of the cell was such that a potential difference between the working and auxiliary electrodes of 12 V would cause a current of about 0·6 A to flow. The working compartment liquor was de-aerated by passing nitrogen over its surface, with the stirrer in operation.

The cells employed for the earlier work differed from the one described above mainly in being slower in operation because of their inferior electrode area : solution volume ratios.

Preliminary work

Amount of uranium per determination. The amount of uranium added in most of the trials was about 200 mg per determination. This amount was rather larger than that normally taken by other workers: it was selected to make it easier to obtain high precision of measurement and to decrease the "blank" and other corrections. The uranium was added as an aqueous uranyl chloride or uranyl nitrate solution of known concentration. Sulphamic acid was always added to the base electrolyte when the nitrate was employed.

Use of gold electrodes. Because information already available indicated that it was probably impracticable to use a platinum working electrode for the uranium(VI)–(IV) reduction, and because our preliminary experiments appeared to confirm this, most of our early experimental work, aimed at replacing the mercury pool, was done with gold electrodes. It was hoped that gold would prove to be more satisfactory than platinum. These gold electrodes were prepared by gold-plating platinum gauze from a cyanide plating bath.

Initially $1M$ sulphuric acid was employed as base electrolyte in the trial uranium determinations. Experiments showed that uranium(VI) could in fact be determined precisely by reduction to uranium(IV) at a gold-plated working electrode, but that the time required for the determination of fixed amounts of uranium under apparently identical conditions varied widely, in the worst cases becoming prohibitively long.

The variation in time required per determination was explicable by assuming that the electrode surface became increasingly "poisoned" with use, so that its effective area became less. In one particular instance it was shown that a molybdenum concentration less than 0·1 % of that of the uranium was sufficient to produce a very marked effect, under the conditions described above.

It was found that the gold surface could be cleaned by anodizing in dilute sulphuric acid, thus enabling the time of determination of uranium in fairly pure solutions to be kept near the minimum. In addition, trials with hydrochloric acid base electrolytes were made, and it became clear that the

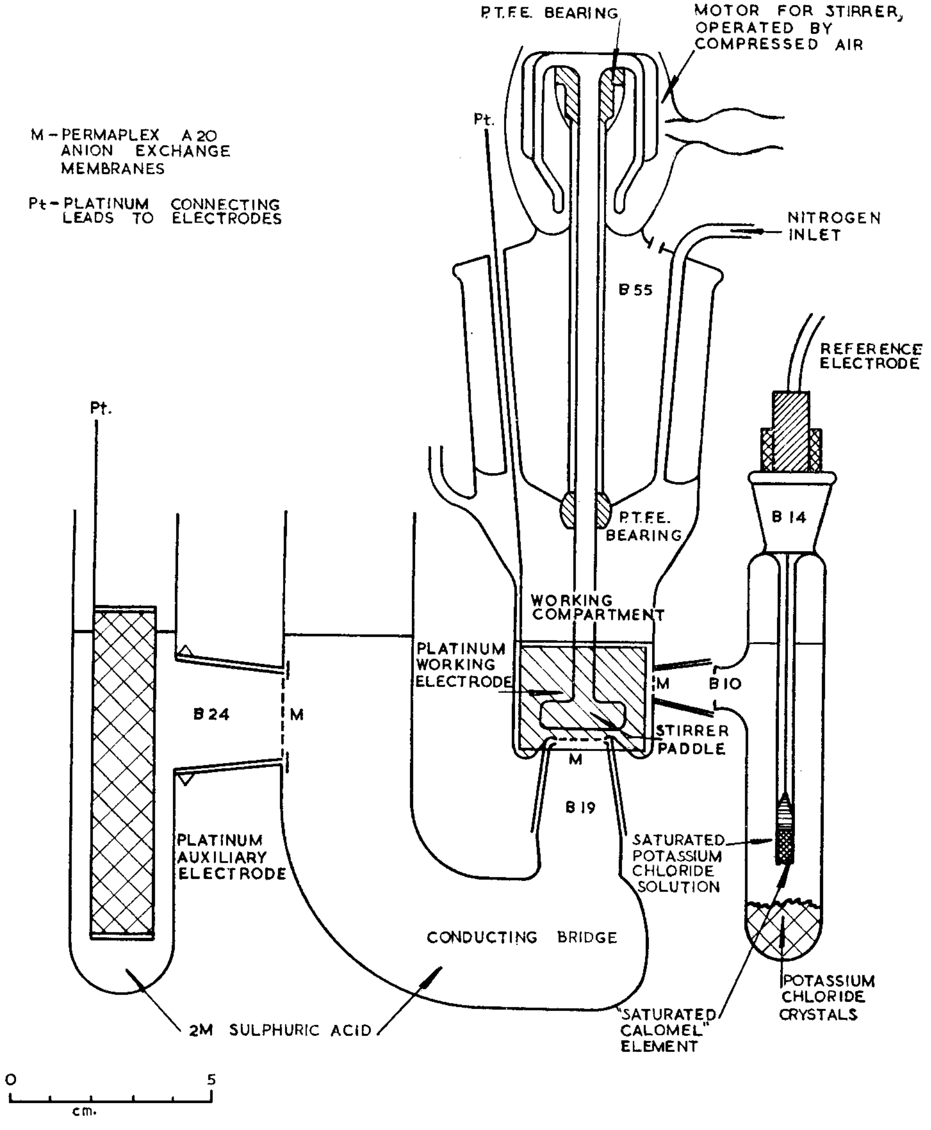


FIG. 1.—Diagram of coulometer cell.

electrode-poisoning effects were substantially less serious in hydrochloric acid than in sulphuric acid.

Application of the platinum working electrode. The combined effect of the anodizing pretreatment in dilute sulphuric acid and the use of 3*M* hydrochloric acid as base solution on the determination of uranium was so beneficial in the case of the gold electrode that it was decided to try the same procedure with a platinum working electrode.

It was shown to be practicable to reduce uranium(VI) to uranium(IV) quantitatively in either 1*M* or 3*M* hydrochloric acid, using a platinum electrode which had previously been anodized in 2*M* sulphuric acid, though the conditions for the avoidance of hydrogen evolution seemed more critical than with the gold cathode; also the minimum time required per determination was somewhat longer than with a gold electrode of the same apparent area.

Despite these drawbacks, the work on platinum electrodes was continued because it had become evident by this time that the gold-plated electrode would be unsuitable for use in a routine procedure, owing to difficulties in preparation and maintenance of the gold deposit.

Effects of foreign metal ions. The effects of foreign metals on the performance of a platinum working electrode in the reduction of uranium(VI) were systematically investigated. Because it seemed possible that optimum performance in previous trials might have depended on the presence of some metal impurity, desirable effects such as the suppression of hydrogen evolution were looked for as well as undesirable electrode-poisoning phenomena. The investigation covered those metals known to be present as impurities in the plutonium/uranium oxides and nitrates received for analysis, and also those easily reducible metals which could be electro-deposited at potentials near those used for the uranium reduction.

The first most important finding was the beneficial effect of copper. It was found that with the $3M$ hydrochloric acid base solution the presence of 1–2 mg of copper(I) per 20 ml could enable potentials as negative as $-0{\cdot}30$ V *vs.* S.C.E. to be used for the uranium reduction (compared with $-0{\cdot}15$ V without copper) without appreciable hydrogen evolution. [The addition of copper as copper(II) entailed a pre-reduction to a limit of $+0{\cdot}10$ V *vs.* S.C.E. to produce copper(I)]. This effect enabled uranium reductions to be performed more rapidly and rendered electrode-poisoning troubles less important. At $-0{\cdot}30$ V, the electrode was not quite negative enough to produce a visible deposit of copper metal.

In addition, it was shown that comparatively large amounts of iron(III), nickel(II), cobalt(II), chromium(III), copper(I) and cadmium(II) had little or no electrode-poisoning effect on a uranium reduction in $3M$ hydrochloric acid.

It was later found that the inhibition of hydrogen evolution at the platinum working electrode, already observed with copper(I), was also shown by lead, tin, antimony, arsenic and bismuth ions to varying extents. Metal ions which begin to electro-deposit at potentials slightly more negative than the desired working electrode potential promoted this inhibition most effectively, although no visible deposit was formed in use.

In some cases this beneficial action was more than outweighed by an electrode-poisoning effect which increased the time required for a uranium determination, and complications also arose when the metal ion had two or more oxidation states, especially when the redox systems behaved irreversibly.

Selection of bismuth(III) as additive. Of the metal ions studied, bismuth(III) appeared to be the most suitable to add to the base solution to improve the performance of the platinum electrode in the reduction of uranium. Bismuth was preferred to copper because of the absence of interfering oxidation states, and because the uranium(VI) reduction could proceed with the working electrode appreciably less negative in the presence of bismuth(III). As in the case of copper the addition of bismuth made electrode-poisoning effects less serious.

Base electrolyte composition. Because of the promising performance of a hydrochloric acid base solution with bismuth(III) added, in conjunction with the platinum electrode, the effects of varying the hydrochloric acid and bismuth concentrations were studied more closely. This work showed that neither concentration was very critical, but that $4{\cdot}5M$ was probably the optimum concentration of hydrochloric acid. Halving or doubling the concentration of bismuth finally chosen made little difference to the effectiveness of the bismuth.

Cell design. A substantial effort was devoted to optimizing the design of the coulometer cell. Importance was attached to making the ratio of area of electrode to solution volume as large as practicable, to keep the time required per determination as short as possible: this would minimize mechanical losses of the cell liquor by spray and through membranes, and the undesirable effects of background currents.

Before conditions for the reliable reduction of uranium(VI) were established, it was found very worthwhile to make use of the highly-reversible iron(II)/iron(III) system to evaluate the performance of experimental designs of cell.

Procedure for the coulometric determination of uranium in uranyl solutions

Reagents. Bismuth(III) solution, $0{\cdot}01M$. Add 20 ml of concentrated hydrochloric acid to 2·8 g of sodium bismuthate. Warm to dissolve, then boil the solution to expel chlorine, cool, and dilute to 1 litre with $4{\cdot}5M$ hydrochloric acid.

Hydrochloric acid, $4{\cdot}5M$.

Sulphamic acid, $1{\cdot}5M$.

Sulphuric acid, $2M$.

Method. Add about 10 ml of $4{\cdot}5M$ hydrochloric acid to the working compartment of the coulometer, followed by 1 ml of $1{\cdot}5M$ sulphamic acid and 1 ml of $0{\cdot}01M$ bismuth(III). Add the sample [not more than 5 ml in volume, containing 150–300 mg of uranium(VI) and less than 10 mmole of nitric acid], then dilute the cell contents to about 20 ml with $4{\cdot}5M$ hydrochloric acid, so that the electrode will just be covered by the solution.

With the working electrode in position, deaerate by passing nitrogen over the surface of the solution for 15 min while the solution is being stirred.

Reduce the solution, to a potential limit of $+0{\cdot}15$ V *vs.* S.C.E., until the current falls below

2 mA. [Any iron(III) and plutonium(IV) present are reduced to iron(II) and plutonium(III) respectively: for "pure" uranyl solutions this step takes less than 30 sec and less than 0·3 C are required.]

Reduce the solution, to a potential limit of −0·20 V *vs.* S.C.E., until the current falls below 2 mA. Note the number of coulombs required. [The total time required for the reduction of 200 mg of uranium(VI) to uranium(IV) is about 7 min: almost 95% of the uranium(VI) is reduced at the maximum available current of 512 mA and thereafter the current is halved about every 20 sec until it drops below 2 mA.]

Calculate the amount of uranium in the portion of sample added as follows:-

$$\begin{array}{c}\text{mg of uranium}\\ \text{in sample}\end{array} = G\left[\begin{array}{c}\text{coulombs required,}\\ \text{extrapolated}\\ \text{to zero current}\end{array} - \begin{array}{c}\text{blank}\\ \text{correction}\end{array}\right]$$

where G is the number of mg of uranium equivalent to 1 C (1·2335 for natural uranium).

When the current falls below 2 mA, the reaction is normally only 0·05–0·1 C short of completion. The blank correction is experimentally determined and normally amounts to about 0·2 C.

Anodizing the platinum working electrode. Cleaning the electrode surface by anodizing in sulphuric acid is essential. It is recommended that it should be carried out when the speed of a uranium(VI) reduction decreases to about one half that with a freshly anodized electrode, *i.e.*, after about eight determinations of uranium in "pure" uranyl nitrate solutions.

For the anodizing process, the cell is filled with 2*M* sulphuric acid, care being taken to exclude chloride, and a current of about 0·5 A passed for 5–10 min with the platinum working electrode acting as anode, so that oxygen is evolved. The cell and electrode are then washed thoroughly with water followed by 4·5*M* hydrochloric acid before use.

New electrodes should be ignited at red heat for a few minutes before the anodizing process.

DISCUSSION

Variations on the final procedure

Reoxidation of uranium(IV) to obtain a confirmatory value. This may be usefully carried out in the case of pure uranium solution samples by first adding 1 ml of 1*M* iron(III) (a ferric alum solution is suitable) to the cell contents and then oxidizing the mixture to a potential limit of +0·65 V *vs.* S.C.E.

When calculating the uranium content from the number of coulombs used in the oxidation step, allowance must be made for any iron found to be present in the sample in the pre-reduction step, the incompleteness of the uranium reduction step, and the oxidation step "blank." These corrections should be comparatively small.

Without the iron(III) addition, the coulometric oxidation of uranium(IV) to (VI) does not proceed sufficiently rapidly.

Successive determination of plutonium and uranium in the same sample. Although the basic method can be used satisfactorily for the successive determination of plutonium(IV) and uranium(VI), in practice it is the determination of "total"—*i.e.*, all oxidation states—plutonium and "total" uranium that is usually required for fuel solutions. Since the plutonium may not be all in a single oxidation state in the sample received, all the plutonium must first be reduced to plutonium(III). Shults[4] has discussed this in detail. The plutonium(III) thus obtained is coulometrically oxidized to plutonium(IV) to obtain one estimate of the total plutonium. A confirmatory estimate is obtained on reduction back to plutonium(III), which must be done before the uranium can be determined. [Uranium is all present as uranium(VI) in fuel solutions normally encountered.]

To make this sequence of events practicable it was found necessary to add sulphuric acid to the base electrolyte. This makes the formal potential of the plutonium(III)/plutonium(IV) more negative, owing to complexing of the plutonium(IV) by sulphate, and enables cycling between the plutonium oxidation states to be accomplished without attack of the working electrode during the oxidation step.

The recommended changes to the experimental conditions of the basic method, to enable plutonium and uranium to be determined successively, are as follows:

Replace the 4·5*M* hydrochloric acid reagent recommended in the basic procedure by a mixture of equal volumes of 4*M* hydrochloric acid and 2*M* sulphuric acid.

Reduce to a potential limit of +0·20 V *vs.* S.C.E. to convert all the plutonium into plutonium(III).

Oxidize to a potential limit of +0·80 V *vs.* S.C.E. to convert all the plutonium into plutonium(IV).

Repeat the reduction to +0·20 V to reconvert all the plutonium into plutonium(III).

Determine the uranium(VI) by reduction to a potential limit of −0·20 V *vs.* S.C.E. as before.

The effects of bismuth(III)

From the work on electrodeposition from extremely dilute solutions described by both Haissinsky[5] and Rogers *et al.*[6,7], it is known that the deposition of sub-monatomic layers of metals on platinum and other "inert" metal cathodes can occur at potentials appreciably more positive than those predicted by the version of the Nernst equation applicable to an electrode entirely covered with the metal being deposited. The potential chosen for the uranium(VI)–(IV) reduction is about 50 mV more positive than that required to deposit macro-amounts of bismuth metal, and it would seem that a similar sub-monatomic layer of bismuth could be formed on the platinum working electrode under the conditions selected for the uranium reduction. The platinum surface will be non-uniform to some extent at the microscopic and sub-microscopic levels, and it is likely that any bismuth which is deposited would first form a monatomic layer on the more reactive parts of the surface. It seems possible that this could provide the platinum electrode with protection against the occurrence of hydrogen evolution at its most vulnerable points by increasing the hydrogen overpotential at these locations. The same argument could of course be used to explain the inhibition of hydrogen evolution at the platinum electrode, caused by copper(I) and some of the other metal ions investigated.

It was also observed that the addition of bismuth or copper ions made electrode-surface poisoning effects less serious. This beneficial effect could be due to the formation of monatomic layers of bismuth or copper over some of the poisoned areas, thus increasing the usable surface area for the uranium(VI) reduction. [Comparative reductions of iron(III) and uranium(VI), made in the earlier work, indicated that it was possible for the same platinum surface to be apparently much more poisoned for the uranium(VI) reduction than for the iron(III) reduction. It seems feasible that a similar state of affairs might hold for the bismuth(III) and uranium(VI) reductions, enabling bismuth to be deposited on regions of the surface which were poisoned with respect to the uranium(VI) reduction.]

It is worth mentioning that bismuth(III) would not have the same effect in coulometric uranium reductions made in chloride-free perchloric, nitric or sulphuric acid base electrolytes. Macro-amounts of bismuth metal would electro-deposit from these base electrolytes at too positive a potential, *i.e.*, at about 0·0 V *vs.* S.C.E., interfering with the uranium(VI) reduction step. The usefulness of bismuth(III) in hydrochloric acid base electrolytes depends on the complexing of the bismuth(III) ion by chloride. This complexing shifts the potential at which macro-amounts of bismuth deposit, to the more negative values encountered in the procedure developed.

Interferences

A preliminary study indicated that appreciable amounts of phosphate, fluoride, molybdenum and mercury ions must be absent from the sample. Substantial amounts of iron, plutonium, nickel, cobalt, chromium(III), copper, cadmium, nitrate, sulphate, perchlorate and sulphamate ions may be present in the sample without effect on the uranium(VI) reduction in the final procedure.

Performance

Scrutiny of many past results from the analysis of uranium standard solutions showed that, for sample aliquots containing about 200 mg of uranium, the coefficient of variation applicable to a single determination is about 0·1 % under "development" conditions and about 0·2% under routine analysis conditions, and results have less than 0·1 % bias when the coulometer calibration is based on electrical measurements.

The procedure developed has been used successfully as a subsidiary method in the routine determination of uranium in pure uranyl nitrate solutions for uranium-accounting purposes during the past four years: several hundred samples have been analysed. A simplified controlled-potential-limit coulometer was employed for this routine work.

The amount of uranium taken and the cell design are important factors in determining the performance of the method. Under the recommended experimental conditions the "blank" correction needed amounts to less than 0·2% of the total number of coulombs used. If it was desired to scale down the procedure to enable much smaller amounts of uranium to be determined without undue loss of performance it would probably be necessary to decrease the cell volume while maintaining the electrode area : electrolyte volume ratio at the original value.

Zusammenfassung—Die experimentellen Bedingungen zur coulometrischen Bestimmung von Uran wurden ermittelt; man reduziert Uran(VI) zu Uran(IV) an einer Platin-Arbeitselektrode mit geregelter Spannung oder geregelter Grenzsapunnung. Dieses Verfahren wurde mit Erfolg als ergänzende Methode bei der Routinebestimmung von Uran in reinen Uranylnitratlösungen verwendet. Die Platinelektrode hat mehrere wichtige praktische Vorteile gegenüber der wohlbekannten Quecksilber-Sumpfelektode bei der coulometrischen Bestimmung von Uran. Die Bestimmungen von Eisen(III) und Uran(VI) oder von Plutonium(IV) und Uran(VI) nacheinander können mit derselben Arbeitselektrode in derselben Lösung ausgeführt werden; auch die coulometrische Oxidation von Uran(IV) zu Uran(VI) ist möglich. Die Rührgeschwindigkeit in der Zellflüssigkeit ist bei der Platinelektrode viel weniger kritisch. Zwei Hauptprobleme mußten gelöst werden, ehe ein praktisch verwertbares Verfahren zustande kam: die Wasserstoffentwicklung während der Reduktion mußte verhindert werden, damit die gewünschte Reaktion auf 100% Stromausbeute kam; ferner mußten Vergiftungserscheinungen der Elektrodenoberfläche unter Kontrolle gebracht werden, sodaß die Reaktionszeit hinreichend kurz gehalten werden konnte. Es zeigte sich, daß eine salzsaure Grundlösung mit ein wenig Wismut(III) die Wasserstoffentwicklung verhinderte; auch die Vergiftung der Elektrodenoberfläche war mit dieser Grundlösung nicht erheblich und ließ sich gering halten, wenn die Elektrode gelegentlich in verdünnter Schwefelsäure anodisch behandelt wurde. Wismut(III) bildet einen Komplex mit Chlorid; dessen Gegenwart erhöht die Wasserstoffüberspannung an der Arbeitselektrode. Während der Uranreduktion findet keine sichtbare Wismutabscheidung an der Elektrode statt. Nitrathaltige Lösungen können analysiert werden, wenn der salzsauren Grundlösung Amidosulfonsäure zugesetzt wird.

Résumé—On a établi les conditions expérimentales qui permettent la détermination coulométrique de l'uranium par réduction de l'uranium(VI) en uranium(IV) sur une électrode de travail en platine, par des techniques de potentiel contrôlé ou de limite de potentiel contrôlé. La

technique a été utilisée avec succès comme méthode subsidiaire dans le dosage de routine de l'uranium dans des solutions de nitrate d'uranyle pures. L'électrode de platine a plusieurs avantages pratiques importants sur l'électrode de masse de mercure bien établie pour le dosage coulométrique de l'uranium. La détermination consécutive des fer(III) et uranium(VI), ou plutonium(IV) et uranium(VI) peut être menée avec la même électrode de travail dans la même solution et l'oxydation coulométrique de l'uranium(IV) en uranium(VI) est réalisable. La vitesse d'agitation de la liqueur de la cellule est beaucoup moins critique dans le cas de l'électrode de platine. Deux problèmes principaux ont dû être surmontés avant qu'une technique pratique ne puisse être réalisée; le dégagement d'hydrogène durant la réduction U(VI)–U(IV) a dû être éliminé de sorte qu'une efficacité de courant de 100% puisse être obtenue pour la réaction désirée, et les phénomènes d'empoisonnement de la surface d'électrode ont dû être contrôlés de sorte que le temps de réaction puisse être maintenu raisonnablement court. On a trouvé que la sélection d'une solution de base d'acide chlorhydrique contenant une petite quantité de bismuth(III) permet d'éviter le dégagement d'hydrogène: également, l'empoisonnement de la surface d'électrode avec cette solution de base n'est pas particulièrement sérieux et peut être maintenu à un bas niveau satisfaisant en anodisant occasionnellement l'électrode en acide sulfurique dilué. Le bismuth(III) forme un complexe avec les ions chlorure et sa présence accroît la surtension de l'hydrogène à l'électrode de travail: il ne se forme pas de dépôt visible de bismuth sur l'électrode durant la réduction de l'uranium. On peut analyser des échantillons contenant du nitrate, étant entendu que l'on ajoute de l'acide sulfamique à cette solution de base d'acide chlorhydrique.

REFERENCES

1. G. L. Booman and W. B. Holbrook, *Anal. Chem.*, 1959, **31,** 10.
2. G. C. Goode, J. Herrington and G. Hall, *Anal. Chim. Acta*, 1964, **30,** 109.
3. I. J. McColm, V. M. Sinclair and R. S. Roche, *Talanta*, 1963, **10,** 387.
4. W. D. Shults, *ibid.*, 1963, **10,** 833.
5. M. Haissinsky, *Z. Elektrochem.*, 1955, **59,** 750.
6. L. B. Rogers and A. F. Stehney, *J. Electrochem. Soc.*, 1949, **95,** 25.
7. L. B. Rogers, D. P. Krause, J. C. Griess and D. B. Ehrlinger, *ibid.*, 1949, **95,** 33.

Talanta, 1970, Vol. 17, pp. 945 to 953. Pergamon Press. Printed in Northern Ireland

AMPEROMETRIC COMPLEX-FORMATION TITRATIONS OF TRACES OF COPPER

F. Freese, H. J. Jasper and G. den Boef
Laboratory for Analytical Chemistry, University of Amsterdam, The Netherlands

(*Received* 17 *February* 1970. *Accepted* 17 *April* 1970)

Summary—Copper has been determined in the submicrogram range by means of a complexometric titration with triethylenetetramine (TRIEN), the end-point being detected by following the anodic wave of the chelating agent at a rotating mercury electrode. The influence of the presence of other metals has been investigated both from the theoretical and the experimental point of view. Because of its higher selectivity TRIEN is preferred to other reagents of the EDTA group. The results show that copper can be determined in the presence of large amounts of most other metals.

In a preliminary communication[1] the principles of the amperometric complex-formation titration of metal ions with indication by means of the anodic wave of the excess of ligand, have been presented. The work of Campbell and Reilley,[2] who used a dropping mercury electrode, can be extended to a higher sensitivity by using a rotating mercury electrode as the indicator electrode. In the present paper the theoretical background of this type of titration will be treated more thoroughly. The theory will be illustrated by the determination ofcopper(II)with triethylentetramine (TRIEN).

THEORETICAL

Titration curves

Considering the titration reaction

$$\mathrm{M} + \mathrm{L} \rightleftharpoons \mathrm{ML}$$

we suppose that changes in volume will be negligible and define $f = c_\mathrm{L}/c_\mathrm{M}$ as the titration parameter, which is a measure of the progress of the titration, having the value $f_\mathrm{e} = 1$ at the equivalence point.

The formula for the titration curve can be derived from

$$K_\mathrm{M}' = \frac{[\mathrm{ML}]'}{[\mathrm{M}]'[\mathrm{L}]'} \tag{1}$$

$$c_\mathrm{M} = [\mathrm{M}]' + [\mathrm{ML}]' \tag{2}$$

$$f = \frac{c_\mathrm{L}}{c_\mathrm{M}} = \frac{[\mathrm{L}]' + [\mathrm{ML}]'}{[\mathrm{M}]' + [\mathrm{ML}]'}\,. \tag{3}$$

Concentrations are primed according to Ringbom,[3] so that all side-reactions are taken into account, K_M' being the conditional constant.

In order to facilitate the handling of these formulae, we propose the use of relative concentrations, dimensionless numbers, defined as

$$m = \frac{[\mathrm{M}]'}{c_\mathrm{M}}\,; \qquad l = \frac{[\mathrm{L}]'}{c_\mathrm{M}}\,; \qquad ml = \frac{[\mathrm{ML}]'}{c_\mathrm{M}}\,.$$

The equations (1), (2) and (3) can now be written as

$$Z_M = K_M'c_M = \frac{ml}{m\,.\,l} \tag{4}$$

$$1 = m + ml \tag{5}$$

$$f = l + ml. \tag{6}$$

Z_M is another dimensionless quantity in which the effects of the analytical concentration of M and the conditional stability constant are combined.

As the experimental part of this paper describes titrations with monitoring of the ligand L, it is useful to find f as a function of l. The titration curve can easily be derived from (4), (5) and (6):

$$f = l + \frac{Z_M l}{1 + Z_M l} = f_1 + f_2. \tag{7}$$

So for the graphical construction of f as a function of l we have to add the linear $f_1 = l$ and the orthogonal hyperbola $f_2 = (Z_M l/1 + Z_M l)$, illustrated in Fig. 1.

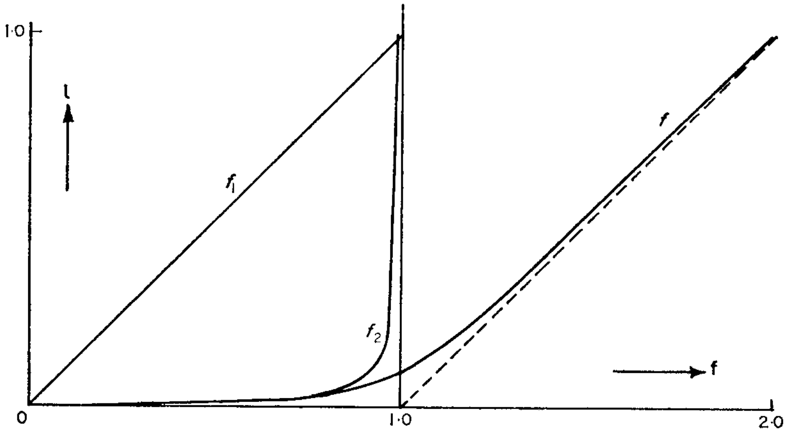


FIG. 1.—l-f curve:

$$f = f_1 + f_2 = l + \frac{Zl}{1 + Zl} \quad \text{for} \quad Z = 100.$$

It is obvious that the shape of the (f–l)-curve and the (f–[L])-curve will be identical. For the calculation of the titration error we will assume that the end-point of the titration will be found graphically by intersecting the tangents for $l = 0$ and $l = 1$ (Fig. 1). As $df/dl = 1 + Z_M/(1 + Z_M l)^2$, these tangents are given by:

$$f = \left(\frac{df}{dl}\right)_0 l = (1 + Z_M)l \sim Z_M l \tag{8}$$

and

$$f = \left(\frac{df}{dl}\right)_1 (l - 1) + f_1,$$

where f_1 is the value of f in the titration curve (7) for $l = 1$, or

$$f = \left\{1 + \frac{Z_M}{(1 + Z_M)^2}\right\}(l - 1) + 1 + \frac{Z_M}{1 + Z_M}$$

which for $Z_M \gg 1$ simplifies to

$$f \sim \left\{1 + \frac{1}{Z_M}\right\} l + 1 - \frac{2}{Z_M}. \tag{9}$$

The tangents (8) and (9) intersect in f_s. It can easily be found that $f_s = 1 - 1/Z_M$. The systematic titration error is therefore,

$$\Delta = -\frac{1}{Z_M}. \tag{10}$$

In earlier work[4] it has been suggested to take $1/\sqrt{Z_M} = m_{f=1} = l_{f=1}$ as a measure of the sharpness. As $1/Z_M$ is directly related to the systematic titration error we propose to use this value as the measure of sharpness. If we accept a systematic error of 1% the value of $Z_M = K'c_M$ has to be greater than 100.

Titration of mixtures of metals

The titration curve for the complexometric titration of two metals M and N has been derived in a previous paper. When the metal N is considered to be an interfering metal it is better to use $f = c_L/c_M$ instead of $f = c_L/(c_M + c_N)$ as was done in the previous paper.[5] With introduction as before of the relative concentration $n = [N]'/c_M$, the titration curve will, in the new notation, change to

$$f = l + \frac{Z_M l}{1 + Z_M l} + \frac{c_N}{c_M} \cdot \frac{Z_N l}{(1 + Z_N l)} \tag{11}$$

$$= f_1 + f_2 + f_3. \tag{12}$$

As we consider the metal N as an interference in the titration of M the complex NL will be much weaker than ML. The titration curve will only have the required linear shape when f_3 is pseudolinear. If we accept a deviation from linearity of 1% we can consider f_3 to be pseudolinear if

$$Z_N l \leqslant 10^{-2}. \tag{13}$$

We can then write (11) as

$$f = (1 + K_N' c_N) l + \frac{Z_M l}{1 + Z_m l}. \tag{14}$$

The factor $(1 + K_N' c_N)$ is the side-reaction coefficient of the side-reaction of L caused by the presence of N. Taking into account this side-reaction coefficient $\alpha_{L(N)}$ in Z_M, equation (14) can be written as

$$f = l' + \frac{Z_M' l'}{1 + Z_M' l'} \tag{15}$$

in which $l' = (1 + K_N' c_N) l = \alpha_{L(N)} l$
and

$$Z_M' = \frac{Z_M}{\alpha_{L(N)}}.$$

The new sharpness criterion will be

$$Z_M' = \frac{K_M' c_M}{1 + K_N' c_N} \geqslant 100. \tag{16}$$

The largest value of l' in practical work will be $l' = 1$. The largest value of l therefore will be

$$l = \frac{1}{1 + K_N' c_N} \, .$$

Substitution in equation (13) leads to the condition for linearity

$$Z_N l = \frac{K_N' c_M}{1 + K_N' c_N} \leqslant 10^{-2}. \tag{17}$$

The presence of the interfering metal N causes a decrease in the slope of the titration curve after the equivalence point by a factor $\alpha_{L(N)}$ and therefore a decrease in the sensitivity of the determination of M. In trace determinations of M we will often work near the limit of sensitivity of the indication system, in which case only a relatively small reduction of the slope can be tolerated.

When a reduction of 50% in the slope is allowed, we get the condition

$$K_N' c_N \leqslant 1 \tag{18}$$

and when a decrease of sensitivity by a factor n can be allowed, the sensitivity condition becomes

$$K_N' c_N \leqslant (n - 1). \tag{19}$$

Recapitulating, we may conclude that the titration of M in the presence of a metal N can be carried out when three conditions are fulfilled, a sharpness criterion, *cf.* equation (16), a condition for linearity, *cf.* equation (17) and a sensitivity condition, mentioned in equation (19).

Up to now we have supposed that the indication signal was perfectly linear in l. In the titrations that will be described the linearity is limited to values of l smaller than 0·1.

It can easily be shown that drawing the tangent at $l = 0{\cdot}1$ will change the sharpness condition to

$$Z_M' = \frac{K_M' c_M}{1 + K_N' c_N} \geqslant 2 \times 10^3 \tag{20}$$

and the linearity condition to

$$\frac{K_N' c_M}{1 + K_N' c_N} \leqslant 10^{-1}. \tag{21}$$

The sensitivity condition, *cf.* equation (19) remains unaltered. The conditions derived above for a sharp indication can only be applied under equilibrium conditions. At low concentrations the conditions for sharp end-points will sometimes be kinetically determined. As our knowledge of the complex-formation and the corresponding stability constants is still incomplete, predictions may sometimes fail.

Anodic indication of L

The reaction at the indicator electrode used for the indication of the excess of ligand is the oxidation of mercury from the electrode according to the reaction

$$Hg^0 + L - 2e \rightarrow HgL$$

The equation of the corresponding reversible polarographic wave at an ordinary DME is

$$E_L = E_0 - 0{\cdot}03 \log K_{HgL} + 0{\cdot}03 \log \alpha_{L(N)} + 0{\cdot}03 \log \frac{\bar{k}_L}{k_{HgL}} + 0{\cdot}03 \log \frac{i}{i_d - i} \quad (22)$$

The ligand will be present as a mixture of several protonated forms. In equation (21) it is assumed that all these forms have the same diffusion coefficient $\bar{k}_L$. The limiting current i_d will be proportional to the sum of the concentrations of all these forms.

The useful potential range for the indication can be found by comparing the wave of the free ligand [equation (22)] with the current–voltage curve for the anodic dissolution of mercury in the absence of the free ligand, which can be represented by

$$E_{Hg} = E_0 - 0{\cdot}03 \log \alpha_{Hg} - 0{\cdot}03 \log \bar{k}_{Hg} + 0{\cdot}03 \log i \quad (23)$$

where α_{Hg} is the side-reaction coefficient taking into account all side-reactions of mercury(II) with the exception of the reaction between mercury(II) and L.

Two possible current voltage curves are given in Fig. 2. The suitable potential range ΔE can be found by subtracting E_L from E_{Hg} for a suitable value of i. We then get

$$\Delta E = E_{Hg} - E_L = 0{\cdot}03 \log K_{HgL} - 0{\cdot}03 \log \alpha_{L(H)} - 0{\cdot}03 \log \alpha_{Hg} + 0{\cdot}03 \log \frac{k_{HgL}}{\bar{k}_{Hg}\bar{k}_L} + 0{\cdot}03 \log (i_d - i)$$

$$\Delta E = 0{\cdot}03 \log K'_{HgL} + 0{\cdot}03 \log \frac{k_{HgL}}{\bar{k}_{Hg}\bar{k}_L} + 0{\cdot}03 \log (i_d - i). \quad (24)$$

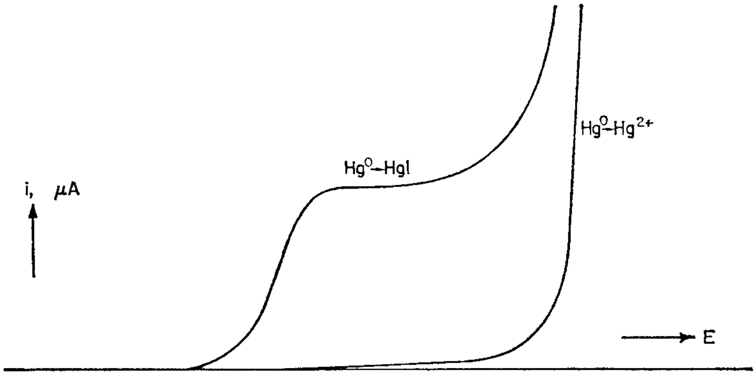


FIG. 2.—Anodic dissolution wave of mercury in the presence and in the absence of the ligand.

The result, as could be expected, is that the useful potential range is directly related to the conditional constant K'_{HgL} of the complex HgL.

The main advantages of anodic amperometry for indication in complexometry are that the method can be used for the titration of nearly all metal ions giving stable complexes, independent of the cathodic behaviour, and the possibility of using a working potential more positive than the half-wave potential of the first reduction wave of oxygen. Reilley and Campbell[2] have given a table of the potential ranges for anodic amperometry in several buffered media.

A rotating mercury electrode has the advantage over a dropping electrode that currents are appreciably larger, that no capacity currents occur, and that there are no current fluctuations due to the growth and fall of the drop. These effects result in a lower limit of determination.

The useful potential range has been discussed above on the basis of reversibility of the reaction at the electrode. However, reactions reversible at the DME might be irreversible at a rotating mercury electrode. In general it can be stated that polarograms at the rotating mercury electrode are not as well developed as at the DME. Moreover the shape of the polarograms depends on the condition of the mercury electrode. Especially when an acid solution is used, a diffusion plateau can hardly be observed. In these and a number of other cases a working potential has to be chosen in a rising part of the current–voltage curve of the free ligand.

As part of the applied voltage is lost in the *iR*-drop, which is not constant, but rises after the end-point of the titration, the potential of the mercury anode shifts to more negative values, resulting in a deviation of the titration curve from linearity. The ascending part of the titration curve bends towards the *f*-axis, as illustrated in Fig. 3. This is the reason why the titrations at a rotating mercury electrode are generally not carried further than to about 10% beyond the end-point.

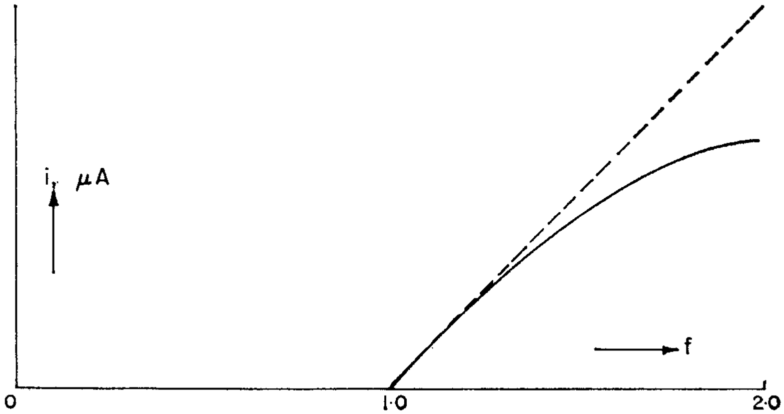


FIG. 3.—Effect of *IR*-drop on indication current after the end-point.

EXPERIMENTAL

Chemicals

Pro analysi chemicals were used. Impurities in the bufier solutions were determined by means of a blank titration. The water used was singly distilled and traces of copper still present were removed by ion-exchange.

Apparatus

Polarograms necessary for the selection of the suitable potential of the indicator electrode were registered with the Metrohm polarograph E 261, using the rotating electrode as working electrode. The titrations were performed in a 10-ml compartment of an H-cell, containing the rotating mercury electrode. The titrant was added from a Metrohm 1-ml syringe burette. The other compartment of the H-cell, separated from the first by a fritted glass disc, was filled with the same supporting electrolyte solution as was the titration compartment, and contained a calomel electrode.

The amperometric titrations were carried out by means of a simple polarographic circuit with a Philips d.c. microammeter PM 2436 for current measurements. As this meter has a higher sensitivity than the polarograph it was preferred for the titrations of low concentrations.

The rotating mercury electrode (750 rpm) consisted of a small piece of platinum wire (25 mm length; 0·75 mm diameter) sealed into glass. The platinum microelectrode is covered with mercury, either by direct electrolysis in a mercury(I) nitrate solution for 1 hr at a current of 10 mA, or by successive electrolyses in a solution of a gold(III) salt and a mercury(I) nitrate solution, both for 1 hr at a current of 10 mA. The electrodes last for a few weeks, after which the mercury layer has to be renewed.

RESULTS

TRIEN was preferred for the determination of copper(II) because of the high value of the stability constant of the complex and the relatively high selectivity compared with the polyaminopolycarboxylic acids. In general, titrations of copper(II) in acid solution are preferred because of the higher selectivity. Determinations in alkaline solution in the presence of other metals will generally require masking. However the anodic wave of TRIEN in a tris-buffer [tris(hydroxymethyl)methylamine] in alkaline solution at pH 9 is much better developed than in acid solution, so that a number of determinations have been carried out at this pH.

For the determinations in acid solution a pH-value of 5 was chosen. At pH 5 $\log K'_{\mathrm{CuL}} = 9{\cdot}4$. According to equation (18) the limit of determination would be somewhat less than $10^{-6}M$.

In Table I some results are given for determinations of copper(II) in $0{\cdot}01M$ acetate buffer at pH 5. The results agree very well with the theoretical predictions.

In Table II some results are given for determinations of $6 \times 10^{-6}M$ copper(II) in the presence of other metals, and in Table III the corresponding results are given for $6 \times 10^{-7}M$ copper(II). The buffer concentration was $0{\cdot}01M$ in all cases.

The amounts of other metals present, mentioned in Tables II and III, are about the maximum allowable limits found experimentally. The interference of more than 1000-fold amounts of metals such as nickel(II), zinc(II) and cadmium(II) can be explained by means of equation (17) derived in the theoretical part.

At pH 5, $\log K'_{\mathrm{NiL}} = 3{\cdot}0$, so when $c_{\mathrm{Ni}} = 6 \times 10^{-3}M$ as in the first experiment of Table II, the product $K'_{\mathrm{NiL}} \cdot c_{\mathrm{Ni}} = 6$ which is not in agreement with condition (18). In this experiment the decrease of the slope after the equivalence point was indeed more than 50%. The maximum allowable amounts of zinc(II), cadmium(II) and cobalt(II)

TABLE I.—DETERMINATION OF Cu(II) WITH TRIEN IN $0{\cdot}01M$ ACETATE BUFFER AT pH 5, VOLUME 5 ml

Cu(II)			Error	Std. devn., %	Titrant concentration
	Amount, μg				
Concentration	Present	Found	%	(no. of detns.)	M
6×10^{-6}	1·90	1·91	0·5	1·3 (8)	10^{-4}
6×10^{-7}	0·190	0·188	−2	1·3 (8)	10^{-5}
6×10^{-8}	0·019	0·021	+10	20 (8)	10^{-6}

TABLE II.—DETERMINATION OF 1·9 μg OF Cu(II) WITH $10^{-4}M$ TRIEN; VOLUME 5 ml

Amount of other metal relative to that of copper		Error, %	Std. devn., % (no. of detns.)	Buffer, masking
Ni	1000	−1·7	1·3(8)	acetate pH 5
Zn	1000	0·0	1·3(8)	acetate pH 5
Cd	1000	−1·2	0·7(8)	acetate pH 6
Cr(III)	1000	−0·6	1·0(8)	acetate pH 6
Pb	10000	0·0	0·6(8)	acetate pH 5
Pb	100000	+2·2	0·7(8)	acetate pH 5
Co	10000	−1·3	1·0(8)	acetate pH 5
Mg	100000	−1·0	1·3(8)	acetate pH 6
Mn(II)	100000	+0·6	0·7(8)	acetate pH 6
Ca	100000	+2·2	1·0(8)	acetate pH 6
Zn	100	−0·6	1·0(8)	Tris pH 9, $10^{-3}M$ NTA
Pb	1000	+1·2	2·0(8)	Tris pH 9, $10^{-3}M$ NTA
Mg	10000	−1·2	1·0(8)	Tris pH 9
Fe(III)	1000	+2·2	1·0(8)	Tris pH 9, citrate
Fe(III)	1000	0·0	0·3(8)	Tris pH 9, oxalate + NTA
Al 1000 + Fe(III) 1000		−0·6	0·7(8)	Tris pH 9, oxalate + NTA

TABLE III.—DETERMINATION OF 0·19 μg OF Cu(II) WITH $10^{-5}M$ TRIEN: VOLUME 5 ml

Amount of other metal relative to that of copper		Error, %	Std. devn., % (no. of detns.)	Buffer, masking
Ca	100000	−0·6	4·0(8)	acetate pH 6
Pb	100000	+4·5	3·3(8)	acetate pH 6
Mg	100000	+2·0	3·7(8)	acetate pH 6
Cd	100000	−1·0	3·7(8)	acetate pH 6
Mn	100000	−2·7	2·0(8)	acetate pH 6
Co	100000	−5·4	7·0(8)	acetate pH 6
Zn	1000	−8·0	3·3(6)	acetate pH 6
Zn	500	−3·3	3·7(8)	acetate pH 6
Ni	1000	+5·0	7·7(4)	acetate pH 6
Ni	200	−1·4	1·3(8)	acetate pH 6
Al	10000	+6·0	4·0(8)	Tris pH 9, oxalate + NTA
Fe(III)	1000	+8·0	2·7(8)	Tris pH 9, oxalate + NTA

TABLE IV.—TITRATION OF 1·9 μg OF Cu(II) ($6 \times 10^{-6}M$) WITH $10^{-4}M$ TRIEN; VOLUME 5 ml

Interference	Error, %	Std. devn., %	Buffer solution
0·01M chloride	−0·7	0·7	0·01M acetate, pH 6
1M chloride	+2·2	1·0	0·8M Tris, pH 9
0·01M bromide	+2·6	0·7	0·01M Tris, pH 9

Note: The time required for all titrations mentioned above is only a few minutes for each.

can be roughly explained in the same manner. The condition given by equation (20) is fulfilled in all experiments mentioned in Tables II and III.

In some cases sample solutions may contain compounds forming complexes with mercury(II), resulting in a current during the whole titration. When such a current is small, titrations can be carried out when the interfering current is electrically compensated. In this way it is possible to carry out the titrations of copper(II) with TRIEN as mentioned above, even in the presence of large amounts of chloride and bromide. Table IV shows some results of such titrations.

Zusammenfassung—Kupfer wurde im Submikrogrammbereich durch komplexometrische Titration mit Triäthylentetramin (TRIEN) bestimmt. Der Endpunkt wurde durch Beobachtung der anodischen Stufe des Chelatbildners an einer rotierenden Quecksilberelektrode ermittelt. Der Einfluss anderer Metalle wurde vom theoretischen und experimentellen Standpunkt aus untersucht. Wegen seiner höheren Selektivität ist TRIEN anderen Reagentien aus der EDTA-Gruppe vorzuziehen. Die Ergebnisse zeigen, dass Kupfer in Gegenwart grosser Mengen der meisten anderen Metalle bestimmt werden kann.

Résumé—On a dosé le cuivre dans le domaine du submicrogramme au moyen d'un titrage complexométrique avec la triéthylènetétramine (TRIEN), le point de fin de dosage étant détecté en suivant la vague anodique de l'agent chelatant sur une électrode de mercure rotative. On a étudié l'influence de la présence d'autres métaux, tant du point de vue théorique qu'expérimental. A cause de sa plus haute sélectivité, on préfère le TRIEN aux autres réactifs du groupe EDTA. Les résultats montrent que l'on peut doser le cuivre en la présence de grandes quantités de la plupart des autres métaux.

REFERENCES

1. F. Freese and G. den Boef, *Talanta*, 1966, **13**, 865.
2. R. T. Campbell and C. N. Reilley, *ibid.*, 1962, **9**, 153.
3. A. Ringbom, *Complexation in Analytical Chemistry*. Interscience, New York, 1963.
4. M. Tanaka and G. Nakagawa, *Anal. Chim. Acta*, 1965, **32**, 123.
5. U. Hannema and G. den Boef, *ibid.*, 1967, **39**, 167.

Talanta, 1970, Vol. 17, pp. 955 to 963. Pergamon Press. Printed in Northern Ireland

SILICA GEL AS A SUPPORT FOR INORGANIC ION-EXCHANGERS FOR THE DETERMINATION OF CAESIUM-137 IN NATURAL WATERS

KIKUO TERADA, HIRONOBU HAYAKAWA, KIYOSHI SAWADA and TOSHIYASU KIBA
Department of Chemistry, Faculty of Science, Kanazawa University,
Kanazawa, Japan

(*Received* 3 *October* 1969. *Revised* 24 *April* 1970. *Accepted* 8 *May* 1970)

Summary—The preparation and characteristics of ammonium molybdophosphate and potassium or ammonium hexacyanocobalt ferrate supported in silica gel, and their application to the determination of ^{137}Cs in natural waters are described. Use of columns of these materials gives better recovery of ^{137}Cs from natural waters (in comparison with co-precipitation with ammonium molybdophosphate), requires less exchanger, so raising the γ-counting efficiency of ^{137}Cs, and permits elimination of other radionuclides by washing with hydrofluoric acid.

SINCE Smit[1] revealed the excellent ion-exchange properties of ammonium molybdophosphate, especially for potassium, rubidium, caesium, silver, mercury(I) and thallium(I), this exchanger has been used for the separation of alkali metals and especially for the radiochemical determination of ^{137}Cs in biological materials, natural waters, sea-water, *etc*,[2–5] but recovery of caesium from sea-water was only 70–80% in large-scale operations.[4,5] If an appropriate column method is available, ^{137}Cs can be concentrated from large volumes of natural waters more efficiently and conveniently. Smit has proposed a column consisting of a physical mixture of the heteropoly acid salt and asbestos fibre[6,7] or filter paper pulp,[8] and of coarse particles of the insoluble ammonium salt of 12-molybdophosphate (AMP),[9] because asbestos or filter paper pulp would reduce the bed capacity per unit volume. The difficulty was to prepare the coarse AMP since it was usually accompanied by a substantial proportion of very fine crystals.

Prout, Russel and Groh[10] have recently described potassium hexacyanocobalt ferrate (KCFC) as an inorganic exchanger and the material was employed by Boni[11] to concentrate radiocaesium from biological and environmental samples such as milk, urine, sea-water and fresh water. Petrow and Levine[12] have recommended ammonium hexacyanocobalt ferrate (NCFC) as an improved exchange material for radiocaesium, because the ammonium salt can obviate the interference by the decay of the potassium in KCFC, in the ^{137}Cs region of the γ-spectrum.

The lack of any satisfactory procedure for elution of the adsorbed caesium made it impossible to reduce the volume of the counting sample and to raise the counting efficiency for γ-activity with an NaI crystal detector. Moreover, a large amount of exchanger had to be thrown away after only one use, since a simple regeneration procedure had not been found. A more convenient material for enrichment of ^{137}Cs from large volumes of natural waters would therefore be desirable.

The present paper describes a simple method of preparing such materials, which will be called AMP-SiO$_2$, KCFC-SiO$_2$ or NCFC-SiO$_2$, and their successful application to natural waters, including sea-water.

EXPERIMENTAL

Reagents

Radioactive nuclides. Caesium-137 as caesium chloride, and cerium-144, cobalt-60, ruthenium-106, strontium-90, zinc-65 and zirconium-95.

Silica gel. Chromatographic grade (WAKOGEL C-100).

Other chemicals. Caesium sulphate used as carrier was of guaranteed reagent-grade, and ammonium molybdate, ammonium monohydrogen phosphate, ammonium nitrate, nitric acid, sodium hexacyanoferrate, potassium hexacyanoferrate and cobalt(II) nitrate were of chemically pure reagent-grade.

Apparatus

Scintillation counter. Well-type, with 45 × 50 mm NaI(Tl) crystal.

G-M counter. Mica-window tube, 28 mg/mm^2, 11·7% counting efficiency for ^{90}Sr(^{90}Y).

γ-Ray spectrometer. Low-background model with transistorized single-channel pulse-height analyser, high-speed scaler and printing scaler.

Glass chromatographic columns. Internal diameter 9·8, 12 and 17 mm, length 140 mm, with a coarse sintered-glass disc and a stop-cock at the bottom.

Preparation of AMP-SiO$_2$

About 240 g of silica gel (42–60, 60–80 and 80–100 mesh) were put into a solution of 100 g of ammonium molybdate and 6 g of ammonium monohydrogen phosphate in 400 ml of distilled water and stirred occasionally. After standing for about 2 hr the contents were heated in an electric air-bath at 105° for a day. The dried material was transferred into a beaker containing a solution of 10 g of ammonium nitrate in 300 ml of 3*M* nitric acid and heated to about 80° on a hot water-bath (with occasional stirring) and digested at that temperature for 3 hr, then the mixture was filtered (coarse cotton cloth spread over a 2-l. beaker) and the residue was washed with distilled water to remove free AMP as thoroughly as possible. The material was transferred on the cloth to a Buchner funnel and covered with another piece of cloth, and was left under suction till almost dry. Finally, the dried material was heated at about 105° for a day and was sieved into 42–60, 60–80 and 80–100 mesh fractions.

Preparation of KCFC-SiO$_2$

About 100 g of silica gel (42–60 and 60–80 mesh) were put into a beaker containing about 200 ml of 0·5*M* potassium hexacyanoferrate and stirred occasionally. After standing for about 2 hr the supernatant liquid was decanted. The impregnated silica gel was then transferred (glass spoon) into a beaker containing about 500 ml of 0·3*M* cobalt(II) nitrate solution, with continuous stirring. A dark green precipitate appeared immediately on the surface of the silica gel. The contents of the beaker were stood for about 2 hr with occasional stirring, then the supernatant liquid and free KCFC were poured off and the remaining KCFC-SiO$_2$ was washed with distilled water; this treatment was repeated until the supernatant liquid became clear. Finally, the product was dried at 115° in an electric air-bath for about 20 hr until it changed colour to purple. The product was sieved (42–60 and 60–80 mesh) and stored in polyethylene bottles.

Preparation of NCFC-SiO$_2$

About 100 g of silica gel (42–80 mesh) were put into a beaker containing about 200 ml of 0·5*M* sodium hexacyanoferrate solution, with occasional stirring. After standing for about 2 hr the supernatant liquid was decanted. The impregnated silica gel was transferred (glass spoon) into a beaker containing about 500 ml of 0·3*M* cobalt nitrate in 0·1*M* ammonium nitrate solution, with continuous stirring. The contents were then treated in the same way as KCFC-SiO$_2$.

Ion-exchange column preparation

The chromatographic tube was filled with a water slurry of 10 g of water-washed 60–80 mesh exchange material. A piece of absorbent cotton was placed on top of the material so that the bed was not disturbed during sample addition. The cotton should be changed several times if a sample contains suspended matter.

Procedure for the determination of ^{137}Cs in a large volume of sample

A volume of water sample to which had been added 70 μg (15 μg for KCFC- or NCFC-SiO$_2$) of Cs$^+$ as carrier and about 1 ml of nitric acid per litre to keep strontium in solution, was passed through the column at a flow-rate of 6–8 l./hr under slight suction from a water-pump, and the effluent was stored in a polyethylene bottle for strontium-90 measurement.

After all the sample had passed through the column, the cotton plug was removed and most of the exchanger was pushed out of the column under air-pressure, then the rest was washed out with a small amount of distilled water. The exchanger was collected in a 50-ml polyethylene centrifuge tube. The water was decanted and *ca.* 30 ml of 46% hydrofluoric acid were added dropwise with occasional shaking. After complete dissolution of the silica the tube was centrifuged for about 20 min at 3000 rpm. The supernatant liquid was rejected and the residue was washed with distilled water and centrifuged twice more. The final residue was transferred with a small amount of ethyl alcohol into a shallow plastic dish having a cover (i.d. *ca.* 60 mm) and was dried under an infrared lamp; its γ-activity was counted with a low-background γ-ray spectrometer.

RESULTS AND DISCUSSION

Characteristics of the exchange materials

AMP-SiO$_2$. The amount of AMP on the silica gel was calculated from the phosphorus content, determined spectrophotometrically as molybdenum blue after dissolution of the AMP in aqueous ammonia (1 + 9). The results obtained are shown in Table I. The increase in loading as the particle-size decreases is probably due to the increase in surface area.

TABLE I.—CHARACTERISTICS OF THE EXCHANGE MATERIALS

Material (M)	Mesh size	M supported, *g* of M/*g* of M-SiO$_2$	Exchange capacity, *mequiv* of Cs/*g* of M-SiO$_2$	Max. flow-rate, *l./hr*
AMP-SiO$_2$	42–60	0·113	0·069 (9·5 mg)	9·0
	60–80	0·187	0·079 (10·8 mg)	7·2
	80–100	0·204	0·101 (13·8 mg)	2·5
KCFC-SiO$_2$	42–60	0·025	0·014 (1·9 mg)	11·5
	60–80	0·029	0·019 (2·6 mg)	8·6
NCFC-SiO$_2$	60–80	0·028	0·018 (2·5 mg)	8·1

The exchange capacity for caesium was measured by passing 100 ml of sea-water, containing about 1·7 mequiv of caesium sulphate, ^{137}Cs tracer and 0·1 ml of nitric acid, at 1 drop/min through a column containing 2 g of the material, dissolving the exchanger with 10 ml of 5*M* sodium hydroxide and heating, making up to standard volume and measuring the γ-activity of an aliquot with a well-type scintillation counter.

KCFC-SiO$_2$ or NCFC-SiO$_2$. The amount of KCFC or NCFC supported on silica gel (Table I) was calculated from the cobalt, iron and potassium or ammonium content of the materials, after removal of silica with hydrofluoric and sulphuric acids. Iron was determined as iron(III) oxide after extraction with IBMK–pentyl acetate solvent mixture, and cobalt as cobalt(III) oxide after precipitation of its 1-nitroso-2 naphthol salt from the aqueous phase. Potassium was determined flame-photometrically and ammonium spectrophotometrically.

The exchange capacity of the KCFC- or NCFC-SiO$_2$ for caesium was measured in the same way as for AMP-SiO$_2$. The exchanger was completely decomposed by hydrofluoric and sulphuric acid treatment and the residue dissolved with hydrochloric acid.

The exchange capacities of AMP-, KCFC- and NCFC-SiO$_2$ for caesium are considered large enough for caesium to be collected by them from large volumes (*e.g.*, 80 or 100 l.) of sea-water, the caesium contents of which have been reported as 0·3–0·8 μg/l.[13–16] This means that the operating capacity of 10 g of AMP-SiO$_2$ (60–80 mesh) is about 19 times the total amount of caesium in 80 l. of sea-water (to which 5·6 mg of Cs^+ have been added as carrier) and that of 10 g of KCFC- or NCFC-SiO$_2$ (60–80 mesh) is at least 17 times the total amount of caesium in 100 l. of sea-water (to which 1·5 mg of Cs^+ have been added as carrier). In the case of fresh water the situation will be more favourable since its caesium content is supposed to be comparable to or less than that of sea-water.

The last column in Table I shows the maximum attainable flow-rate for columns containing 5 g of adsorbing material of different sizes. Exchanger of 60–80 mesh size is the most suitable for treatment of large volumes of sample because the exchange capacity for caesium is higher than that of 42–60 mesh material and the maximum attainable flow-rate is higher than that of 80–100 mesh material.

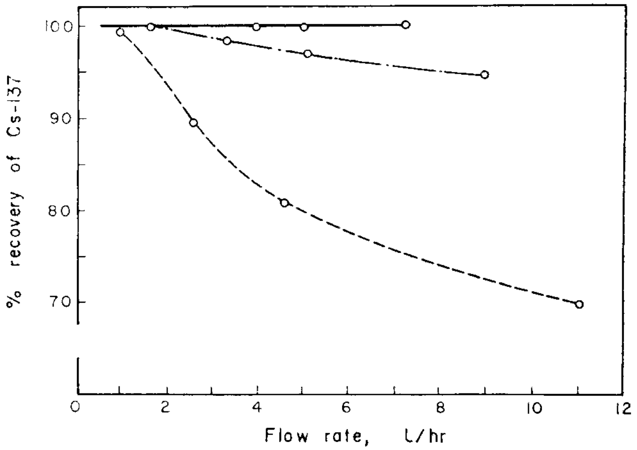


FIG. 1.—Relationship between the flow-rate and recovery of ^{137}Cs.
—O— 5 g of AMP-SiO$_2$
--O-- 2 g of AMP-SiO$_2$
---O--- 1 g of AMP-SiO$_2$
Sample, 3 l. of sea-water; 12-mm diameter column.

It was also confirmed that ^{137}Cs is not adsorbed by silica gel itself from a water sample containing the specified amount of nitric acid.

Effect of flow-rate

It was expected that the operating capacity of the exchanger would be related to the flow-rate of water sample. The results for 1, 2, 3 and 5 g of 60–80 mesh exchange material are shown in Figs. 1 and 2. The maximum attainable flow-rates for 1, 2, 3 and 5 g of the exchanger were about 15, 11, 9 and 7·2 l./hr respectively for AMP-SiO$_2$, and 30, 18, 13 and 8·6 l./hr for KCFC-SiO$_2$. Quantitative adsorption might be expected if 5 g of either exchanger were used with a flow-rate less than 7 l./hr.

Effect of volume of sample

Two exchanger columns (12 mm bore, 80 mm length, 5 g of 60–80 mesh exchanger), were connected vertically in series and sea-water containing caesium carrier and tracer was passed through them. After passage of each 20 l. of sample, a fresh lower column was substituted and the flow was continued until 100 l. of sample had passed through. Then the ^{137}Cs adsorbed on each exchanger was measured as described above. The

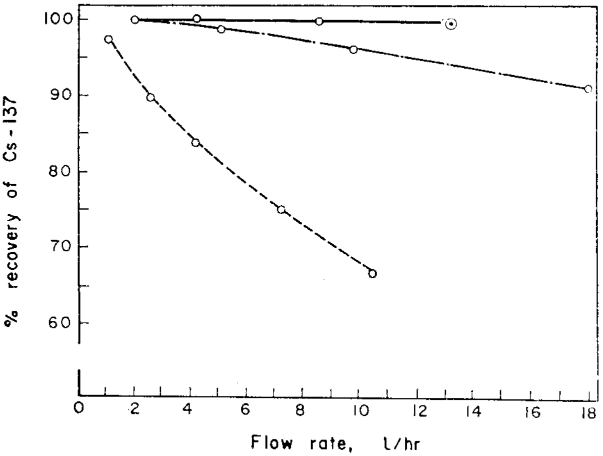


FIG. 2.—Relationship between the flow-rate and the recovery of ^{137}Cs.
—○— 5 g of KCFC-SiO$_2$
—⊙— 3 g of KCFC-SiO$_2$
-—○—- 2 g of KCFC-SiO$_2$
---○--- 1 g of KCFC-SiO$_2$
Sample, 3 l. of sea-water; 12-mm diameter column.

results are illustrated in Fig. 3. Adsorption was nearly quantitative for the first 40 l. of sample and then decreased rapidly. Larger amounts of sample may be treated if a wider column is used with a larger amount of exchanger; *e.g.*, 80–100 l. (60–80 mesh) of sea-water and tap-water were treated with 10 g of exchanger in a 17 × 80 mm column and the yield was satisfactory at a flow-rate of about 10 l./hr for AMP-SiO$_2$, and also for KCFC-SiO$_2$ (Fig. 3).

Effect of caesium carrier

Although the caesium content of sea-water is reported to be 0·3–0·8 μg/l., it was found that addition of caesium carrier enhanced the adsorption yield of ^{137}Cs on the exchanger. The effect of caesium sulphate as carrier was therefore examined. The results are shown in Table II. For sea-water the effect of the carrier was not remarkable, but for tap-water it was very appreciable, *e.g.*, the recovery of caesium by AMP-SiO$_2$ increased from 87·6 to 98·8% on addition of 0·07 ppm of caesium carrier. However, larger amounts of carrier decreased the adsorption of ^{137}Cs. Consequently, the amount of caesium carrier, especially in fresh water, is critically important.

Other factors affecting adsorption of ^{137}Cs

When sea-water is passed through AMP-SiO$_2$, the yellow colour of the material fades gradually as AMP dissolves, but the addition of 1 ml of nitric acid per litre of water prevents this, the pH of the sample becoming about 2, the most favourable for formation of ammonium molybdophosphate. When the acidified sample is introduced into the column through an ordinary rubber tube, reduction of AMP occasionally occurs and the exchanger becomes dark blue. A polyethylene tube

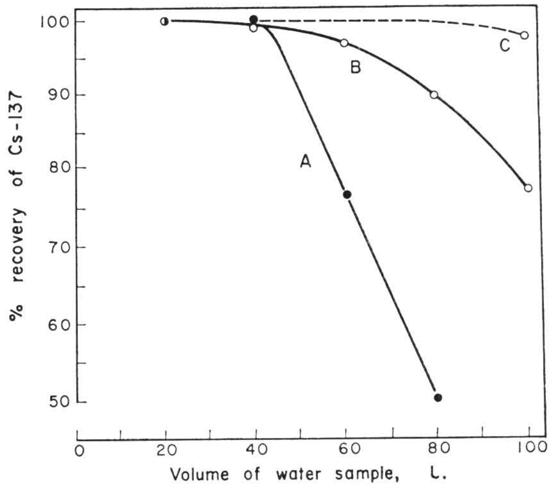


FIG. 3.—Relationship of the volume of sample and recovery of ^{137}Cs.
A: AMP-SiO_2, 5 g; column 12-mm bore.
B: KCFC-SiO_2, 5 g; column 12-mm bore.
C: KCFC-SiO_2, 10 g; column 17-mm bore.
Flow-rate 6 l./hr.

TABLE II.—EFFECT OF ADDITION OF CAESIUM CARRIER ON RECOVERY OF ^{137}Cs

Exchanger (5 g)	Cs added (as Cs_2SO_4),* *ppm*	Recovery of ^{137}Cs, %	
		Sea-water†	Fresh water
AMP-SiO_2	0	97·3	87·6
	0·07	98·6	98·8
KCFC-SiO_2	0	98·9	86·7
	0·015	99·1	98·7

* 40-l. samples; flow-rate 7 l./hr.
† Sea-water contained 0·0005 ppm Cs originally.

has no such effect and should therefore be used. The temperature of the sample water has no effect in the range 5–35°.

Adsorption properties for other radionuclides

As a check, recovery experiments for other radionuclides believed to exist in sea-water were carried out after addition of a known amount of each to 3 l. of sea-water which contained the amounts of caesium carrier and nitric acid mentioned above. The samples were processed with 5 g of exchanger at a flow-rate of 3 l./hr. It was found that AMP-SiO_2 scarcely adsorbed other radionuclides except for radiozirconium–niobium, about 12% of the original amount being adsorbed, but KCFC-SiO_2 can concentrate not only ^{137}Cs, but 34% of radiocerium, 29% of radiocobalt, 15% of radioruthenium–rhodium, 26% of radiozinc and 24% of radiozirconium–niobium as shown in Table III. However, it was thought that the degree of adsorption of these nuclides might decrease considerably when a large volume of sea-water was treated, and this was confirmed by the 3·5% adsorption of radiozirconium–niobium when

40 l. of doped sea-water were passed through the AMP-SiO_2 column. Table III shows that AMP-SiO_2 is more selective than KCFC-SiO_2 for ^{137}Cs. Radiostrontium was not adsorbed at all. NCFC-SiO_2 behaved similarly to KCFC-SiO_2.

TABLE III.—RECOVERY OF VARIOUS RADIONUCLIDES

Radionuclide	Adsorbed by		Remaining after HF treatment	
	AMP-SiO_2 (5 g) %	KCFC-SiO_2 (5 g) %	AMP-SiO_2 %	KCFC-SiO_2 %
^{137}Cs	99*	100	95	100
^{144}Ce–^{144}Pr	0·2	34	0	0
^{60}Co	0·3	29	0	0
^{106}Ru–^{106}Rh	0·4	15	0	0
^{90}Sr–^{90}Y	0	0	0	0
^{65}Zn	0·7	26	0	0
^{95}Zr–^{95}Nb	12·1	24	0	0
^{95}Zr–^{95}Nb	3·5	—	0	0

* Sample: 40 l. of sea-water.

However, as it was impossible to match the chemical forms of the active species used in these experiments with those present in sea-water, the results given in Table III are not in themselves conclusive evidence of recovery of the radionuclides in a sample. Either way, these adsorbed radionuclides have to be removed from the exchanger before the activity measurement of ^{137}Cs. After several tests it was found that the interfering nuclides adsorbed could be easily eliminated by dissolution of the silica in hydrofluoric acid, whereby the nuclides other than ^{137}Cs went into solution while ^{137}Cs was held on the AMP and KCFC or NCFC because these adsorbents are not readily attacked by hydrofluoric acid. As shown in Table III, during the treatment with hydrofluoric acid about 4% of the caesium was lost from the solid phase (AMP-SiO_2), but the other nuclides could be eliminated completely from the exchanger. The loss of ^{137}Cs from KCFC- or NCFC-SiO_2 was negligible. Furthermore, this procedure reduces the volume of the counting sample, and the counting efficiency for Cs-137 is increased by about 20%.

Effect of the potassium in KCFC

According to Petrow *et al.*,[12] the contribution of potassium-40 γ-radiation in 8 g of KCFC to the caesium region of the spectrum was equivalent to 10 pCi of ^{137}Cs. The counting system used by us is closely similar to theirs, but the amount of KCFC used is only about 250 mg, which should produce a response of about 0·3 pCi of Cs-137 in the caesium region. However, the blank value for KCFC-SiO_2 was less than 0·1 pCi, which was only about 0·5% of the total count, so the exchanger itself was regarded as without effect on the results.

Determination of ^{137}Cs in surface sea-water

Table IV shows the results of ^{137}Cs analyses, by the present method, of four surface water samples collected from the Japan Sea. Counting was done with a gamma-ray spectrometer for about 20 hr to obtain sufficient total counts to minimize the statistical counting error. These values are in satisfactory agreement with those determined by Miyake *et al.*[17] (who employed the ordinary co-precipitation method with

TABLE IV.—Cs-137 CONTENT OF SURFACE WATER OF JAPAN SEA (AUGUST, 1967)

St. No.	Lat. N	Long. E	Cs-137, pCi/l.*		
			a	b	c
5	38°06′	134°27′	0·26 ± 0·01	0·23 ± 0·01	0·24 ± 0·04
12	41°02′	132°15′	0·22 ± 0·01	0·22 ± 0·01	0·21 ± 0·04
15	40°14′	135°12	0·22 ± 0·01	0·20 ± 0·01	
18	39°31′	138°11′	0·23 ± 0·01	0·23 ± 0·01	

* a Data obtained with AMP-SiO_2 method.
b Data obtained with KCFC-SiO_2 method.
c Data obtained by Miyake *et al.*

ammonium molybdophosphate) for surface water samples collected from the same station of the Japan Sea at the same time.

CONCLUSION

Caesium-137 can be separated almost quantitatively from large volumes of natural waters with AMP-SiO_2 and KCFC- or NCFC-SiO_2 chromatographic columns. AMP-SiO_2 is more easily prepared than coarse AMP crystals and more convenient to use than AMP-asbestos, because of its mechanical strength and homogeneity. In spite of their exchange capacity being smaller than that of ordinary AMP and KCFC, AMP-SiO_2 and KCFC-SiO_2 can catch ^{137}Cs quantitatively even at high flow-rate of sample. This fact seems to indicate a highly effective adsorption surface and a rapid ion-exchange process in the columns.

The apparatus for the enrichment of ^{137}Cs is so simple that it is readily used on board ship, for freshly collected samples.

Acknowledgement—The authors wish to express their thanks to the staff members of the Maizuru Marine Observatory for their kind help in collection of sea-water samples, and to the staff members of the Geochemical Laboratory of the Meteorological Research Institute for the use of the instruments for the γ-activity measurements. They are also indebted to the Ministry of Education for financial support for this research.

Zusammenfassung—Darstellung und Eigenschaften von auf Silicagel aufgezogenem Ammoniummolybdophosphat und Kalium- oder Ammoniumhexacyanokobaltferrat sowie ihre Anwendung auf die Bestimmung von ^{137}Cs in natürlichen Wässern werden beschrieben. Säulen aus diesen Materialien geben bessere Ausbeuten an ^{137}Cs aus natürlichen Wässern (verglichen mit der Mitfällung mit Ammoniummolybdophosphat), erfordern weniger Austauscher, wodurch die γ-Zählausbeute von ^{137}Cs ansteigt, und ermöglichen die Entfernung anderer Radionuklide durch Wachen mit Flußsäure.

Résumé—On décrit la préparation et les caractéristiques de molybdophosphate d'ammonium et d'hexacyanocobalt-ferrate de potassium ou d'ammonium supportés en gel de silice, et leur application au dosage de ^{137}Cs dans les eaux naturelles. L'emploi de colonnes de ces produits donne une meilleure récupération de ^{137}Cs d'eaux naturelles (par comparaison à la co-précipitation avec le molybdophosphate d'ammonium), nécessite moins d'échangeur, élevant ainsi l'efficacité du comptage γ de ^{137}Cs, et permet l'élimination d'autres radionucléides par lavage à l'acide fluorhydrique.

REFERENCES

1. J. van R. Smit, *Nature*, 1958, **181**, 1530.
2. N. Yamagata and T. Yamagata, *Bull. Chem. Soc. Japan*, 1958, **31**, 1063.
3. N. Yamagata, K. Iwashima and E. Tajima, *J. At. Energy Soc. Japan*, 1962, **4**, 534.
4. N. Yamagata, *Nature*, 1963, **200**, 157.
5. Y. Miyake, K. Saruhashi, Y. Katsuragi and T. Kanazawa, *J. Radn. Res. Japan*, 1961, **2**, 25.
6. J. van R. Smit, W. Robb and J. J. Jacobs, *J. Inorg. Nucl. Chem.*, 1959, **12**, 104.
7. J. Krtil, *ibid.*, 1961, **22**, 247.
8. H. L. Caron and T. T. Sugihara, *Anal. Chem.*, 1962, **34**, 1082.
9. J. van R. Smit, *J. Inorg. Nucl. Chem.*, 1965, **27**, 227.
10. W. E. Prout, E. R. Russel and H. J. Groh, *ibid.*, 1956, **27**, 473.
11. A. L. Boni, *Anal. Chem.*, 1966, **38**, 89.
12. H. G. Petrow and H. Levine, *ibid.*, 1967, **39**, 360.
13. M. Ishibashi and T. Hara, *Rec. Oceanogr. Wks. Japan*, N.S. 2, 1955, **2**, 45.
14. A. A. Smales and L. Salmon, *Analyst*, 1955, **80**, 37.
15. E. Bolter, K. K. Turekian and D. F. Schutz, *Geochim. Cosmochim. Acta*, 1964, **28**, 1459.
16. C. Feldman and T. C. Rains, *Anal. Chem.*, 1964, **36**, 405.
17. Y. Miyake, K. Saruhashi, Y. Katsuragi and T. Kanazawa, paper presented at the Annual Assembly of the Oceanogr. Soc. Japan, Maizuru, November, 1968.

Talanta, 1970, Vol. 17, pp. 965 to 971. Pergamon Press. Printed in Northern Ireland

ATOMIC-FLUORESCENCE CHARACTERISTICS AND ANALYTICAL DETERMINATION OF MANGANESE IN AN AIR-ACETYLENE FLAME

L. Ebdon, G. F. Kirkbright and T. S. West
Chemistry Department, Imperial College, London, S.W.7., U.K.

(*Received* 16 *March* 1970. *Accepted* 15 *May* 1970)

Summary—The atomic-fluorescence characteristics of manganese atoms in a premixed nitrogen-shielded air–acetylene flame are described. Excitation is obtained at 280 nm from a microwave-excited electrodeless discharge tube. A detection limit of 0·001 ppm for the determination of manganese by atomic-fluorescence spectroscopy is obtained by measurement of the resonance fluorescence observed at this wavelength. In addition to several other weaker atomic-fluorescence signals observed from manganese atoms in the flame, weak resonance fluorescence at 258 and 260 nm from manganese ions stimulated by ion line-emission from the source has been recorded. Linear calibration graphs for atomic-fluorescence measurement at 280 nm are obtained over the range 0·0025–10 ppm of manganese in aqueous solution. Of 26 foreign anions and cations examined for interference at the 1000-fold weight excess level only four produced interference. Large amounts of Si, Th and V interfere by scattering of the incident radiation, while Mg causes depression of the atomic fluorescence by a chemical effect.

Atomic fluorescence has been observed for manganese at 279·5 nm, a 150-W xenon arc source being used for excitation, in air–hydrogen, air–propane and hydrogen–oxygen–argon flames, with detection limits of 0·15, 0·3 and 1 ppm respectively.[1,2] Ellis and Demers[3] reported a detection limit of 0·004 ppm at 279·5 nm for the atomic fluorescence of manganese, and used a 450-W xenon arc source. In the general application of electrodeless discharge tubes and particular instrumental detection systems to the detection of atomic fluorescence for a range of elements, both Winefordner *et al.*[4] and West and co-workers[5] have observed the atomic fluorescence of manganese at 279·5 nm, the detection limits being 0·006 and 0·014 ppm in an argon–hydrogen diffusion flame[4] and an air–hydrogen flame[5] respectively.

The detection and determination of manganese by flame emission spectroscopy (FES) and atomic-absorption spectroscopy (AAS) is well established. Recently, several very low detection limits have been obtained for manganese by FES: 0·1 ppm in an oxy-acetylene flame, (Fassel and Golightly[6]), 0·1 ppm in an air–acetylene flame and 0·024 ppm in a premixed oxygen-enriched air–acetylene flame (Chapman and Dale[7]), and 0·005 ppm in a premixed nitrous oxide–acetylene flame (Pickett and Koirtyohann[8]); all at 403·1 nm. Hobbs, Kirkbright and West[9] have reported detection of manganese by FES in a nitrogen-shielded air–acetylene flame; the detection limit obtained in the conventional air–acetylene flame at 403·3 nm was 0·1 ppm, while with the shielded flame a detection limit of 0·01 ppm was obtained. Several workers have studied the determination of manganese by AAS. Beyer[10] and Slavin[11] obtained detection limits (at 279·4 nm) of 0·05 and 0·005 ppm respectively. The manganese line at 403·3 nm is less sensitive and Allen[12] reports spectral interference at the manganese 403·3073 nm line from the gallium line at 403·2982 nm. Silicon appears to be the only major chemical interference, and the addition of lanthanum has been reported to suppress this.[13] To the best of our knowledge no study of the atomic-fluorescence spectral characteristics of manganese has been reported, nor one of the analytical utility of manganese atomic fluorescence in an air–acetylene flame. This paper describes the preparation and properties of the microwave-excited electrodeless discharge tubes employed as sources, and the sensitive and selective determination of manganese by atomic-fluorescence spectroscopy in a nitrogen-shielded air–acetylene flame. A comparison has been made with flame emission spectroscopy, the same detector system being used.

EXPERIMENTAL

Apparatus

A Unicam SP 900A flame spectrophotometer was employed. The use of this instrument for AFS has been described elsewhere.[1] The indirect cyclone nebulizer unit of this instrument was employed without modification. The nebulizer spray rate was 3 ml/min at the pressures used. An EMI 9601B photomultiplier was fitted in place of the standard EMI 9529B supplied with this instrument, to obtain higher sensitivity in the ultraviolet region.

The manganese electrodeless discharge tube was operated at 2450 MHz with a 200-W Microtron 200 Mark II power generator and three-quarter wave Broida-type resonant cavity (Electromedical Supplies, Ltd., Wantage, Type 210L). The cavity was modified by the addition of a side-wall tuning stub. The tube output was modulated at 50 Hz as previously described.[14]

A premixed air–acetylene flame was used throughout this investigation. Nitrogen shielding was used to separate the secondary diffusion zone from the primary reaction zone, the burner being the type described by Hobbs, Kirkbright and West.[9] The burner head was placed 50 mm in front of the monochromator entrance slit. The rim of the flame-shield device was raised so that the monochromator did not view the primary zone. In fluorescence measurements the source was positioned at 90° to the burner–monochromator axis and in the same horizontal plane, so that the distance between the electrodeless discharge tube and the centre of the flame was 50 mm.

Reagents

Manganese stock solution. A 1000-ppm stock solution was prepared by dissolving 3·60 g of crystalline manganese(II) chloride (analytical grade) in 1 litre of 0·5*M* hydrochloric acid. This solution was diluted as required immediately before use.

Diverse ions. Solutions were prepared from analytical-reagent grade salts.

ATOMIC FLUORESCENCE SPECTROSCOPY

Preparation of electrodeless discharge tube

The preparation of manganese electrodeless discharge tubes from manganese(II) iodide and manganese,[4] manganese(II) iodide,[15] manganese(II) chloride[5] and the element and chlorine[16] has previously been reported. In this study these methods of preparation were examined in an attempt to produce the most stable and intense tubes which had good operating life times. The tubes were prepared by the general procedure described elsewhere.[16] Argon-filled tubes were found to be more stable and to have a longer operating life time than those containing helium. The most satisfactory results were obtained for tubes which contained *ca.* 1 mg of manganese(II) chloride (analytical-reagent grade $MnCl_2 . 4H_2O$ dehydrated under vacuum) and an argon filler-gas pressure of 4 mbar.

Operation and spectral characteristics of manganese discharge tube

The electrodeless discharge tubes were operated in the three-quarter wave resonant cavity with a power input of 50 W. After an initial running-in period of between 1 and 2 hr, only a 5-min warm-up period was required after initiation of the discharge. After this warm-up and under these operating conditions, the line-to-background ratios at 279·4 nm and 403·1 nm were typically greater than 100:1, while the short term output stability of the radiation at these wavelengths was ±3%. The discharge obtained exhibits the lines of the resonance spectrum of manganese. The tubes also emit the most intense lines of the Mn(II) spectrum, *i.e.*, from the $3d^5$ $4s^1$ $a\,^7S_3$ ion. The presence of these ionic lines does not appear to impair the analytical usefulness of the tubes for atomic-fluorescence work. The relative intensities of the most useful manganese lines obtained with these operating conditions are shown in Table I.

TABLE I.—AFS RELATIVE SOURCE AND FLUORESCENCE INTENSITIES AND DETECTION LIMITS

Wavelength, *nm*	Spectrum*	Transition† (refs. 18, 19)	Relative intensities from source§	Relative fluorescence intensities§	Limit of detection for manganese, *ppm*
257·6	II	$a\,^7S_3 - z\,^7P_4{}^0$	34	12	1·5
259·4	II	$a\,^7S_3 - z\,^7P_3{}^0$	33	8	12
260·6	II	$a\,^7S_3 - z\,^7P_2{}^0$	32	8	12
279·5	I	$a\,^6S_{5/2} - y\,^6P_{7/2}{}^0$	100‡	100‡	0·001‡
279·8	I	$a\,^6S_{5/2} - y\,^6P_{5/2}{}^0$			
280·1	I	$a\,^6S_{5/2} - y\,^6P_{3/2}{}^0$			
293·3	II	$a\,^5S_2 - z\,^5P_1{}^0$	2	4‡	90‡
293·9	II	$a\,^5S_2 - z\,^5P_2{}^0$	5		
294·9	II	$a\,^5S_2 - z\,^5P_3{}^0$	6	3	90
304·5	I	$a\,^6D_{5/2} - v\,^6P_{7/2}{}^0$	4	11	30
357·8	I	$a\,^6D_{5/2} - x\,^6P_{7/2}{}^0$	8	7	50
383·4	I	$a\,^6D_{5/2} - z\,^6F_{7/2}{}^0$	6	8	67
403·1	I	$a\,^6S_{5/2} - z\,^6P_{7/2}{}^0$	312‡	49‡	0·02‡
403·3	I	$a\,^6S_{5/2} - z\,^6P_{5/2}{}^0$			
403·4	I	$a\,^6S_{5/2} - z\,^6P_{3/2}{}^0$		30‖	

* Normal state of valence electrons: Mn(I) $3d^5\,4s^2\,^6S_{5/2} = 0$; Mn(II) $3d^5\,4s^1\,^7S_3 = 0$.

† Lowest state of Mn(I) is $a\,^6S_{5/2}$ and of Mn(II) $a\,^7S_3$.

‡ Unresolved lines.

§ Relative to 280-nm triplet, and uncorrected for response characteristics of photomultiplier.

‖ Relative intensity at 403 nm with 280-nm source radiation filtered out.

Atomic fluorescence measurements

When 10-ppm manganese solutions were nebulized into the air-acetylene flame with the electrodeless discharge tube in operation, atomic-fluorescence signals were observed at each of the wavelengths shown in Table I. The most intense fluorescence was obtained from the 280- and 403-nm triplet lines which arise from transitions to the ground state. The individual lines of these triplets were unresolved with the spectral band-pass available. The use of an optical wide-band filter to prevent irradiation of the flame by the 280 nm radiation from the source revealed that the fluorescence emission signal at 403 nm orginated from both resonance fluorescence and some stepwise fluorescence from deactivation of the excited $y\,^6P_{3/2}{}^0$, $y\,^6P_{5/2}{}^0$ and $y\,^6P_{7/2}{}^0$ state atoms by radiationless transitions to the $z\,^6P_{3/2}{}^0$, $z\,^6P_{5/2}{}^0$ and $z\,^6P_{7/2}{}^0$ excited states. The use of an optical filter to prevent irradiation of the flame by the 403-nm radiation from the source, revealed as expected that excitation at 403 nm did not contribute to the fluorescence radiation observed at 280 nm.

The suitability of both fluorescence signals (280 and 403 nm) for the analytical determination of manganese was investigated. Lower flame background intensity, lower thermal emission intensity for manganese and freedom from spectral interference[12] is observed at 280 nm, however, and all analytical AFS measurements were made at this wavelength.

The emission at 260 nm for the most intense lines of the Mn(II) spectrum has been observed to stimulate ionic resonance fluorescence from manganese in the $3d^5 4s^1$, $a\,^7S_3$ ionic state in the air–acetylene flame. Assuming that thermal equilibrium prevails in the air–acetylene flame, the calculated degree of ionization produced when a 10-ppm manganese solution is nebulized into a nitrogen-shielded air–acetylene flame at 2450 K is $0{\cdot}6 \times 10^{-3}\%$. Although the population of ions is low, the *gf* values (*i.e.*, products of the statistical weights and oscillator strengths) and source intensities of the 257·6, 259·4 and 260·6 Mn(II) lines are high. The net result is a resonance ionic fluorescence signal of appreciable intensity. Although the *gf* values of the Mn(II) lines at 293·3, 293·9 and 294·9 nm are high, the source intensities at these lines are low and they are not due to transitions to the ground state. For this reason, and because of the relatively high background at these wavelengths, only very weak ionic fluorescence was observed at these wavelengths. The fluorescence from manganese ions was suppressed at all the observed lines on addition of 1000 ppm of potassium as potassium chloride to the solutions nebulized.

Optimum operating conditions

The use of both conventional unshielded and nitrogen-shielded air–acetylene flames was investigated. At 280 nm the atomic-fluorescence signal intensity was reproducibly 30% greater in the shielded flame and the signal noise levels obtained were decreased by a factor of 2 on shielding. The nitrogen-shielded air–acetylene flame was chosen for all further measurements and a nitrogen flow-rate of 14 l./min was employed.

The most intense fluorescence at 280 nm was obtained with an air flow-rate of 6·5 l./min and an acetylene flow-rate of 1·1 l./min (the ranges investigated were 5–7·5 and 0·9–1·4 l./min respectively). De Waele and Harjadi[17] have reported the relation of the optimum burner height to concentration of manganese in atomic-absorption spectroscopy. Although we found an optimum height of observation in the flame, it was not markedly dependent on concentration. With the optimum burner height the monochromator views the interconal region of the flame between *ca.* 6 and 26 mm above the burner head.

The effect of variation of the monochromator slit-width on the atomic-fluorescence signal-to-background noise ratio was investigated under otherwise optimum conditions. The optimum slit-width at 280 nm was 0·4 mm; this corresponds to a spectral bandwidth of approximately 1·6 nm. The use of a lens to focus radiation from the source into the flame did not improve the attainable detection limit for manganese.

Calibration data and detection limits

With the optimum operating conditions established, linear atomic-fluorescence calibration graphs were obtained at 280 nm over the range from 0·0025 to 10 ppm of manganese in aqueous solution. The fluorescence at 280 nm suffers self-absorption above 10 ppm and at above this concentration the calibration graphs curve towards the concentration axis. Linear atomic-fluorescence calibration graphs were obtained over the range 0·1 to 15 ppm of manganese in aqueous solution when fluorescence measurements were made at 403 nm.

The detection limits obtained at each of the ten wavelengths for which atomic fluorescence was observed are shown in Table I. The detection limit was defined as that concentration of manganese in aqueous solution which produced a signal equivalent to twice the standard deviation of the background noise measured near the limit of detection.

Interference studies

The effect, on the atomic fluorescence intensity produced at 280 nm by a 0·5-ppm manganese solution, of the presence of a 1000-fold excess by weight of a range of cations and anions has been examined. The results of this investigation are summarized in Table II. Of the 26 ions studied at this concentration only 4 produced serious interferences; three of the most refractory elements (thorium, silicon and vanadium) gave a positive interference by particulate scattering of incident radiation from the source. Two of these, thorium and silicon, gave negligible interferences when only a 100-fold weight excess was employed. Magnesium seriously reduced the fluorescence signal even when only a 100-fold weight excess was present. Magnesium similarly depressed the manganese atomic-absorption signal and apparently interferes by reducing the population of manganese atoms in the flame. The interference of silicon in the atomic-absorption spectrophotometry of manganese has previously been reported and the use of lanthanum as a releasing agent proposed.[13]

TABLE II.—EFFECTS OF FOREIGN IONS ON FLUORIMETRIC DETERMINATION OF 0·5 ppm OF MANGANESE AT 280 nm

Effect on AFS signal	Foreign ion (1000-fold weight excess)
No interference	Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Mo^{6+}, Cd^{2+}, Pb^{2+}, PO_4^{3-}, SO_4^{2-}, NO_3^-, NH_4^+, Na^+, Th^{4+}*
Negligible interference (<3%)	K^+, Ca^{2+}, Ba^{2+}, W^{6+}, Hg^{2+}, Si^{4+}*, Sn^{2+}, Ta^{5+}, Ga^{3+}
Interference	Th^{4+}(+4%), Si^{4+}(+5%), V^{5+}(+16%), V^{5+}*(+8%), Mg^{2+}(−39%), Mg^{2+}*(−11%)

* 100-fold weight excess.

FLAME EMISSION SPECTROSCOPY

Investigation of the detection of manganese by flame emission spectroscopy was made both in the conventional and nitrogen-shielded flames, and the optimum operating conditions established. The effect of variation of acetylene flow-rate between 0·9 and 1·2 l./min on the emission intensity at 403 nm was investigated. The optimum acetylene flow-rate was found to be 1·07 l./min for both unshielded and shielded flames. The effect of varying the air-flow rate between 6·5 and 7·5 l./min was also investigated. For the unshielded flame an optimum air flow-rate of 7·0 l./min was used, while for the nitrogen-shielded flame the optimum flow-rate was 7·5 l./min. The optimum flow-rate for the nitrogen shielding gas for this latter flame was found to be 14 l./min.

With these optimum conditions, the optimum height of observation was found to be in the region 13–33 mm above the burner head for both flames.

The optimum slit-widths and the detection limits at each wavelength are shown in Table III. The use of the most intense line emission, at 403 nm, gives rise to the lowest detection limit.

TABLE III.—SUMMARY OF DETECTION LIMITS BY FLAME EMISSION

Wavelength*, *nm*	Unshielded flame Slit width, *mm*	Unshielded flame Limit of detection, *ppm*	Shielded flame Slit width, *mm*	Shielded flame Limit of detection, *ppm*
279·5 279·8 280·1	0·175	0·08	0·19	0·05
354·78 354·80	0·08	1·5	0·13	1·2
356·95 356·98	0·08	1·0	0·12	1·0
403·1 403·3 403·4	0·04	0·02	0·09	0·01

* All lines were unresolved.

ATOMIC ABSORPTION

Reference has already been made to the many studies of the atomic-absorption spectrophotometry (AAS) of manganese. A brief study of the AAS of manganese was made with the same apparatus as described here for fluorescence measurements, adapted as reported in an earlier paper from this laboratory.[14] The limits of detection for an aqueous manganese solution were found to be 0·1 and 0·4 ppm at 279·5 and 403·1 nm respectively.

CONCLUSION

This study indicates that manganese may be determined with extremely high sensitivity by atomic-fluorescence spectroscopy when a high-intensity source of radiation is used. The apparatus we have employed was originally designed for flame emission spectroscopy. Consequently, while this apparatus permits the sensitive detection of manganese by atomic-emission spectroscopy, the attainable sensitivities for manganese by atomic-absorption spectroscopy are poorer than those reported by other workers using instrumentation specifically designed for atomic-absorption work. The atomic-fluorescence detection limit obtainable is *ca.* one order of magnitude lower than the best attainable flame emission detection limit. Good selectivity is also available in the determination of manganese by atomic-fluorescence spectroscopy using the flame and nebulizer system described. Some physical scattering interference in the presence of high concentrations of elements which form refractory oxides in the air–acetylene flame has been observed, and chemical interference from magnesium has also been recorded.

TABLE IV.—DETECTION LIMITS FOR MANGANESE

Wavelength, *nm*	Detection limits, *ppm* Atomic fluorescence	Atomic absorption	Flame emission
280	0·001	0·1	0·05
403	0·02	0·4	0·01

Acknowledgement—We are grateful to the Ministry of Technology for support of this work.

Zusammenfassung—Die Atomfluoreszenzeigenschaften von Manganatomen in einer vorgemischten Luft-Acetylen-Flamme mit Stickstoffmantel werden beschrieben. Eine mit Mikrowellen erregte elektrodenlose Entladungsröhre dient zur Anregung bei 280 nm. Messung der Resonanzfluoreszenz bei dieser Wellenlänge führt zu einer Nachweisgrenze von 0,001 ppm für die atomfluoreszenzspektrometrische Bestimmung von Mangan. Außer mehreren anderen schwächeren Atomfluoreszenzsignalen von Manganatomen in der Flamme wurde schwache Resonanzfluoreszenz bei 258 und 260 nm an Manganatomen registriert, die durch Linienemission von Ionen aus der Lichtquelle angeregt wurde. Im Bereich 0,0025 bis 10 ppm Mangan in wäßriger Lösung werden bei 280 nm lineare Eichkurven bei der Atomfluoreszenzmessung gefunden. Unter den 26 bei 1000-fachen Überschuß untersuchten fremden Anionen und Kationen störten nur vier. Große Mengen Si, Th und V stören durch Streuung der einfallenden Strahlung, während Mg die Atomfluoreszenz durch einen chemischen Effekt vermindert.

Résumé—On décrit les caractéristiques de fluorescence atomique d'atomes de manganèse dans une flamme air–acétylène préalablement mélangés et protégée à l'azote. On obtient l'excitation à 280 nm à partir d'un tube à décharge sans électrode excité aux micro-ondes. On obtient une limite de détection de 0,001 p.p.m. pour la détermination du manganèse par spectroscopie de fluorescence atomique en mesurant la fluorescence de résonance observée à cette longueur d'onde. En addition à plusieurs autres signaux de fluorescence atomique plus faibles observés à partir d'atomes de manganèse dans la flamme, on a enregistré une faible fluorescence de résonance à 258 et 260 nm à partir d'ions manganèse provoqués par émission de raie d'ion de la source. On obtient des graphiques d'étalonnage linéaires pour la mesure de fluorescence atomique à 280 nm dans le domaine 0,0025–10 p.p.m. de manganèse en solution aqueuse. Des 26 anions et cations étrangers examinés pour leur interférence en quantité 100 fois supérieure, quatre seulement apportent une gêne. De grandes quantités de Si, Th et V interfèrent par dispersion de la radiation incidente, tandis que Mg cause un abaissement de la fluorescence atomique par une influence chimique.

REFERENCES

1. R. M. Dagnall, K. C. Thompson and T. S. West, *Anal. Chim. Acta*, 1966, **36**, 269.
2. D. C. Manning and P. Heneage, *At. Absorption Newsletter*, 1967, **6**, 124.
3. D. W. Ellis and D. R. Demers, Paper presented at 153*rd Nat. Mtg. Am. Chem. Soc.*, Miami Beach, Florida, April 1967.
4. K. E. Zacha, M. P. Bratzel, J. D. Winefordner and J. M. Mansfield, *Anal. Chem.*, 1968, **40**, 1733.
5. R. M. Dagnall, M. R. G. Taylor and T. S. West, *Spectroscopy Letters*, 1968, **1**, 397.
6. V. A. Fassel and D. W. Golightly, *Anal. Chem.*, 1967, **39**, 466.
7. J. F. Chapman and L. S. Dale, *Analyst*, 1969, **94**, 563.
8. E. E. Pickett and S. R. Koirtyohann, *Spectrochim. Acta.*, 1968, **23B**, 235.
9. R. S. Hobbs, G. F. Kirkbright and T. S. West, *Analyst*, 1969, **94**, 554.
10. M. Beyer, *At. Absorption Newsletter*, 1965, **4**, 212.
11. W. Slavin, *Appl. Spectry.*, 1966, **20**, 281.
12. J. E. Allan, *Spectrochim. Acta*, 1969, **24B**, 13.
13. J. T. H. Roos and W. J. Price, *Analyst*, 1969, **94**, 89.
14. L. Ebdon, G. F. Kirkbright and T. S. West, *Anal. Chim. Acta*, 1969, **47**, 563.
15. J. M. Mansfield, M. P. Bratzel, H. O. Norgordon, D. O. Knapp, K. E. Zacha and J. D. Winefordner, *Spectrochim. Acta*, 1968, **23B**, 389.
16. R. M. Dagnall and T. S. West, *Appl. Opt.*, 1968, **7**, 1287.
17. M. M. De Waele and W. Harjadi, *Anal. Chim. Acta*, 1969, **45**, 21.
18. C. H. Corliss and R. Bozman, *Experimental Transition Probabilities for Spectral Lines of Seventy Elements*. National Bureau of Standards, Washington, 1962.
19. C. E. Moore, *Atomic Energy Levels as Derived from the Analysis of Optical Spectra*, Vol.II . National Bureau of Standards, Washington, 1952.

Talanta, 1970 Vol. 17, pp. 973 to 986. Pergamon Press. Printed in Northern Ireland

REDOXAUSTAUSCHER UND IHRE ANWENDUNGEN—XV

REDUKTION VON EISEN(III) AN REDOXITEN UND ANSCHLIEẞENDE OXYDIMETRISCHE BESTIMMUNG*

BRUNO SANSONI und WOLFGANG WIEGAND†
Institut für Strahlenschutz der Gesellschaft für Strahlenforschung mbH., Radiochemisch-analytische Abteilung 8042 Neuherberg bei München und Chemisches Institut der Universität Marburg/Lahn

(*Eingegangen am* 4. *Januar* 1966. *Angenommen am* 14. *April* 1970§)

Zusammenfassung—Als Beispiel für die Reduktion von Kationen an Redoxiten wird die quantitative Reduktion von 50 bis 200 mg Eisen(III) in schwefelsaurer Lösung an einem Leukomethylenblau- und Ferrocen-Harz auf Polystyrolbasis beschrieben. Im Durchlauf wird Eisen(II) potentiometrisch mit $0{,}1N$ Cer(IV)-sulfatlösung bestimmt. Unter optimalen Bedingungen ergibt sich im Bereich von 100 bis 200 mg Eisen eine Standardabweichung von $\pm 0{,}04$ bis $\pm 0{,}14$ mg. Im Gegensatz zu Metallreduktioren stören Cu^{2+}, Bi^{3+}, TiO^{2+}, Sn^{4+}, Ce^{4+} und AsO_4^{3-} nicht. Die Methode wurde zur Direktbestimmung von Eisen in Erzen, Martinschlacke und Spezialstählen angewendet.

OXYDIMETRISCHE Bestimmungen behaupten sich in der Makro- bis Halbmikroanalyse neben photometrischen Methoden, da sie zuverlässig sind und oft weniger durch Begleitelemente gestört werden.[1,2] Die ihnen vorausgehende Reduktion des zu bestimmenden Stoffes erfolgt meist in einer Säule mit aufgeschichteten Metallkörnern (Jones-Reduktor),[3,4] gelegentlich flüssigen Amalgamen[1,5] und seltener durch gelöste Reduktionsmittel. Bekannteste Beispiele sind die Reduktionen von Eisen(III) oder Transuranen am Cadmiumbzw. Blei-Reduktor für anschließende quantitative Bestimmungen oder Trennungen.

Im Jahre 1952 haben Sansoni[6] und Cassidy[7] unabhängig voneinander die von ihnen entwickelten Redoxaustauscher[7,8,9] als unlösliche Jones-Reduktoren vorgeschlagen. Die erste analytische Anwendung[10] beschrieb einen mit Anthrahydrochinon beladenen Anionenaustauscher, an dem von 50 bis 100 mg Eisen(III) in schwefelsaurer Lösung 96% als Eisen(II) im Durchlauf wiedergefunden wurden.[10,11] Später verwendeten Erdey, Inczédy und Markovits[12] am Anionenaustauscher gebundenes Chlorostannat(II) in $3M$ Salzsäure bei erhöhter Temperatur. Inczédy[13] arbeitete im Citratpuffer bei pH 6 mit 0,025–1 mg Eisen am Variaminblau-Kationenaustauscher.

Wesentlich allgemeiner anwendbar sind jedoch unlösliche Redoxite mit kovalent eingebauten Redoxsystemen. Sie sind auch für stark saure bis stark alkalische Medien geeignet und verunreinigen die Lösung nicht mit eluierten Redox-Ionen.

---

* XIV. Mitteilung R. Winkler, B. Sansoni, K. Starke, *Chem. Zvesti*, 1967, **21**, 571. XII. Mitteilung B. Sansoni, R. Winkler, K. Starke, *Angew. Chem.* 1966, **78**, 645. Vorgetragen GDCH-Fachgruppe "Analytische Chemie," Stuttgart 1960 (Referat *Angew. Chem.*, 1961, **72**, 569) sowie XX. IUPAC-Kongreß Moskau 1965 (Abstracts E/F, S. 94). Herrn Prof. Dr. R. Klement, München, zum 70. Geburtstag.

† Jetzt: Mannesmann-AG, Röhrenwerk Witten, 581 Witten/Ruhr.

§ Publication delayed at authors' request.

Störungen durch ionenaustauschende Gruppen entfallen. Aus diesen Gründen hatten wir bereits im Jahre 1953 ein Polystyrolharz mit nachträglich chemisch eingebautem Leukomethylenblau eingesetzt.[10,11] Jedoch war die anschließende oxydimetrische Titration mit Permanganat zu ungenau,[14] da etwas Leukomethylenblau ausblutete und die Erkennung des Farbumschlags des Permanganates störte.

Im folgenden wird die quantitative Reduktion von Eisen(III) zu Eisen(II) an verbesserten Redoxiten beschrieben. Die anschließende Eisenbestimmung erfolgt mit Cer(IV) und potentiometrischer Endpunktsanzeige. Im Verlauf der Arbeit werden die allgemeinen Arbeitsbedingungen analytischer Anwendungen von Redoxiten studiert und mit denen bei Ionenaustauschern verglichen.

THEORETISCHER TEIL

Als Redoxite standen das Tonmineral Nontronit[15] sowie Polystyrolharze mit chemisch eingebautem Ferrocen,[16] Leukomethylenblau[10,11] und Anilinohydrochinon[17] nach Sansoni und Sigmund zur Verfügung. Die beiden ersteren übertragen nur Elektronen, die beiden letzteren zusätzlich Protonen. Eisen(III) wird an den genannten Redoxiten in schwefelsaurer Lösung nach dem Schema

$$\mathrm{Fe^{3+}} + \boxed{\mathrm{R}} \rightleftharpoons \boxed{\mathrm{R^{+}}} + \mathrm{Fe^{2+}} \qquad \text{oder} \tag{1}$$

$$2\mathrm{Fe^{3+}} + \boxed{\mathrm{H_2R}} \rightleftharpoons \boxed{\mathrm{R}} + 2\mathrm{Fe^{2+}} + 2\mathrm{H^{+}} \tag{2}$$

reduziert.

Die Gleichgewichtskonstante K für die Reduktion von Eisen(III) am Redoxit in beliebigem Medium ergibt sich nach

$$-\Delta G = RT.\ln K = n \cdot F \cdot \Delta E_{50\%} \tag{3}$$

unter den üblichen thermodynamischen Voraussetzungen für 25° zu

$$\log K = \frac{n}{0{,}0591} \cdot \Delta E_{50\%}$$

$$\text{bzw. } K = 10^{(n/0{,}0591)\cdot \Delta E_{50\%}}. \tag{4}$$

Darin bedeutet ΔG die Änderung der Freien Energie während eines Formelumsatzes, n die Anzahl der übertragenen Elektronen, F die Faradaykonstante und $\Delta E_{50\%}$ [Volt] die Differenz der Realpotentiale $E_{50\%}$ beider Teilreaktionen im jeweiligen Medium:

$$\Delta E_{50\%} = E_{50\%,\mathrm{Fe^{2+}/Fe^{3+}}} - E_{50\%,\mathrm{Redoxit}}. \tag{5}$$

Die Reduktion sollte freiwillig ablaufen, wenn

$$-\Delta G = n \cdot F \cdot \Delta E_{50\%} > 0. \tag{6}$$

$E_{50\%}$ kann aus Abb. 1 als Ordinatendifferenz entnommen werden. Dort sind die von Bock und Herrmann[18] gemessenen Realpotentiale des $\mathrm{Fe^{2+}/Fe^{3+}}$-sulfates für verschiedene Mineralsäuren in Abhängigkeit von deren Konzentration und die Realpotentiale der Redoxite in Abhängigkeit von der Schwefelsäurekonzentration aufgetragen.[9,19] In erster Näherung wird dabei angenommen, daß die Potentiale der Redoxite unter reversiblen Bedingungen gemessen wurden und unabhängig von der

Art der verwendeten Mineralsäuren sind.[19] Da diese Bedingungen nicht streng erfüllt sind, sind hier nur halbquantitative Aussagen möglich.

Danach läßt sich voraussehen, daß Eisen(III) in Perchlorsäure an allen vier Redoxiten vollständig, in Schwefelsäure und Salzsäure nur an den drei Redox-Harzen glatt, an Nontronit teilweise, in Phosphorsäure auch an den Harzen unvollständig und in der hier nicht eingetragenen Flußsäure fast nicht mehr reduziert wird.

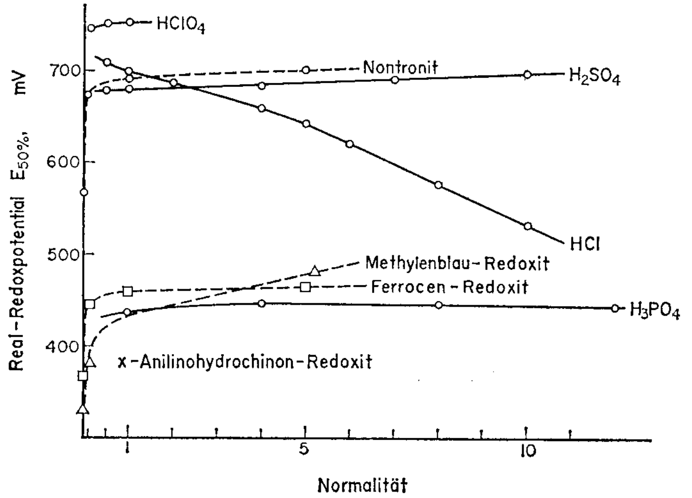


Abb. 1.—Vergleich der Realpotentiale $E_{50\%}$ von Fe^{3+}/Fe^{2+} und Redoxiten in verschiedenen Mineralsäuren bei 20,0°.
——— Realpotentiale des Eisensystems[18]
- - - - - Realpotentiale des Redoxites in Schwefelsäure.[17,19]

Nach einem Potentialvergleich zwischen Redoxiten und elektrochemischer Spannungsreihe sollten an Nontronit außer Eisen(III) nur Chrom(VI), Thallium(III), Selen(VI), Vanadin(V), Quecksilber(II); am Ferrocen-Harz zusätzlich Arsen(V), Molybdatosilikat und Molybdän(VI); am Leukomethylenblau-Harz unter Umständen noch Uran(VI) reduziert werden. Diese Näherung vernachlässigt allerdings Unterschiede zwischen Real- und Normalpotentialen. Bei Arsen(V) lassen höhere Aktivierungsenergien nur langsame Reaktionsgeschwindigkeiten voraussehen.

Als Ergebnis der Betrachtung ist das Anilinohydrochinon-Harz wegen seines tiefen Redoxpotentiales zu unspezifisch. Der wesentlich selektivere Nontronit hingegen ist in 1*N* Schwefelsäure nicht mehr ausreichend stabil. Daher werden in vorliegender Arbeit die schnell reagierenden Leukomethylenblau- und Ferrocen-Harze (gelegentlich auch das Anilinohydrochinon-Harz) verwendet.

EXPERIMENTELLER TEIL

Geräte

Säulen. Es werden Säulen nach Abb. 2 mit den Abmessungen 240 × 12 bzw. 340 × 12 m (Kapillarrohr innen 2-mm Durchmesser) verwendet.

Säulenaggregat. Jeweils 5 Säulen stehen in einem Plexiglasgestell nach Abb. 3 und werden dur ein gemeinsames Verteilerrohr mit Schliffhähnen undansätzen verbunden. In gleicher Weise werd 4 dieser so erhaltenen Aggregate zusammengeschaltet. Damit können dann insgesamt 20 Säul

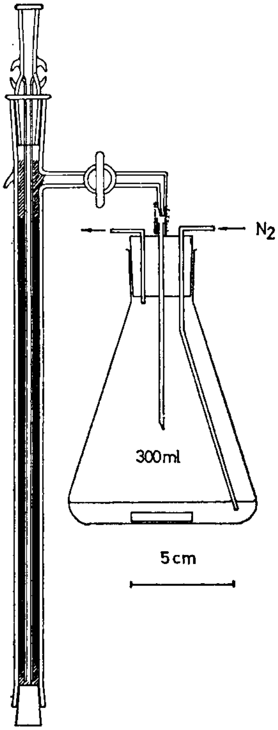


Abb. 2.—Austauschersäule mit aufsteigender Flüssigkeitsströmung.[27,28] Dazu ein 100-ml Vorratsbecher mit 12,5 NS Schliff; Quarz- oder Polyacrylfaserwatte ist schraffiert.

gleichzeitig, unter Luftabschluß und halbautomatisch über Nacht über eine gemeinsame Leitung gewaschen werden.

Waschwasser. Eine Redoxaustauscheranlage[9,20] liefert pro Regeneration etwa 2500 Liter sauerstoffarmes Leitfähigkeitswasser mit $\leqslant 40\,\mu g\, O_2/l$, $\approx 2 \cdot 10^{-8}\Omega^{-1} \cdot mm^{-1}$, pH 6,6 – 6,8 (21 ± 1°). Bei Verwendung von nur ausgekochtem und mit Inertgas gespültem oder auch normalem Ionenaustauscherwasser wird ein entsprechender Anteil Reduktionskapazität der zu waschenden Säule verbraucht. Diese Arbeitsweise ist jedoch bei etwas geringeren Ansprüchen durchaus möglich. Eine ausführliche Beschreibung der Anlage wird in Mitteilung XVIII dieser Reihe erfolgen.

Meßgeräte. Präzisions-pH-Meter 35 (Knick); Pt-Kalomel-Einstabmeßkette 480 NS (Ingold); justierbare Spritzpipetten 5 bis 15 ± 0,002 ml (Jacobs, Kopenhagen); 10 ml-Kolbenbürette (Ströhlein). Strahlungsmeßgerät FH 90 und Szintillationszählrohr FH 421 (Frieseke & Höpfner).

Redoxite. Die Redox-Harze werden aus Poly-4-aminostyrol der Korngröße 0,3–0,5 mm hergestellt.[9] Es befinden sich jeweils 8 g Methylenblau-Harz in den 240-mm Säulen und 11 g Ferrocen-Harz bzw. 11 g Anilinochydrochinon-Harz in den 340-mm Säulen. Alle Redoxite werden vor der ersten Anwendung mehrmals reduziert und oxydiert. Das Leukomethylenblau-Harz war bereits etwa 150mal einem Redox-Cyclus unterworfen worden. Von der Synthese der noch gebundene und unerwünschte kationenaustauschende Gruppen sind in 1*N* Schwefelsäure ohne Wirkung. Einzelne wenige Chargen der selbst hergestellten Redox-Harze halten nach der Regeneration durch Anionenaustausch gelegenlich Spuren Dithionit fest. Diese müssen dann durch kurzes Waschen mit schwach sauerstoffhaltigem Wasser oxydiert oder durch Blindbestimmungen berücksichtigt werden. Meist erübrigte sich dies jedoch.

Lösungen

Ammoniakalische Dithionitlösung. 25 bis 50 g $Na_2S_2O_4$ (gereinigt, Riedel-DeHaen, werden in 30 ml konz. Ammoniaklösung sowie 500 ml Wasser gelöst.

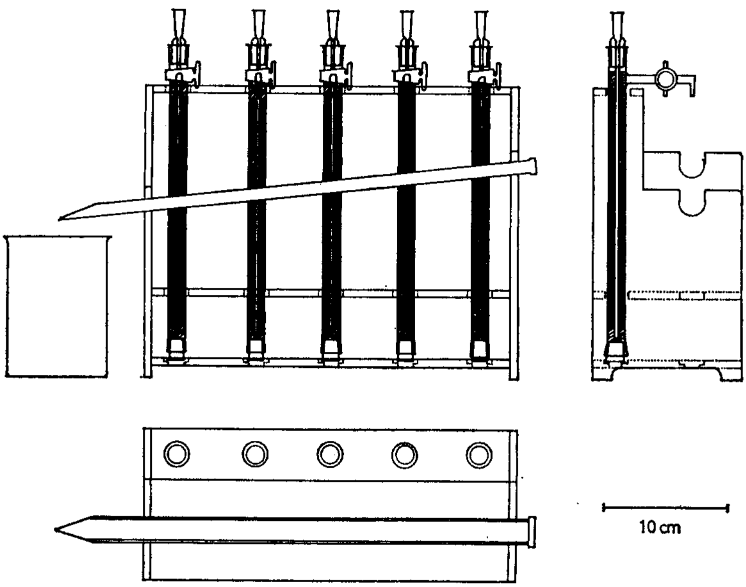


Abb. 3.—Aggregat für 5 Säulen.
Plexiglasgestell für gemeinsames Waschen nach Aufsetzen eines gemeinsamen Verteilerstückes auf die 5 Säulen.

Schwefelsaure Eisen(III)-*sulfatlösung*. Die erforderliche Menge $NH_4Fe(SO_4)_2 \cdot 12\,H_2O$ (*p.a.*) wird in 1*N* Schwefelsäure gelöst, mit dieser Säure auf 2 Liter aufgefüllt und komplexometrisch (Indikator Sulfosalicylsäure) eingestellt.[21]

0,1*N Cer*(IV)-*sulfatlösung* in 1*N* H_2SO_4, wird mit potentiometrischer Endpunktsanzeige[2] bei 40–50° gegen As_2O_3 unter Zugabe von 2 Tropfen OsO_4-Lösung eingestellt.

Osmiumtetroxidlösung: 250 mg OsO_4 werden in 100 ml Wasser gelöst.

0,1*N Permanganatlösung* wird gegen Natriumoxalat eingestellt.

Markierte Eisen(III)-*lösung*: 2 mCi einer fast trägerfreien ^{59}Eisen(III)-sulfatlösung (Harwell, mit Spur Citronensäure stabilisiert) mit Eisen(III)sulfatlösung in 1*N* Schwefelsäure auf 100 ml aufgefüllt (Träger 15 mg Fe/ml).

Regeneration

Die Redoxite werden mit Wasser vorgequollen, in die Säulen gefüllt und mit je 100 ml Dithionitlösung bei einer Durchlaufgeschwindigkeit von etwa 1,5 ml/min bis zum vollständigen Farbumschlag reduziert. Dann wird das Säulenaggregat zusammengesetzt und über Nacht mit etwa 2 Liter Waschwasser pro Säule bei etwa 2,2 ml/min (1 Tropfen/5 sec) sorgfältig dithionitfrei gewaschen. Die letzten 100 ml Durchlauf dürfen 1 Tropfen 0,01*N* Permanganatlösung innerhalb einer Minute nicht entfärben. Andernfalls muß noch weiter gewaschen werden.

Reduktion von Eisen(III)

Man versieht die regenerierten Säulen mit 100-ml Schliff-Vorratsbechern und befestigt am Säulenauslauf jeweils einen dreifach durchbohrten Gummistopfen mit Ein- und Ausleitungsrohr für Inertgas. In die zum Auffangen des Durchlaufes bestimmten 300-ml Erlenmeyerkolben gibt man zuvor je 25 ml konz. Schwefelsäure, 25 ml sirupöse Phosphorsäure (beide *p.a.*) und 50 ml Wasser. Dann werden sie an dem Gummistopfen des Auslaufrohres der Säulen befestigt und gemeinsam mit nachgereinigstem Stickstoff (Linde) gespült. Die zu reduzierende Eisen(III)-lösung gibt man mit der Kolbenbürette oder Spritzpipette in den unteren Teil des Vorratsbechers, ohne dessen Wand zu berühren, läßt die Lösung mit 2,2 ml/min durchlaufen und wäscht dreimal mit je 1,5 ml und dann insgesamt 250 ml Schwefelsäure nach. Bei dieser Anordnung bleibt die Luft weitgehend ausgeschlossen.

Eisenbestimmung. Auf die Erlenmeyerkolben wird nun ein anderer Gummistopfen mit Einstabmeßkette sowie Gasein- und ausleitungsrohr gesetzt und unter magnetischem Rühren mit Cer(IV)-sulfatlösung titriert. Gelegentlich ergaben unvollständig ausgewaschene Spuren Dithionit bei der Titration kleine Vorstufen, die vom Gesamtverbrauch abgezogen werden müssen. Deren Berücksichtigung bereitete jedoch im allgemeinen keine Schwierigkeit.

Optimale Reduktionsbedingungen

Da es sich um das erste Beispiel einer analytischen Anwendung von Redoxiten handelt, wurde der Einfluß verschiedener Faktoren auf die Reduktion von Eisen(III) näher untersucht.

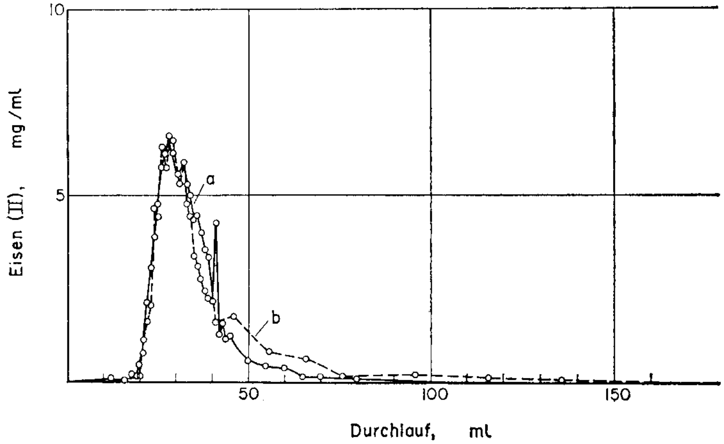


ABB. 4.—Reduktionskurven für Eisen(III) am Leukomethylenblau-Redoxit. Reduktion von(*a*) 109,0 mg und(*b*) 117,3 mg Fe(III) in 6,70 ml 1*N* Schwefelsäure mit 0,5 ml/min an 8,00 g Leukomethylenblau-Harz; Säulen 240 × 12 mmi, Waschen mit 250 ml 1*N* Schwefelsäure.

Stabilität der Redoxite

Die verwendeten Redoxite sind ausreichend stabil. So wurden durch 55 g Ferrocen-Harz 13 Liter 1*N* Schwefelsäure innerhalb von 260 Stunden (etwa 0,8 ml/min) filtriert, auf 300 ml eingeengt und neutralisiert. Weder mit Thiocyanat noch mit α,α'-Dipyridyl oder Sulfosalicylsäure konnte Eisen nachgeweisen werden. Das vorher schon etwa 150mal zu verschiedenartigen Reduktionen verwendete Leukomethylenblau-Harz gab selbst nach zwei Jahren Stehen unter 1*N* Schwefelsäure keine Farbstoffspuren ab. Indessen ließ seine Reaktionsgeschwindigkeit nach etwa 300 Redox-Umwandlungen merklich nach. Das Anilinohydrochinon-Harz färbte die überstehende 1*N* schwefelsaure Lösung nach einigen Wochen leicht braun.

Reduktionsverlauf von Eisen(III)

Der Verlauf der Reduktion von Eisen(III) zu Eisen(II) und dessen Auswaschen in der Säule ist den Reduktionskurven in Abb. 4 und 5 zu entnehmen. Etwa Hundert mg Eisen(III) werden in wenig 1*N* Schwefelsäure an 8 g Leukomethylenblau-Harz reduziert, mit der gleichen Säure gewaschen und im Durchlauf Eisen(II) portionsweise mit Permanganat titriert. Nach Abb. 4 gelangt der Hauptanteil an Eisen(II) bereits in die ersten 80 ml Durchlauf. Zum vollständigen Auswaschen genügen 150 ml. Zwei gleiche, hintereinander geschaltete Säulen mit der doppelten Harzmenge brauchen kaum mehr Waschflüssigkeit. Die Übereinstimmung der zwei Reduktionskurven aus getrennten Versuchen in Abb. 4 zeigt die gute Reproduzierbarkeit der Reduktion in der Säule.

Das Ferrocen-Harz ermöglicht noch etwas schärfere Elutionsbanden (Abb. 5, Kurve *d*). Hier benötigt die doppelte Eisenmenge in einer um 40% längeren Säule mit 11 g Harz (Kurve *c*) etwa 40 ml Waschlösung mehr. In allen Fällen genügen 250 ml vollauf.

Durchbruchskurven für Gesamteisen

Die entsprechenden Versuche mit radioaktiv markierter Eisen(III)-lösung ergaben nach Abb. 6 im Durchlauf des Leukomethylenblau-, Ferrocen-, bzw. Anilinohydrochinon-Harzes nur mehr analytisch vernachlässigbare Konzentrationen von 0,03; 0,06; 0,6 μg Gesamteisen pro ml. Auch hier ist die Elutionsbande am Ferrocen-Harz schärfer, hingegen läßt sich das Leukomethylenblau-Harz etwas schneller eisenfrei waschen.

Adsorption von Eisenspuren

In einem weiteren Versuch verblieben im ungünstigsten Fall des Anilinohydrochinon-Harzes nach Waschen mit 250 ml $1N$ Schwefelsäure nur etwa 0,07 μg Eisen auf der Säule. Damit ist nachgewiesen, daß eine Übertragung des Verfahrens auch in den Mikromaßstab möglich ist. Unter vorliegenden Bedingungen sind Reste von ionenaustauschenden Gruppen am Redox-Harz ohne Wirkung. Die Konzentration der gebundenen Eisenspuren steigt zum Säulenende linear an. Das läßt den Schluß zu, daß längeres Auswaschen noch weitgehende Elution erlaubt. Auch am oberen Quarzwattebauch, gefetteten Schliff sowie Auslaufrohr verblieben nur $\leqslant$0,09; $\leqslant$0,06; $\leqslant$0,02 μg Eisen.

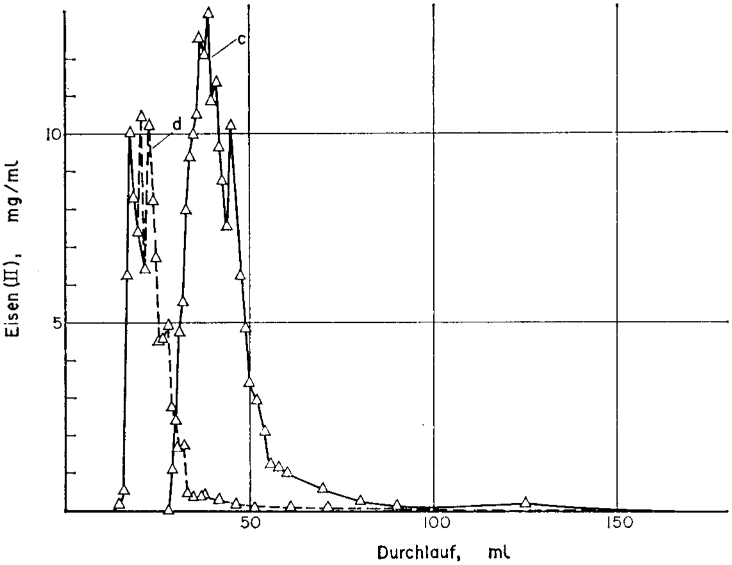


ABB. 5.—Reduktionskurven für Eisen(III) am Ferrocen-Redoxit. Reduktion von(*c*) 203,2 mg Fe(III) an 11,0 g Ferrocen-Harz in 6,70 ml $1N$ Schwefelsäure (Säule 340 × 12 mm), (*d*) 101,6 mg Fe(III) an 7,50 g Harz (Säule 240 × 12 mm) i jeweils 0,5 ml/min.

Durchlaufgeschwindigkeit

Sie darf maximal für das Leukomethylenblau-Harz 0,5 ml/min und für das Ferrocen-Harz 0,8 ml/min betragen. Das wesentlich langsamer reagierende Anilinohydrochinon-Harz erlaubt nur Durchlaufgeschwindigkeiten von unter etwa 0,2 ml/min.

Eisenkonzentration

Sie hat einen untergeordneten Einfluß. Jedoch ergaben bei 200 mg Fe an 11 g Ferrocen-Harz Volumina der aufgegebenen Eisen(III)-lösung von 90 ml an aufwärts zunehmende Minusfehler.

Nutzbare Reduktionskapazität

Sie beträgt für die angegebene Säule mit 8 g Leukomethylenblau-Harz etwa 120 mg Eisen(III), entsprechend 0,23 mMol/g oder 85% ihrer Gesamt-Kapazität. Dieser Wert liegt im Vergleich zu 60–80% bei Ionenaustauschern^{22} günstig.

Temperatur

Änderungen zwischen +10 und +25° waren ohne sichtbaren Einfluß. Stärkere Temperaturerhöhung läßt jedoch bei langsamen Redoxreaktionen eine merkliche Erhöhung der Reaktionsgeschwindigkeit und damit Verbesserung des Säulenbetriebes erwarten.

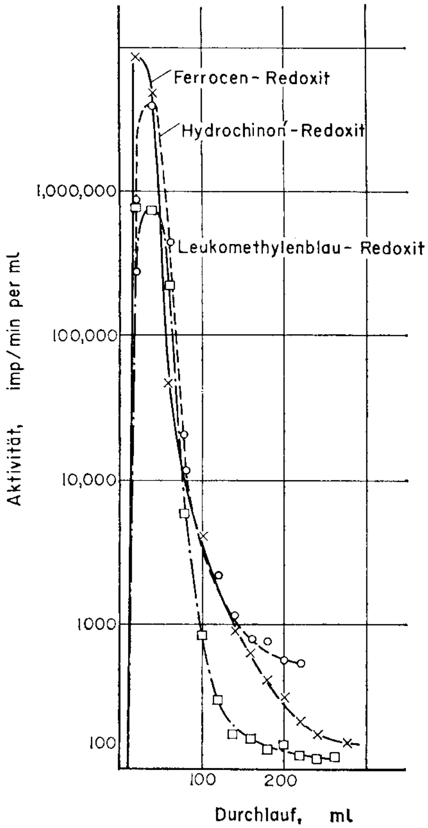


ABB. 6.—Durchbruchskurve für Eisen(II + III) einer mit ^{59}Fe markierten Eisen(III)-Lösung.
Leukomethylenblau- (8,0 g), Ferrocen- (7,5 g) und Anilinohydrochinon- (11 g) Redoxite in 240 × 11 mm Säulen; 6,70 ml 1*N* schwefelsure, radioaktiv markierte Eisen(III)-sulfatlösung (15 mg Fe/ml) jeweils mit 0,5 ml/min filtriert und mit 250 ml 1*N* Schwefelsäure gewaschen. 10^3 Impulse entsprechen 0,61 μg Eisen.

pH-*Wert und Lösungsmittel*

Die für die Reduktion der Eisen(III)-Lösung maßgebenden Redoxpotentiale ändern sich mit pH-Wert, Komplexbildung oder Fällung in der Lösung. Das zeigt deutlich der Unterschied zwischen verschiedenen Mineralsäuren:

Schwefelsäure. Unter Versuchsbedingungen lassen sich 100 mg Eisen(III) am Leukomethylenblau-Harz in 0,5 bis 10*N* oder 200 mg am Ferrocen-Harz in 0,5 bis 5*N* Schwefelsäure quantitativ reduzieren und damit bestimmen. Höhere Säurekonzentrationen führten im zweiten Fall zu Überwerten.

Salzsäure. Unter sonst gleichen Bedingungen gelingt hier die quantitative Bestimmung nur in dem schmalen Bereich von 1 bis 2*N*. Ober- und unterhalb treten starke Minusfehler auf. Oberhalb von 7 bis 8*N* wird auch die cerimetrische Titration unmöglich, über 10*N* beginnt Chlorentwicklung in der Säule. Weitergehende Reduktion gelingt jedoch auch hier in längeren Säulen. Salzsäure ist aber grundsätzlich infolge der Bildung von Chloroferrat(III)-Komplexen ungünstiger als Schwefel- oder Perchlorsäure.

Phosphorsäure. Unter analogen Bedingungen bewirkt 0,5 bis 15*N* Phosphorsäure von 25 bis 51% ansteigende Minusfehler. Sie beruhen auch hier auf zunehmender Bildung von Phosphatoferrat(III)-Komplexen. In der Säule vorübergehend ausfallende weiße Niederschläge—vermutlich Eisenphosphat—lösen sich beim Waschen mit 1*N* Schwefelsäure wieder auf. 15*N* Phosphorsäure greift das Leukomethylenblau-Harz an. Infolgedessen liefert hier die cerimetrische Bestimmung falsche Werte.

Kanalbildung

Die in Ionenaustauschersäulen auftretenden Kanäle sind meist zunächst nicht sichtbar. Sie können jedoch am Leukomethylenblau-Harz infolge des starken Farbumschlages während der Oxydation von hellbraun nach blauschwarz mit dem Auge gut beobachtet werden. Die grün (Mischfarbe) gefärbten Kanäle wandern der Front des oxydierten Harzes mehr oder weniger stark voraus.

Bei den untersuchten Fällen verringerte sich die störende Kanalbildung einmal mit steigender H^+-Konzentration und zum anderen bei konstanter H^+-Konzentration mit zunehmender Bildung von Ferrat(III)-Komplexen. So traten bei 0,05*N* Schwefelsäure in der Übergangsschicht bis zu mehrere Zentimeter lange Bänder auf, bei 10*N* Phosphorsäure war die wandernde Front bis auf 1–2 mm scharf zusammengezogen. Die Kanalbildung läßt sich außerdem herabsetzen durch Verwendung kleinerer Korngrößen des Redoxites, gleichmäßigere Packung und sorgfältigere Justierung der Säule, Aufteilung einer überlangen Säule in mehrere kleine, ferner langsamere Durchlaufgeschwindigkeit und möglicherweise Beschleunigung der Reaktion durch Temperaturerhöhung.

Modellbestimmungen

Unter den vorausgehend ermittelten optimalen Reduktionsbedingungen wurden oxydimetrische Modellbestimmungen reiner Eisen(III)-Lösungen ohne und mit Zusatz von Fremdelementen ausgeführt.

Reine Eisen(III)-Lösungen

Die potentiometrische Titration des in den Durchlauf gelangten Eisen(II) mit 0,1*N* Cer(IV)-sulfat ergab für reine Lösungen von Eisen(III)-sulfat in 1*N* Schwefelsäure für jeweils *n* Bestimmungen folgende Standardabweichungen *s* und Variationskoeffizienten *V* (relative Standardabweichung):[23]

TABELLE I.—CERIMETRISCHE BESTIMMUNG REINER EISEN(III)-LÖSUNGEN

Redoxit	Gegeben, *mg*	Eisen(III) gefunden, *s*, *mg*	*V*%	*n*	Bemerkungen
Leukomethylenblau-Harz	100,1	±0,14	±0,14	12	
	200,2	±0,25	±0,12	4	(a)
Ferrocen-Harz	101,6	±0,04	±0,04	6	(b)
	194,5	±0,10	±0,05	4	(a, b)
	203,2	±0,09	±0,04	21	(a, b)

8 g Leukomethylenblau-Harz (240 × 12 mm), 11 g Ferrocen-Harz (350 × 11 mm) i Eisen (III)-sulfat in 1*N* Schwefelsäure (15,2 mg Fe/ml); 2,2 ml/min; 250 ml 1*N* Schwefelsäure; 20 – 23°C
(a) 2 Säulen hintereinander; (b) Dosierung der Eisenlösung mit Kolbenpipette.

Die scheinbar höhere Präzision der Bestimmung am Ferrocen-Harz ist dadurch bedingt, daß die relativ konzentrierte Eisen(III)-Lösung mit einer Kolbenpipette anstatt einer normalen 10 ml-Bürette vorgelegt wurde. Sie ist grundsätzlich auch am Leukomethylenblau-Harz zu erreichen. Gelegentliche Korrekturen für Blindbestimmungen an einzelnen Harz-Chargen sind bereits vorgenommen. Zwei Bestimmungen von 100 mg Eisen(III) an 11 g Anilinohydrochinon-Harz ergaben bei entsprechend verringerter Durchlaufgeschwindigkeit Fehler von etwa + 0,2%.

Einfluß von Fremdelementen

In Übereinstimmung mit den Aussagen des theoretischen Teiles wird die Eisenbestimmung (Tabelle II) nicht gestört durch Alkali- und Erdalkali-Ionen, Zink, Mangan(II), Nickel(II), Kobalt(II), Aluminium, Seltene Erden, Chrom(III), Cadmium, Thallium(I), Zirkon und Thorium sowie bemerkenswerterweise auch Kupfer(II), Wismut(III), Titan(IV), Zinn(IV), Cer(IV) und Arsen(V). Die letztgenannten 6 Elemente werden durch Metallreduktoren ebenfalls reduziert und stören daher dort die oxydimetrische Bestimmung von Eisen.

TABELLE II.—EISEN(III)-BESTIMMUNG NEBEN NICHT STÖRENDEN BEGLEITELEMENTEN

Eisen, *mg*		Fehler, %	Fremdionenzusatz	
Gegeben	Gefunden		Ion	Salz
8 g Leukomethylenblau-Redoxit, Säule 240 × 10 mm:				
150,0	150,3	+0,2	Na^+	750 mg Na_2SO_4
150,0	150,4	+0,3	Na^+	5000 mg $Na_2{}^2SO_4$
150,0	150,1	+0,1	Mg^{2+}	150 mg $MgSO_4 \cdot 7\,H_2O$
150,0	150,3	+0,2	Zn^{2+}	150 mg $ZnSO_4 \cdot 7\,H_2O$
150,0	149,9	−0,1	Mn^{2+}	750 mg $MnSO_4 \cdot H_2O$
150,0	150,6	+0,4	Co^{2+}	750 mg $CoSO_4 \cdot 7\,H_2O$
150,0	149,8	−0,1	Ni^{2+}	750 mg $NiSO_4 \cdot 7\,H_2O$
100,1	100,2	+0,2	Cr^{3+}	750 mg $KCr(SO_4)_2 \cdot 12H_2O$
150,0	150,5	+0,3	Cr^{3+}	750 mg $KCr(SO_4)_2 \cdot 12H_2O$
150,0	150,1	+0,1	Al^{3+}	750 mg $AlCl_3 \cdot 6\,H_2O$
100,1	100,3	+0,2	TiO^{2+}	750 mg $TiO\,(SO_4)_2$
150,0	150,2	+0,1	Cd^{2+}	750 mg $CdSO_4 \cdot 8/3\,H_2O$
150,0	150,0	0,0	Cu^{2+}	750 mg $CuSO_4 \cdot 5\,H_2O$
150,5	150,2	−0,1	Bi^{3+}	750 mg $Bi(NO_3)_3 \cdot 5\,H_2O$
150,0	150,1	+0,1	Sn^{4+}	750 mg $Sn(SO_4)_2 \cdot 4\,H_2O$
100,1	100,0	−0,1	As(V)	750 mg Na_2HAsO_4
100,1	100,0	−0,1	Ce^{4+}	750 mg $Ce\,(SO_4)_2 \cdot 4\,H_2O$
11 g Ferrocen-Redoxit, Säule 340 × 10 mm:				
194,46	194,51	+0,03	Na^+	500 mg $Na_2SO_4 \cdot 10\,H_2O$
	194,57	+0,06	K^+	500 mg K_2SO_4
	194,51	+0,03	$NH_4{}^+$	500 mg $(NH_4)_2SO_4$
			Mg^{2+}	500 mg $MgSO_4 \cdot 7\,H_2O$
			Li^+	500 mg LiCl
194,46	194,51	+0,03	Mn^{2+}	500 mg $MnSO_4 \cdot 7\,H_2O$
	194,68	+0,08	Zn^{2+}	500 mg $ZnSO_4 \cdot 7\,H_2O$
	194,57	+0,06	Ni^{2+}	500 mg $NiSO_4 \cdot 7\,H_2O$
			Co^{2+}	500 mg $CoSO_4 \cdot 7\,H_2O$
194,46	194,51	+0,03	Al^{3+}	500 mg $Al_2(SO_4)_3 \cdot 18\,H_2O$
	194,62	+0,08	Cu^{2+}	500 mg $CuSO_4 \cdot 5\,H_2O$
	194,51	+0,03	Cd^{2+}	500 mg $CdSO_4 \cdot 8/3\,H_2O$
0,0	0,0	—	Ti(IV)	500 mg $Ti(SO_4)_2$
			Zr^{4+}	500 mg $ZrO(NO_2)_2$
			Th^{4+}	500 mg $Th(NO_3)_4$
			Tl^+	500 mg Tl_2SO_4
0,0	0,0	—	Nd^{3+}	100 mg Nd_2O_3
			Pr^{3+}	100 mg Pr_2O_3
			Sm^{3+}	100 mg Sm_2O_3
			Y^{3+}	100 mg Y_2O_3
0,0	0,0	—	As(V)	250 mg Na_2HAsO_4
0,0	0,0	—	Be^{2+}	250 mg $Be(CH_3COO)_2$
0,0	0,0	—	Cr^{3+}	500 mg $Cr_2(SO_4)_3 \cdot aq$

(Versuchsbedingungen wie in Tabelle I.).

Zusammen mit Eisen(III) werden durch die Redoxite Vanadin(V) zu (III/IV), Molybdän(VI) zu (V/VI), Spuren von Uran(VI) zu (IV) und Cer(IV) zu (III) reduziert. Mit Ausnahme des letzteren stören diese Begleitelemente die Bestimmung von Eisen(III).

ANWENDUNGEN

Analyse von Schlacke und Erz[14]

Die untersuchten Stoffe, je eine Martinschlacke, ein Schwedenerz und ein Agglomerat enthielten nach Werksangaben 13,4; 62,6; 61,0% Eisen. Die Reduktion am Zink-Reduktor mit anschließender Titration mit Permanganat ergab 13,7; 62,8; 61,6% Eisen. Reduktion an dem früher verwendeten, noch ausblutenden Leukomethylenblau-Harz und Titration mit Permanganat[14] führten im Mittel von jeweils 3 Bestimmungen zu 13,8; 63,1; 62,0% Eisen.

Eisenbestimmung in Stahl

Der als Beispiel gewählte hochlegierte Stahl X 10 Cr, Ni, Nb 18/9 (AISI Nr. 347) enthält etwa 70% Eisen, ferner u.a. Chrom, Nickel und Niob. Die cerimetrische Bestimmung nach der Redoxaustauschermethode führte zu folgendem Ergebnis:

TABELLE III.—BESTIMMUNG DES EISENS IN STAHL

Redoxit	Einwaage, *mg*	Eisengehalt, *mg*		Fehler %	
		theor.	gefunden	abs.	rel.
Leukomethylen-blau-Harz	113,54	69,05	$69{,}3_0$	+0,25	+0,4
	113,54	69,05	$69{,}2_5$	+0,20	+0,3
(2 × 8,0 g)					
Ferrocen-Harz	113,54	69,05	$69{,}2_5$	+0,20	+0,3
(11 g)	113,54	69,05	$69{,}3_0$	+0,25	+0,4

Die gefundenen Eisenwerte liegen scheinbar um 0,3 bis 0,4% zu hoch. Da jedoch der theoretische Gehalt nach einer der üblichen Restmethoden bestimmt worden war, entsprechen die nach vorliegender Direktmethode gefundenen Werte dem tatsächlichen Gehalt wahrscheinlich besser.

Arbeitsvorschrift

Man löst 500–600 mg Metallspäne in 50 ml 6*N* Salzsäure unter Zugabe von 10 Tropfen 30% igem H_2O_2 und 10—20 Tropfen konz. Salpetersäure bei Siedetemperatur. Ausgeschiedene Kieselsäure und Kohlenstoff werden abfiltriert. Das auf 10 bis 15 ml eigeengte Filtrat wird dann in eine Lösung von etwa 15 g Natriumhydroxid (*p.a.*) und 3 g Natriumperoxid in 100 ml Wasser gegeben und 10 Minuten mit Siedestäbchen gekochrt. Hierauf filtriert man das evtl. noch $TiO_2 \cdot xH_2O$ enthaltende Eisen(III)-hydroxid ab und wäscht dreimal mit 20–30 ml 60°-heißem Wasser. Der Niederschlag wird vom Filter mit etwa 80–100 ml heißer 6*N* Saltsäure gelöst und dieses mit 50 ml heißem Wasser nachgespült. Das auf 10–15 ml eingeengte Filtrat wird nochmals wie oben gefällt und der Niederschlag gelöst. Man wäscht mit 50 ml heißem Wasser nach und engt mit 5 ml konz. Schwefelsäure bis zum Auftreten von SO_3-Nebeln ein. Dann füllt man auf 100 ml auf. Die etwa 1*N* schwefelsaure Eisenlösung wird nun mit einer Spritzpipette entnommen und nach der allgemeinen Arbeitsvorschrift in zwei hintereinander geschalteten Säulen mit je 8,0 g Leukomethylenblau-bzw. einer Säule mit 11 g Ferrocen-Harz reduziert. Im Durchlauf wird Eisen(II) potentiometrisch mit 0,1*N* Cer (IV)-sulfat titriert.

DISKUSSION

1. Elutionsstabile Redoxite ermöglichen oxydimetrische Bestimmungen von gelösten Redoxsystemen. Im Gegensatz zu Metallreduktoren und den meisten Redox-Ionenaustauschern wird die Lösung tatsächlich nicht durch Ionen des Reagenz verunreinigt. Für das untersuchte Beispiel der Reduktion von Eisen(III) zu (II) in 1*N* Schwefelsäure ($E_{50\%} = +0{,}68$ V) eignen sich auf Grund von Realpotential, Reaktionsgeschwindigkeit, Stabilität sowie deutlich sichtbarem Farbumschlag vor allem das Leukomethylenblau- und Ferrocen-Harz ($E_{50\%} = +0{,}42$ bzw. $+ 0{,}47$ V).

2. Nach Lage ihrer Redoxpotentiale sind die meisten bisher bekannten Redoxite (Abb. 27 in Citat 9) mildere und damit wesentlich selektivere Reduktionsmittel als Metallreduktoren. Im vorliegenden Fall wird die Reduktion von Eisen(III) am Redoxit im Gegensatz zum Metallreduktor nicht durch Kupfer(II), Wismut(III), Titan(IV), Zinn(IV) und Arsen(V) gestört. Ein Redoxit mit dem Redoxpotential des Nontronites ($E_{50\%} = +0{,}65$ V) sollte selektiv nur Eisen(III) und Vanadin(V) neben allen anderen in Zitat[25] (dort Abb. 27) aufgeführten Redoxsystemen reduzieren.

3. Ein Potentialvergleich zwischen Redoxiten und gelösten Redoxsystemen der elektrochemischen Spannungsreihe erlaubt qualitative Vorhersagen über störende Fremdionen und halbquantitative über den Grad der Reduzierbarkeit beliebiger Redoxsysteme in unterschiedlichem Medium. Beim betrachteten System Eisen (III/II) stimmten Vorhersage und Experiment durchweg gut überein. Das zeigt den Wert[9,24] der Messung von Realpotentialen $E_{50\%}$ der Redoxite auch dann, wenn sie wegen irreversibler Oxydationsanteile, teilweise nicht streng reversibler Gleichgewichtseinstellung und etwas unterschiedlichem Medium für thermodynamische Berechnungen nicht brauchbar sind.

4. Geeignete Redoxite eröffnen wegen ihrer höheren und gut abgestuften Redoxpotentiale vielleicht die Möglichkeit, Transurane aus höheren Oxydationsstufen in einem Schritt sofort in mittlere zu überführen. Metallreduktoren reduzieren fast immer zur niedrigsten Stufe.

5. Im untersuchten Beispiel wird die Reduktion von Eisen(III) in der Reihenfolge Perchlor-, Schwefel-, Salz-, Phosphor-, Flußsäure sowie für jeweils eine dieser Mineralsäuren mit steigender H^+-Konzentration schwieriger. Das ist durch Stabilisierung von Fe(III) infolge Komplexbildung bzw. Verschiebung des Redoxgleichgewichtes (2) durch steigende H^+-Konzentration zu erklären. Die Selektivität der Redoxite läßt sich somit auch durch geeignete Komplexbildung und Einstellung des pH-Wertes der jeweiligen Aufgabe anpassen.

6. Die allgemeinen Arbeitsbedingungen der analytischen Anwendung von Redoxaustauschern entsprechen in vorliegendem Falle hinsichtlich Säulenbetrieb, Gestalt der Durchbruchskurve, Austauschkapazität, optimaler Korngröße und Kanalbildung denen der Ionenaustauscher. Ähnliche Durchlaufgeschwindigkeiten erfordern jedoch die Verwendung etwas längerer Säulen mit einer größeren Austauschermenge. Allerdings reagierte das Redox-Harz vom Hydrochinon-Typ langsamer.

7. Im Gegensatz zum Ionenaustausch erfordert die Regeneration der Säulen nur wenig mehr als die stöchiometrische Menge an Reduktions-bzw. Oxydationsmitteln.[11] Der beim Ionenaustausch erforderlichen hohen Konzentration an Regenerationsmittel entspricht hier ein ausreichend hohes bzw. niedriges Redoxpotential.

Das Auswaschen des Reduktionsmittels muß verständlicherweise im allgemeinen unter Ausschluß von Luftsauerstoff in Waschwasser und Apparatur erfolgen, wobei sich die mit aufsteigendem Flüssigkeitsstrom arbeitende Austauschersäule nach Abb. 2 besonders bewährt hat.[11]

Organische Redox-Harze sind zwar gegen so starke Reduktionsmittel wie Dithionit ausreichend stabil, werden jedoch von starken Oxydationsmitteln leicht irreversibel angegriffen.[20,25] Demgegenüber sind rein anorganische Redoxaustauscher auch gegen starke Oxydationsmittel vollständig stabil.[15,26]

8. Reste von ionenaustauschenden Gruppen stören häufig die analytische Anwendung von Redoxaustauschern. Die coulometrisch und radiometrisch bestimmten

Kapazitäten für derartige unerwünschte, bei der Synthese verbleibende Gruppen, lagen bei den verwendeten Redox-Harzen in der Größenordnung von nur 0,04 mEq/g.[9] Bei der Reduktion von Eisen(III) machte sich in 1*N* Schwefelsäure jedoch keinerlei störender Kationenaustausch bemerkbar. Anionenaustauschende Restgruppen können dagegen während der Regeneration und des Waschens Spuren Regenerationsmittel, z.B. Dithionit-Anionen binden. Bei der späteren Elution wird dadurch die anschließende oxydimetrische Titration gestört. Soferne man daher bei der Synthese von Redox-Harzen nicht vermeiden kann, daß das Harzgerüst unerwünschte positiv oder negativ geladene Gruppen enthält, kann man wie oben beschrieben, versuchen, Dithionitspuren durch Waschen mit schwach sauerstoffhaltigem Wasser rasch weg zu oxydieren oder man muß—wie bei Metallreduktoren—Blindbestimmungen ausführen.

Die Arbeit wurde im Jahre 1960 ausgeführt. Für die Einarbeitung in radiochemische Arbeitsmethoden danken wir herzlich Herrn Prof. Dr. Dr. H. Graul, Dr. Schaumlöffel und Dipl. Chem. Steiner, Isotopenabteilung der Strahlenklinik der Universität Marburg/Lahn, sowie für materielle Unterstützung dem Herrn Bundesminister für wissenschaftliche Forschung, der Deutschen Forschungsgemeinschaft und Herrn Dir. Dr. W. Hagge, Farbenfabriken Bayer, Leverkusen.

Summary—As an example of the reduction of cations on redox exchangers, the reduction of 50–200 mg of iron(III) on leucomethyleneblue- and ferrocene-resin of a polystyrene type, is described. The iron(II) was titrated potentiometrically with cerium(IV). Under optimum conditions, the standard deviation was 0·04–0·14 mg. In contrast to their behaviour on metal reductors, there is no interference from Cu^{2+}, Bi^{3+}, TiO^{2+}, Sn^{4+}, Ce^{4+} and AsO_4^{3-}. The method has been used for the direct determination of iron in ores, slags and special steels.

Résumé—Comme exemple de la réduction de cations sur des échangeurs redox, on décrit la réduction de 50–200 mg de fer(III) sur une résine bleu de leucométhylène et ferrocène d'un type polystyrène. Le fer(II) a été titré potentiométriquement au cérium(IV). Dans les conditions optimales, l'écart type est de 0,04–0,14 mg. En contraste avec leur comportement sur des réducteurs métalliques, il n'y a pas d'interférence de Cu^{2+}, Bi^{3+}, TiO^{2+}, Sn^{4+}, Ce^{4+} et AsO_4^{3-}. On a utilisé la méthode pour le dosage direct du fer dans les minerais, scories et aciers spéciaux.

LITERATUR

1. I. M. Kolthoff, R. Belcher, V. A. Stenger und G. Matsuyama, *Volumetric Analysis*—III, Interscience, New York, 1957.
2. W. Petzold, *Die Cerimetrie*, Verlag Chemie, Weinheim/Bergstr., 1955.
3. H. W. Stone und D. N. Hume, *Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 598.
4. C. Yoshimura, *Nippon Kagaku Zasshi*, 1952, **73**, 362, 701; 1953, **74**, 116, 747, 818i, 1955, **76**, 409.
5. W. I. Stephen, *Ind. Chemist*, 1953, **29**, 31, 79, 169.
6. B. Sansoni, *Naturwissenschaften*, 1952, **39**, 281.
7. H. G. Cassidy, *Proc. Natl. Acad. Sci. U.S.*, 1952, **38**, 934.
8. G. Manecke, in *Methoden der organischen Chemie*, Ed. Houben-Weyl, 4. Aufl., I.1.S. 609.
9. B. Sansoni, *Neue chemische Arbeitsmethoden durch heterogene Reaktionen: Redoxaustauscher und numerometrische Titration*, Verlag UNI-Druck, München 1968.
10. *Idem*, XIII.IUPAC-Kongreß, Stockholm, 1953, Abstr. S. 52.
11. *Idem*, *Diss.*, Univ. München, 1956.
12. L. Erdey, J. Inczédy und I. Markovits, *Talanta*, 1960, **4**, 25.
13. J. Inczédy, *Acta Chim. Acad. Sci. Hung.*, 1961, **27**, 185.
14. K. Dorfner, *Diss.*, Marburg/Lahn, 1959.

15. B. Sansoni und O. Sigmund, *Angew. Chem.*, 1962, **74,** 695.
16. *Idem*, *ibid.*, 1961, **73,** 299.
17. O. Sigmund, *Diss.*, Marburg/Lahn, 1963.
18. R. Bock und H. Herrmann, *Z. Anorg. Allgem. Chem.*, 1953, **273,** 1.
19. B. Sansoni, in *Anomalien bei Ionenaustauschervorgängen*, 1961, S. 411, Akademieverlag, Berlin, 1962.
20. B. Sansoni, O. Sigmund, E. Bauer, W. Wiegand und L. Perera, *Angew. Chem.*, 1961, **73,** 763.
21. *Komplexometrische Bestimmungsmethoden mit Titriplex*, 3. Aufl., Merck, Darmstadt.
22. O. Samuelson, *Ion Exchangers in Analytical Chemistry*, Almquist und Wiksell, Stockholm, 1952.
23. G. Gottschalk, *Statistik in der quantitativen chemischen Analyse*, Ferdinand Enke Verlag, Stuttgart, 1962.
24. B. Sansoni und O. Sigmund, unveröffentlicht.
25. B. Sansoni und L. Perera, unveröffentlicht.
26. R. Winkler, *Diss.*, Marburg/Lahn, 1966: B. Sansoni, R. Winkler und K. Starke, *Angew. Chemie*, 1966, **78,** 645.
27. B. Sansoni, *Chemiker Z.*, 1954, **78,** 580.
28. *Idem*, *Chem. Tech.* (*Berlin*), 1958, **10,** 580.

Talanta, 1970, Vol. 17, pp. 987 to 997. Pergamon Press. Printed in Northern Ireland

REDOXAUSTAUSCHER UND IHRE ANWENDUNGEN—XVI

ENTFERNUNG VON WASSERSTOFFPEROXID AUS WÄSSERIGER LÖSUNG AN REDOX- UND IONENAUSTAUSCHERN*

BRUNO SANSONI und ELISABETH BAUER-SCHREIBER
Institut für Strahlenschutz der Gesellschaft für Strahlenforschung mbH.,
Radiochemisch-analytische Abteilung, 8042 Neuherberg bei München und
Chemisches Institut der Universität Marburg/Lahn

(*Eingegangen am* 6. *Januar* 1966. *Angenommen am* 14. *April* 1970†)

Zusammenfassung—Wasserstoffperoxid läßt sich aus wässeriger Lösung durch Reduktion an einem mit Dithionit oder vor allem Sulfit beladenem Anionenaustauscher (Lewatit M 600) sowie durch katalytische Zersetzung am OH^--Anionenaustauscher halbkontinuierlich und automatisch entfernen. Dazu werden einfache Säulenanordnungen beschrieben, die sowohl den Ausschluß störender Labordämpfe als auch einen quasi-Säulenbetrieb bei durch Gasentwicklung stark aufgewirbelter Austauscherschicht ermöglichen.

WASSERSTOFFPEROXID stört die Weiterverarbeitung von Lösungen in Strahlenchemie, Kerntechnik und Analytik.[1] Es bildet sich durch Enzymeinwirkung, hemmt aber das Wachstum anaerober Bakterien und kann den zur Bildung von Carcinomen führenden krankhaften Gärungsstoffwechsel der Zelle auslösen. Nicht zuletzt beruht die Strahlenschädigung des Organismus teilweise mit auf intermediär gebildeten Peroxiden und OH^--Radikalen.[2]

Wasserstoffperoxid kann durch Reduktion, Oxydation, katalytische Zersetzung oder Abtrennung aus Lösungen entfernt werden.[2] Im folgenden interessierte die Reduktion des Wasserstoffperoxides an Redoxaustauschern als Teilschritt der Entfernung von gelöstem Sauerstoff aus Wasser. Dabei wurde die katalytische Zersetzung an OH^--Anionenaustauschern beobachtet.

Daraus ergeben sich Anregungen für die Entfernung radiolytisch gebildeter Peroxide im Kühlwasserkreislauf von Atomreaktoren. Verschiedene Membranen der physiologischen Zelle haben den Charakter von Redoxaustauschern.[3] Overberger[4] hat Redoxite als unlösliches Prophylaktikum für Strahlenschäden im Organismus zur Reduktion von $.OH^-$-Radikalen und Peroxiden verwendet.

Wasserstoffperoxid hat eine negative Bildungsenergie von −134 kJ/Mol bei 25°. Seine Aktivierungsenergie von etwa 75 kJ/Mol hindert den Zerfall. Die kathodische Reduktion verläuft in saurer Lösung[5,6] nach

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \qquad E^\circ = +1{,}77\,V, \tag{1}$$

---

* XV. Mitteilung B. Sansoni W. Wiegand, *Talanta*, 1970, **17**, 973. Vorgetragen Chemische Gesellschaft Marburg/Lahn (Januar 1960) und GDCH-Hauptversammlung Aachen, 1961 (Referat, *Angew. Chem.*, 1961, **73**, 763).

Herrn Dir. Dr. Walter Hagge, Leverkusen-Bayerwerk, zum 70. Geburtstag.

† Publication delayed at authors' request.

und in alkalischer[7] nach

$$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^- \qquad E^\circ = +0{,}88\ V. \tag{2}$$

Die katalytische Zersetzung

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2 \tag{3}$$

erfolgt besonders leicht in alkalischem Medium. Die Reaktionen (1) bis (3) verlaufen über Radikale.[7] Wasserstoffperoxid ist in wässeriger Lösung eine sehr schwache Säure[8] mit $K = 2{,}24 \cdot 10^{-12}$.

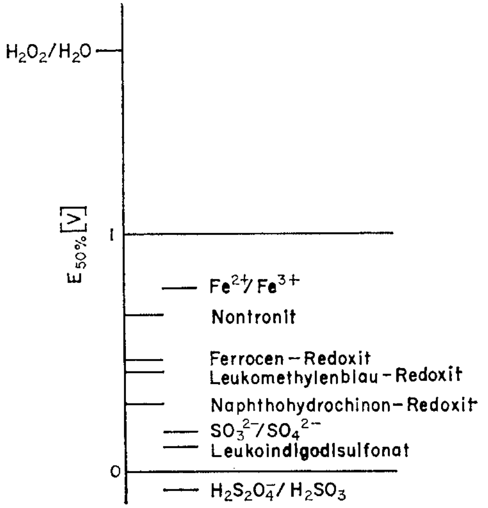


ABB. 1.—Vergleich der Redoxpotentiale von H_2O_2/H_2O und Redoxaustauschern. Normalpotentiale für H_2O_2/H_2O und gelöste Ionen,[5,6] Realpotentiale für Redox-Harze in 1N und für Nontronit in 0,01N Schwefelsäure.[11]

Nach Abb. 1 sollte Wasserstoffperoxid durch alle angegebenen Redoxaustauscher zu Wasser reduziert werden können. Für Anwendungen in salzfreier-Lösung genügen einfache Redox-Ionenaustauscher. Ihr Gerüst ist relativ beständig. Anionen wie Dithionit, Sulfit, Thiosulfat, Phosphit vermeiden die bei verschiedenen Kationen[9] sowie Redoxiten beobachtete störende katalytische Zersetzung.[10] Durch Oxydation gebildetes Sulfat ist indifferent und stört bei Elution durch salzhaltige Lösungen weniger als entsprechende Redox-Kationen. Die an den Reaktionen (1) bis (3) beteiligten Radikale können organische Redoxgruppen an Redoxiten irreversibel angreifen und diese unbrauchbar machen.

EXPERIMENTELLE TEIL

Geräte

Die Reduktionsversuche wurden in Schliffsäulen (180 × 10 mm nach Abb. 2) unter Ausschluß störender Laborluft ausgeführt. Die 300 ml-Erlenmeyerkolben stehen auf einem in entsprechender Höhe angebrachten Plexiglasstreifen. Die katalytische Zersetzung erfolgte in den Apparaturen nach Abb. 3 und 4. Sie erlauben bei nicht zu schneller Durchlaufgeschwindigkeit und etwas Übung auch bei starker Gasentwicklung einen quasi-Säulenbetrieb. In der Anordnung Abb. 3 entweichen die Gasblasen durch das Kapillarrohr. In Abb. 4 soll der schräg eintauchende Glasstab (1–2 mm Durchmesser) das Aufsteigen der Gasblasen erleichtern. In beiden Fällen dient das untere Drittel der Säulenfüllung als Sicherheit für etwa durchgebrochene Peroxidspuren.

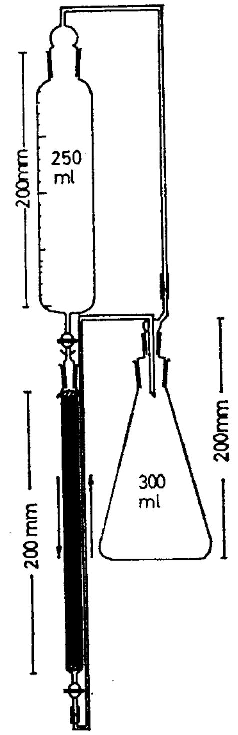


Abb. 2.—Schliffsäule mit Ausschluß störender Laborluft.

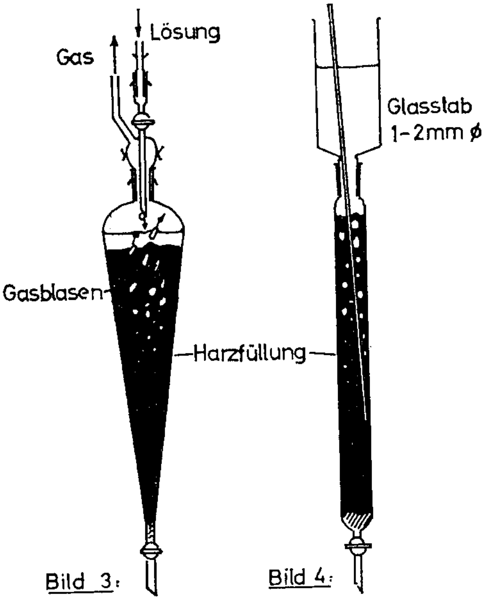


Bild 3:

Bild 4:

Abb. 3 und 4.—Apparaturen für quasi-Säulenbetrieb bei starker Gasentwicklung.

Außerdem wurden verwendet: Fraktionsteiler RadiRac (LKB) mit 10-ml Syphon, Polarograph Polarecord (Metrohm), Leitfähigkeitsmesser CDM II mit 0,2-ml Durchflußzelle(Radiometer).

Die Redoxaustauscheranlage[9,11] lieferte sauerstoffarmes Wachwasser mit $\sim 0{,}2\cdot 10^{-7}\,\Omega^{-1}.\,mm^{-1}$ $\leqslant 40\,\mu g\ O_2/l$ und pH 6,6–6,8 (bei 21 ± 1°). Gegebenenfalls kann auch ausgekochtes und mit N_2 gespültes vollentsalztes Waschwasser verwendet werden.

Redox-Ionenaustauscher

Ionenaustauscher. Stark saurer Lewatit S100 und stark basischer Lewatit M 600 werden wie üblich mit 4*M* Salzsäure in die H^+-bzw. Cl^--Form gebracht, sorgfältig eisenfrei, anschließend neutral gewaschen, an der Luft getrocknet und gesiebt. Ein Teil des Anionenaustauschers wird anschließend mit 2*M* Natriumlauge unter CO_2-Ausschluß in die OH^--Form übergeführt.

Die Anionenaustauschkapazität von Cl^--Lewatit M 600 ergab sich für die Siebfraktion 0,1–0,2 mm zu 3,27 mEq Cl^-/g Trockengewicht; 0,6–0,75 mm zu 3,18; 0,75–1,00 mm zu 3,22; ungesiebt zu 3,22 und ist damit innerhalb der Fehlergrenzen befriedigend konstant. Dagegen nahm der Feuchtigkeitsgehalt bei konstanter Luftfeuchtigkeit mit steigender Korngröße etwas zu: Korngröße 0,1–0,2 mm 16,5%; 0,2–0,3 mm 21,2%; 0,3–0,4 mm 22,7%; 0,4–0,5 mm 23,5% 0,5–0,6 mm 23,7%; 0,6–0,75 mm 23,5%; 0,75–1,00 mm 24,5%.

$S_2O_4^{2-}$-Anionenaustauscher. Jeweils 7,00 g lufttrockener Cl^--Lewatit M 600 (0,6–0,75 mm) werden in der Säule nach Abb. 2 mit 200 ml ammoniakalischer Dithionitlösung bei etwa 1 Tropfen/sec (3–4 ml/min) in die Dithionit-Form übergeführt und mit etwa 300 ml sauerstoffreiem Wasser dithionitfrei gewaschen. Dabei soll die oberste Harzschicht nicht mit Luft in Berührung kommen. Andernfalls muß mit jeweils konstantem Kapazitätsverlust gearbeitet werden. Die Sulfat-Form des Austauschers wird unmittelbar mit frischer Dithionitlösung regeneriert.

SO_3^{2-}-Anionenaustauscher. Entsprechend werden 7,00 g Cl^--Lewatit M 600 (0,6–0,75 mm) mit etwa 100 ml Sulfitlösung in die Sulfit-Form gebracht. Nach Oxydation wird das gebundene Sulfat ebenfalls mit 10%iger Natriumsulfit-Lösung ausgetauscht.

Reagenzien

Ammoniakalische Dithionitlösung. Jeweils kurz vor Gebrauch werden etwa 50 g $Na_2S_2O_4$ (gereinigt, Riedel-DeHaen in 1 Liter 1*M* Ammoniaklösung (chem. rein) gelöst.

Sulfitlösung. 100 g Na_2SO_3 (*p.a.*) in 1 Liter vollentsalztem Wasser.

Wasserstoffperoxidlösung. 30%iges H_2O_2 (Perhydrol, *p.a.*) wird kurz vor Gebrauch verdünnt und mit 0,1*N* Thiosulfat jodometrisch eingestellt.

Analytische Bestimmungen

Ionenaustauschkapazitäten wurden volumetrisch,[12] Redoxkapazitäten mit Eisen(III)-sulfat[11,13,14] Wasserstoffperoxid jodometrisch nach Kolthoff[15] und gelegentlich im Durchlauf auch polarographisch bestimmt.[16]

ERGEBNISSE

Nach Vorversuchen mit einer größeren Anzahl von Redox-Ionenaustauschern wurden die mit Dithionit und Sulfit beladenen Anionenaustauscher eingehender untersucht.

Reduktion am $S_2O_4^{2-}$-Anionenaustauscher

Der Dithionit-Anionenaustauscher ist nach Abb. 5 ausreichend stabil. Sene Reduktionskapazität verändert sich in der gut verschlossenen Säule während 24 Stunden kaum und sinkt nach 100 Stunden auf etwa die Hälfte.

In drei Versuchsreihen wurden zunehmende Volumina wässerige 0,1*N* Wasserstoffperoxidlösung an $S_2O_4^{2-}$-Lewatit M 600 in Säulen nach Abb. 3 unter möglichst konstanten Bedingungen reduziert. Abbildung 6 enthält das Ergebnis der Einzelversuche als Durchbruchskurve. Dabei wurde (*a*) die in der Säule entfernte und (*b*) im Durchlauf gefundene Wasserstoffperoxidmenge gegen die vorgegebene aufgetragen und jeweils als mEq H_2O_2 auf das Trockengewicht (g) des Austauschers bezogen. Der Sättigungswert von (*a*) ergibt eine Gesamt-Reduktionskapazität[17] von 2,6–2,7 mEq H_2O_2/g, der Durchbruchspunkt von (*b*) eine nutzbare Durchbruchskapazität[17] von 2,5 mEq H_2O_2/g. Die Abszissendifferenz des Sättigungs- und Durchbruchspunktes entspricht einer ausgenutzten Gesamt-Kapazität der Säule von etwa 95%. Für Ionenaustauscher werden 60–80% angegeben.[18] Dieser hohe Wert deutet auf rasche und vollständige Gleichgewichtseinstellung in jedem Säulenabschnitt.

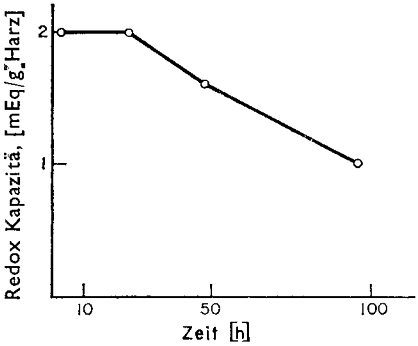


ABB. 5.—Stabilität von $S_2O_4^{2-}$-Permutit ES (5).
Säule 180 × 10 mm; 10 g Cl^--Permutit ES (0,3–0,5 mm) in $S_2O_4^{2-}$-Form; 20–25°C; diffuses Sonnenlicht.

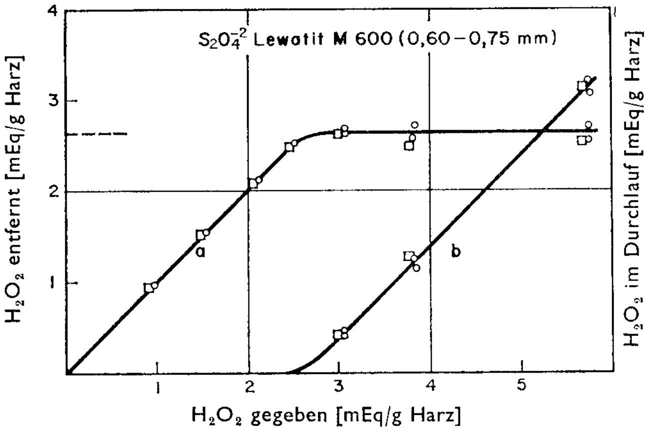


ABB. 6.—Reduktion von Wasserstoffperoxid an $S_2O_4^{2-}$-Lewatit M 600.
Säulen 180 × 10 mm (Abb. 2) mit 7,00 g lufttrockener Harzeinwaage an Cl^--Lewatit M 600; (0,6–0,75 mm); 1,1 ml/min; 24–25°C; diffuses Sonnenlicht.

Die gefundene Gesamt-Reduktionskapazität ist erheblich kleiner als die theoretisch für den Übergang von S(III) zu S(IV) zu erwartende von etwa 9,5 mEq/g. Das hat mehrere Gründe. Erstens enthielt frisch der Originalflasche entnommenes $Na_2S_2O_4$ (gereinigt, Riedel-DeHaen) nur etwa 74 Gew.-% des theoretischen Gehaltes an Dithionit, daneben 11% Thiosulfat und 12% Sulfit. Zweitens sinkt der Reduktionswert des am Austauscher gebundenen Dithionites infolge Oxydation der obersten Schichten durch den Luftsauerstoff in Apparatur und Waschwasser. Drittens ist im angewendeten schwach ammoniakalischen Medium die Beladung des Lewatit M 600 nicht mehr ganz vollständig. So führte eine Beladung mit wässriger, also schwach saurer Dithionitlösung zu Gesamt-Redoxkapazitäten von 3,4–3,8 mEqFe^{3+}/g. Viertens entstehen aus 1 Mol $S_2O_4^{2-}$, 2 Mol SO_3^{2-} bzw. SO_4^{2-}. Das bedeutet notwendigerweise eine teilweise Elution von Sulfit- bzw. Sulfat. Der an der Luft aufgefangene Durchlauf einer wässerigen Wasserstoffperoxidlösung enthielt je nach

Basizität des Anionenaustauschers 18 bis 24 Äquivalent-% der mit H_2O_2 gemessenen Gesamt-Reduktionskapazität als Sulfat bzw. Schwefelsäure. Damit erfolgt die Oxydation von Dithionit am Anionenaustauscher zwar sehr schnell, jedoch unübersichtlich.

In der ersten Versuchsreihe (o) von Abb. 6 wurde Cl^--Lewatit M 600 zunächst mit 2*M* Natronlauge in die OH^-- und dann erst mit ammoniakalischer Dithionitlösung in die $S_2O_4^{2-}$-Form übergeführt; in der zweiten und dritten wurde direkt in die $S_2O_4^{2-}$-Form gebracht. Die Übereinstimmung ist in Anbetracht der etwas erhöhten Raumtemperatur sowie des diffusen Sonnenlichtes (geringe katalytische Peroxidzersetzung an der Glaswandung) befriedigend. Das zeigt, daß auch ein Überspringen der OH^--Form vollständige Regeneration ermöglicht. Außerdem hat sich die Kapazität des Anionenaustauschers nach dreimaliger Oxydation–Reduktion nicht merklich verändert.

Reduktion am SO_3^{2-}-Anionenaustauscher

Der Sulfit-Anionenaustauscher reagiert nach

$$SO_3^{2-}\text{-Iat.} + H_2O_2 \rightleftharpoons SO_4^{2-}\text{-Iat.} + H_2O. \qquad (4)$$

Die Reaktion ist langsamer, aber einfacher und übersichtlicher als bei Dithionit. Infolge konstant bleibender Anionenladung wird die Lösung grundsätzlich nicht verunreinig. Sulfit erfordert überdies geringere Betriebskosten.

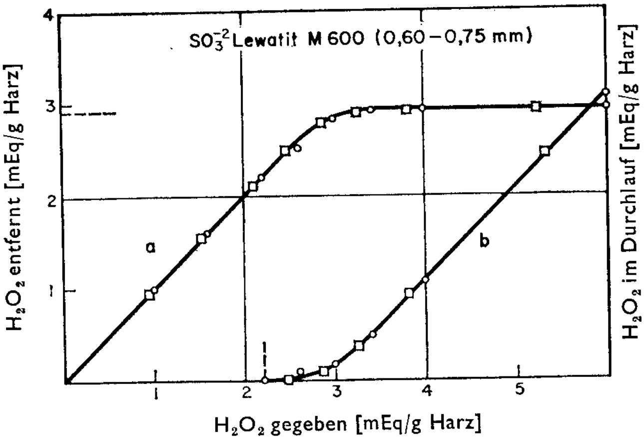


ABB. 7.—Reduktion von Wasserstoffperoxid an SO_3^{2-}-Lewatit M 600. 7,00 g lufttrockene Harzeinwaage an Cl^--Lewatit M 600; Korngröße; ungesiebt; sonst wie für Abb. 6.

Der Sulfit-Anionenaustauscher ist gegen Autoxydation so stabil wie eine entsprechend verschlossen aufbewahrte wässerige Sulfitlösung. Die Gesamt-Reduktionskapazität nimmt innerhalb von 44 Tagen nur um 6% ab. Auch das Gerüst des Anionenaustauschers ist ausreichend beständig. So blieb die Anionenaustauschkapazität von Lewatit M 600 nach 6 Redoxumwandlungen mit Sulfit bzw. 0,1*N* Wasserstoffperoxid mit 3,18 bis 3,19 $mEqCl^-$ g konstant. Die unter gleichen Bedingungen wie beim Dithionit-Anionenaustauscher aus Einzelversuchen zusammengesetzte *Durchbruchskurve* für etwa 1*M* Wasserstoffperoxidlösung zeigt Abb. 7. Die Gesamt-Reduktionskapazität beträgt nach Kurve (*a*) etwa 240 mg H_2O_2 pro Säule oder 2,9 mEq H_2O_2/g. Durchlauf erfolgt nach (*b*) ab 165 mg H_2O_2, entsprechend knapp 70% der Gesamt-Reduktionskapazität. Letzterer Wert entspricht durchaus denen des Ionenaustauschers, liegt aber niedriger als beim Dithionit-Anionenaustauscher. Das ist eine Folge der langsameren Oxydation des Sulfites.

Die gemessene *Gesamt-Reduktionskapazität* stimmt gut mit dem aus der Anionenaustauschkapazität berechneten Wert von 3,2 mEq H_2O_2/g überein. Die geringe Differenz ist durch teilweise Autoxydation des festen bzw. im oberen Säulenteil gebundenen Sulfites durch Luftsauerstoff sowie geringe Peroxidverluste infolge Zerfalls an den Glaswänden bedingt.

Die Werte aus zwei Versuchsreihen (Abb. 7) streuen erheblich weniger als beim Dithionit-Anionenaustauscher (Abb. 6). Das ist durch den übersichtlicheren Reaktionsverlauf und die geringere Reaktionsgeschwindigkeit der Sulfitoxydation mit Luftsauerstoff zu erklären. Auch hier kann die erschöpfte Sulfat-Form mit 5–10%iger Natriumsulfitlösung direkt regeneriert werden.

Eine Erhöhung der *Durchlaufgeschwindigkeit* von 0,1 auf 5 ml/min hat kaum Einfluß auf die mit einem H_2O_2-Überschuß bestimmte Gesamt-Reduktionskapazität. Ein schwacher Anstieg unterhalb von 0,5 ml/min wird nur durch die bei längerer Wartezeit spürbar werdende Selbstzersetzung des Wasserstoffperoxides an Gefäßwänden und Harzoberfläche vorgetäuscht. Andererseits hängt die wirklich nutzbare Durchbruchskapazität stärker von der Durchlaufgeschwindigkeit ab. Es kann aber auch hier die beim Ionenaustausch übliche von 1 ml/min angewendet werden.

Die *Korngröße* des Anionenaustauschers ist von 0,1 bis 1,0 mm praktisch ohne Einfluß auf die wie vorher bestimmte Gesamt-Reduktionskapazität. Streuungen sind wiederum durch langsam beginnende Selbstzersetzung des Peroxides bedingt.

Die *Konzentration* der Wasserstoffperoxidlösung ist im Bereich von 0,1–2,5*M* nach drei Versuchsreihen ohne Einfluß auf die in der Säule reduzierte Peroxidmenge.

Geringe Mengen an *Stabilisatoren* wie Diphosphat, Barbitursäure, Harnstoff, ferner Zusatz von 1% Phosphorsäure sowie 0,04*N* Schwefelsäure, aber auch 0,02*M* Natronlauge zeigten praktisch keinen Einfluß auf die Reduktion in der Säule.

Die störende Gasentwicklung durch Selbstzersetzung des Wasserstoffperoxides beginnt oberhalb etwa 25° deutlich zu werden. Bei $<$23–24° wurde nur gelegentlich schwache Gasentwicklung beobachtet. Sie störte den Säulenbetrieb nicht wesentlich.

Wasserstoffperoxid kann ohne Störungen am Sulfit-Anionenaustauscher nur in dem pH-Bereich von etwa 4,5 bis 7 reduziert werden. Im stärker sauren Gebiet wird Schwefeldioxid abgespalten, im stärker alkalischen tritt Selbstzersetzung des Peroxides unter deutlicher Gasentwicklung ein. Ebenso stören Fremdsalzkonzentrationen ab etwa 0,01*N* durch Elution von Sulfit.

Abbildung 8 zeigt die Durchbruchskurve für die Reduktion von fast 2 Liter 0,15*M* Wasserstoffperoxidlösung im kontinuierlichen Säulenbetrieb an etwa 100 g Sulfit-Anionenaustauscher. Es trat während der Reduktion praktisch keine Gasentwicklung in der Säule auf.

Reduktion und katalytische Zersetzung an Redoxiten

Steigender Salzgehalt der Wasserstoffperoxidlösung bewirkt, von einigen Ausnahmen abgesehen, zunehmende Elution des reduzierenden Ions vom Anionenaustauscher. In diesem Fall sind Redoxite mit elutionsstabil eingebauter Redox-Gruppe geeigneter.

Als Beispiel wurde eine 0,3%ige Wasserstoffperoxidlösung in 1*M* Natriumsulfat an einem Leukomethylenblau-Polystyrol-Redoxit[13] quantitativ reduziert, ohne daß die Lösung verunreinigt wurde. Der gleiche Redoxit war früher zur Prüfung seiner Stabilität nach jeweils vorherigen Reduktionen mit Dithionit über hundert Male mit 0,1%iger wässeriger Wasserstoffperoxidlösung oxydiert worden. Dabei nahm die Reduktionskapazität um weniger als 15% ab.

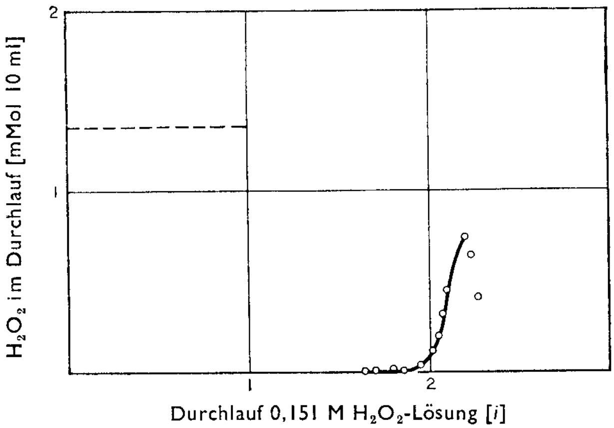


ABB. 8.—Kontinuierliche Entfernung von 0,151*M* Wasserstoffperoxid durch Reduktion an SO_3^{2-}-Lewatit M 600.
100 g Cl^--Lewatit M 600 (0,6–0,75 mm; 22,6% Feuchtigkeit) in SO_3^{2-}-Form übergeführt; bei 20–23°C mit durchschnittlich 3 ml/min filtriert.

Verschiedene andere Polystyrol-Harze mit eingebauten Hydrochinon/Chinonsystemen[13,14] sowie Ferrocen[12] entwickelten aus Wasserstoffperoxid deutlich Sauerstoff. Besonders stark katalysierte das Fe^{3+}/Fe^{2+}-haltige Tonmineral Nontronit die Peroxidzersetzung.

Stärker konzentrierte Wasserstoffperoxidlösung oder lange Einwirkung auch verdünnterer Lösung greifen jedoch die meisten organischen Redoxite mehr oder weniger stark irreversibel an.

Katalytische Zersetzung am OH^--Anionenaustauscher

Verdünnte Wasserstoffperoxidlösungen zersetzen sich am festen OH^--Anionenaustauscher katalytisch.[9] Dabei erwärmt sich die Lösung mehr oder weniger stark.

Im Gegensatz zur entsprechenden Hydroxidlösung verunreinigt die Festbase die Lösung nicht. Die OH^--Ionen können in salzfreier Lösung das Austauschergerüst nicht verlassen. Daher kann die Reaktion auch in einem sehr großen Lösungsvolumen an einer relativ sehr kleinen, aber hoch konzentrierten Menge OH^--Ionen ortsgebunden ablaufen. Normaler Säulenbetrieb wird allerdings durch die starke Gasentwicklung unmöglich.

Die Anordnungen Abb. 3 und 4 zeigen Möglichkeiten auf, den entwickelten Sauerstoff abzuleiten. Sie erlauben einen angenäherten quasi-Säulenbetrieb mit aufgewirbelter Schicht. Die Hauptmenge Peroxid soll bereits im oberen Säulenteil zersetzt werden. Das untere Drittel bleibt als Reserve zur Entfernung gelegentlich durchbrechender Peroxidspuren verfügbar. Ein solches Vordringen der Peroxidfront in der Säule ist am Ausbleichen der rotbraunen Farbe des OH^--Lewatit M 600 oder, noch empfindlicher, durch beginnende Gasentwicklung zu erkennen.

Als Beispiel bringt Abb. 9 die Durchbruchskurve für 1*M* Wasserstoffperoxidlösung. Der Versuch dauerte vier Wochen, zeitweise war der Durchlauf verlangsamt oder ganz unterbrochen. Die nutzbare Durchbruchskapazität dieser OH^--Anionenaustauschersäule betrug etwa 370,2 mEq H_2O_2/g. Das entspricht formal dem 128-fachen derjenigen des Sulfit-Anionenaustauschers.

Ähnlich dem OH^--Anionenaustauscher wirken auch mit Fe^{2+}/Fe^{3+} und ganz besonders mit MnO_4^-/MnO_2 belegte Ionenaustauscher. Dagegen blieb eine Beladung mit H^+, Na^+ oder Cu^{2+} ohne sichtbare Wirkung. Zum Beispiel fanden sich im Durchlauf einer Säule mit 9 g Lewatit S 100 von aufgegebenen 53,9 mEq Wasserstoffperoxid in der angegebenen Reihenfolge der Beladungen 53,7; 53,8 und 53,3 mEq wieder.

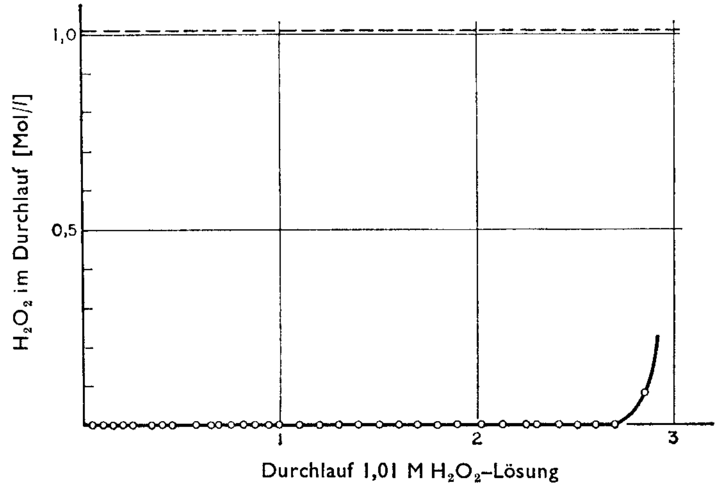


Abb. 9.—Katalytische Zersetzung von 1,01*M* Wasserstoffperoxid an OH^--Lewatit M 600 im quasi-Säulenbetrieb.
20 g Cl^--Lewatit M 600 (0,6–0,75 mm, 22,6% Feuchtigkeit) in OH^--Form übergeführt; bei 20–23°C mit 1 ml/min, jedoch mit Unterbrechungen, filtriert. Säule nach Abb. 4.

DISKUSSION

Vorliegende Arbeit zeigt die Vorteile von einfachen Redox-Ionenaustauschern mit nur irreversibel oxydierbaren Anionen bei der Reduktion ungeladener Moleküle in salzfreier oder salzarmer Lösung. Während Redoxite durch irreversibel Oxydation langsam zerstört werden, ist das Ionenaustrauschergerüst relativ stabil, einfach zugänglich und leicht regenerierbar. Günstig sind Redoxsysteme, welche bei der Oxydation indifferente Anionen wie Sulfat ergeben und bei geringfügiger Elution nicht stören.

Die Entfernung von Wasserstoffperoxid durch Reduktion zu Wasser gelingt besonders rasch am Dithionit-Anionenaustauscher. Auch geringe Sauerstoffspuren werden noch erfaßt. Dithionit hat jedoch den Nachteil eines unübersichtlichen Reaktionsmechanismus, einer Verdoppelung der Anionenladung während der Oxydation und dadurch Elution von Sulfit oder Sulfat. Diese kann bei nur teilweiser Beladung des Anionenaustauschers von diesem selbst, sonst aber durch eine nachgeschaltete Säule mit OH^--Anionenaustauscher entfernt werden. Für andere Zwecke stört die Verunreinigung der Lösung durch Sulfat oder Schwefelsäure jedoch häufig nicht.

Demgegenüber hat der schon von Austerweil[20] zur Entfernung von gelöstem Luftsauerstoff erwähnte Sulfit-Anionenaustauscher den Vorteil eines einfacheren Mechanismus und konstanter Anionenladung. Die Lösung wird nicht verunreinigt. Der Sulfit-Anionenaustauscher ist unter Luftabschluß sehr beständig. Die Grenzen seiner Anwendbarkeit (pH 4,5 bis 7) sind durch die Stabilität von Sulfit einerseits und beginnende Selbstzersetzung des Peroxides andererseits bedingt.

Besondere Bedeutung hat eine halbkontinuierliche und automatische Reduktion des Wasserstoffperoxides am Sulfit-Anionenaustauscher, wenn sie mit einer Vollentsalzung an Ionenaustauschern gekoppelt werden kann. Zum Schutz vor eventuellen Spurenverunreinigungen der behandelten Lösung wird man eine kleine OH^-—und H^+-Ionenaustauschersäule nachschalten. Eine wichtige mögliche Anwendung wäre der einer Radiolyse ausgesetzte Kühlwasserkreislauf entsprechender Atomreaktoren.

Hohe Peroxidkonzentrationen erfordern beim Reduktionsverfahren häufige Regenerationen. Hier erreichte die halbkontinuierliche Zersetzung am OH^--Anionenaustauscher den etwa 130-fachen Umsatz. Die Lösung darf allerdings keine Salzspuren enthalten. Diese tauschen OH^--Ionen aus und blockieren dadurch den Katalysator. Außerdem katalysieren Eisenspuren den oxydativen Angriff des Ionenaustauschergerüstes ungewöhnlich stark.[9]

Die Arbeit wurde im Jahre 1959 ausgeführt. Wir danken für materielle Unterstützung vielmals dem Herrn Bundesminister für wissenschaftliche Forschung, der Deutschen Forschungsgemeinschaft sowie Herrn Dir. Dr. W. Hagge von den Farbenfabriken Bayer in Leverkusen.

Summary—Hydrogen peroxide can be removed semi-continuously from aqueous solution by reduction on an anion-exchange resin in the dithionite or sulphite form, or by catalytic decomposition on a resin in the OH^--form. Simple column arrangements suitable for this purpose providing for exclusion of air, and for quasi-column operation when the resin is vigorously agitated by the evolution of considerable amounts of gas, are described.

Résumé—L'eau oxygénée peut être éliminée de manière semi continue d'une solution aqueuse par réduction sur une résine échangeuse d'anions sous la forme dithionite ou sulfite, ou par décomposition catalytique sur une résine sous forme OH^-. On décrit des dispositifs de colonne simples convenant à cette fin, prévoyant l'exclusion de l'air et l'opération pratique en colonne lorsque la résine est vigoureusement agitée par le dégagement de quantités considérables de gaz.

LITERATUR

1. W. Machu, *Das Wasserstoffperoxid und die Perverbindungen*, Springer-Verlag, Wien, 1951.
2. W. C. Schumb, C. N. Scatterfield und R. L. Wentworth, *Hydrogen Peroxide*, Reinhold, New York, 1955.
3. T. Bersin, *Ion Exchangers in Organic and Biochemistry*, eds. C. Calmon and T. R. E. Kressman, Interscience, New York, 1957.
4. C. Overberger, *J. Am. Chem. Soc.*, 1955, 77, 3675.
5. G. Charlot, D. Bezier und J. Courtot, *Constantes Selectionnes Potentiels d'Oxydo-Reduction*, Pergamon Press, Paris, 1958.
6. W. M. Latimer, *Oxidation Potentials*, 2nd Ed., Prentice-Hall, Englewood Cliffs, N.J., 1952.
7. K. J. Vetter, *Elektrochemische Kinetik*. Springer-Verlag, Berlin, 1961.
8. M. G. Evans und N. Uri, *Trans. Faraday Soc.*, 1949, **45**, 224.
9. B. Sansoni, O. Sigmund, E. Bauer, W. Wiegand und L. Perera, *Angew. Chem.*, 1961, **73**, 763.

10. E. Blasius, *Chromatographische Methoden in der analytischen und präparativen anorganischen Chemie, unter besonderer Berücksichtigung der Ionenaustauscher*, Ferdinand Enke Verlag, Stuttgart, 1958.
11. B. Sansoni, *Neue chemische Arbeitsmethoden durch heterogene Reaktionen: Redoxaustauscher und numerometrische Titration*, Verlag UNI-Druck, München, 1968.
12. S. Fisher und R. Kunin, *Anal. Chem.*, 1955, **27**, 1191.
13. B. Sansoni, *Diss.*, Univ. München, 1956.
14. O. Sigmund, *Diss.*, Univ. Marburg/Lahn, 1963.
15. I. M. Kolthoff, *Z. Anal. Chem.*, 1921, **60**, 400.
16. J. Heyrovský und P. Zuman, *Einführung in die praktische Polarographie.* VEB-Verlag Technik, Berlin, 1959.
17. B. Sansoni, in *Anomalien bei Ionenaustauschvorgängen*, 1961, Akademie Verlag, Berlin, 1962.
18. O. Samuelson, *Ion Exchangers in Analytical Chemistry*, Almquist und Wiksell, Stockholm, 1952.
19. B. Sansoni und O. Sigmund, *Angew. Chem.*, 1961, **73**, 299.
20. G. V. Austerweil, *Franz. Patent Nr.* 855849 (1940).

Talanta, 1970, Vol. 17, pp. 999 to 1003. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

Apparatus for the determination of melting points, molecular weights, freezing points and purity, and for the study of melting

(*Received* 10 *June* 1969. *Revised* 4 *May* 1970. *Accepted* 12 *May* 1970)

AN APPARATUS for the rapid precise determination of molecular weights has been developed. It is based on the measurement of melting point lowering, because there are difficulties in obtaining accurate values for freezing points.[1,2] Notice is taken of the conditions which affect precision and arise from processes occurring in the melting system. An equation is deduced for accurate calculation of the melting point, from an estimate of the time at which the melting point occurred, and the co-ordinates of two points in the melting region of the time–temperature record.

EXPERIMENTAL

The vessel was a 10-ml Pyrex glass bulb with two ground-glass necks, the one for filling and emptying having a ground-glass stopper, and the other containing a sealed-in thermistor arranged to have its tip immersed 5 mm into the liquid. The vessel contained 7 g of liquid and five glass balls 6 mm in diameter. The thermistor (FS 23), Standard Telephones and Cables Ltd.) had a resistance of 2000 Ω at 20°, and temperature coefficient 132 Ω/K, and was made one of the ratio arms of a Wheatstone bridge, the out-of-balance current being amplified and recorded on the chart of a recording potentiometer adjusted to give full-scale deflection for the concentration range being used.

The flask was filled with a known weight of solvent and immersed in a freezing-bath for 1 min. It was then placed in an insulated container mounted on the arm of a reciprocating machine and swung uniformly, 90 times a minute, through an arc of 120°.

The temperature–time trace of the pure solvent formed a base line from which subsequent melting-point lowerings could be measured. Some examples are shown in Fig. 1.

Conditions to be observed in design

1. Crystallization of the solvent should be rapid.
2. Residual supercooling in the solid/liquid system or in the temperature measuring device is undesirable.
3. Rapid heat exchange between solid and liquid is necessary so that equilibrium between the two phases can be established quickly.
4. Melting should proceed through a series of equilibrium states, each state, for partially frozen solutions, being in accordance with the freezing point law.
5. The temperature-sensing device must detect small changes accurately. The temperature measured should be that of the solution in equilibrium with frozen solid.
6. At the melting point the concentration of the solution in equilibrium with solid must be constant.
7. The melting point should be relatively indifferent to the rate of melting.
8. A clearly defined melting point is desirable.
9. The apparatus should be simple to use, and the time of measurement short.

DISCUSSION

Crystallization of the organic liquids used, of water and of molten naphthalene and diphenylamine was rapid and clearly defined, largely because of the presence of the glass balls. The melting point was well defined on the recorder trace and by calculation could be measured accurately. The time required to remelt the partially frozen liquid was short, usually about 5 min. The thermistor tip was small and hence the temperature response rapid. Efficiency of mixing was the main factor involved in satisfying the other conditions, and was achieved by means of the glass balls, the uniformity of the mechanical motion and the jerk at the end of each stroke. The uniformity of motion was most important. The efficiency was demonstrated by the smoothness of the trace for pure solvent and by the shape of that for a solution. The shape of the curve follows from the freezing point depression law, which may be expressed as

$$T_L - T_1 \equiv \Delta T_1 = \frac{kn}{w_0 + st_1} \tag{1}$$

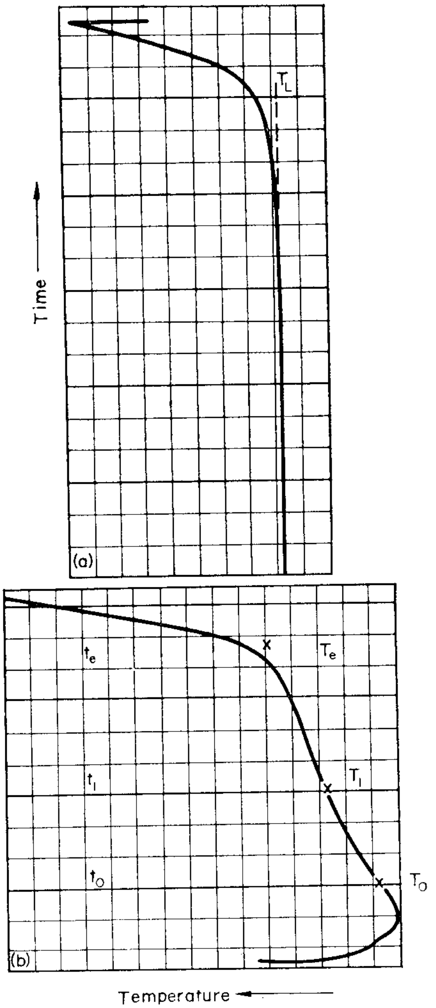


FIG. 1.—Examples of time–temperature curves; (*a*) pure solvent; (*b*) solution.

where k = the cryoscopic constant, n = moles of solute, w_0 = weight of solvent at beginning of melting, T_L = melting point of solvent, s = speed of melting, t_l = time of melting to temperature T_l.

For any given trace for melting, the only variables are T and t and when plotted against each other they should give a concave curve. The shape of the trace in Fig. 1(*b*) illustrates this. That all such traces were curved confirms the efficiency of mixing.

The rate of heat exchange between the two phases was not only a function of mixing, but also of crystal size and the thermal properties of the two phases. Thus the heat exchange was least for pure solvents where the crystals were large, and greatest for the solvent cyclohexane, the latent heat of which was so low that melting was too rapid for a trace like Fig. 1 to be developed.

Determination of the melting point

The melting point of solvents (T_L) is that portion of the trace which gives a constant temperature over an interval of time. The melting point for solutions can be taken as that temperature where the amount of frozen solid becomes vanishingly small (T_e). At this point,

$$T_L - T_e = \Delta T_e = \frac{kn}{w} \qquad (2)$$

where w is the weighed amount of solvent.

The expression used to calculate the melting point is

$$\Delta T_e = \frac{\Delta T_1 \Delta T_0 \alpha}{\Delta T_0(\alpha + 1) - \Delta T_1} \tag{3}$$

where $\Delta T_1 = T_L - T_1$ and $\Delta T_0 = T_L - T_0$ are two temperature differences on the trace, corresponding to times of melting t_1 and t_0, $\alpha = (t_1 - t_0)/(t_e - t_1)$, and where t_e is the time at T_e (see Fig. 1).

From equations (1) and (2) we obtain

$$w_0 + st_1 = \frac{\Delta T_e w}{\Delta T_1}, \tag{4}$$

and as

$$w_0 \Delta T_0 = kn = \Delta T_e w,$$

then

$$\frac{\Delta T_e w}{\Delta T_0} + st_1 = \frac{\Delta T_e w}{\Delta T_1}. \tag{5}$$

Thus,

$$s = \frac{\Delta T_e w}{t_1}\left[\frac{1}{\Delta T_1} - \frac{1}{\Delta T_0}\right] \tag{6}$$

If the rate of melting is the same throughout the melting process, and it is probable that this is so over a small temperature range and relatively short melting times, then the expression above is true whatever the temperature points chosen. Hence,

$$\frac{\Delta T_e w}{t_1 - t_0}\left[\frac{1}{\Delta T_1} - \frac{1}{\Delta T_0}\right] = \frac{\Delta T_e w}{t_e - t_1}\left[\frac{1}{\Delta T_e} - \frac{1}{\Delta T_1}\right] \tag{7}$$

This gives:

$$\left[\frac{1}{\Delta T_1} - \frac{1}{\Delta T_0}\right] = \frac{t_1 - t_0}{t_e - t_1}\left[\frac{1}{\Delta T_e} - \frac{1}{\Delta T_1}\right]$$

or

$$\frac{1}{\Delta T_1} - \frac{1}{\Delta T_0} = \frac{\alpha}{\Delta T_e} - \frac{\alpha}{\Delta T_1}$$

or

$$\frac{(\alpha + 1)}{\Delta T_1} = \frac{1}{\Delta T_0} + \frac{\alpha}{\Delta T_e}$$

whence

$$\Delta T_e = \frac{\Delta T_1 \Delta T_0 \alpha}{\Delta T_0(\alpha + 1) - \Delta T_1}. \tag{8}$$

Estimation of precision

The precision of cryosopic results is usually expressed in terms of temperature as this is the unit of measurement. It was thought that concentration would be a more meaningful term. The cryoscopic constant k estimated from the slope of a plot of melting point depression *vs.* molal concentration m, may be used to estimate the concentration m' corresponding to any given value of ΔT_e,

$$m' = \Delta T_e/k.$$

The differences $(m - m')$ can then be used as a measure of precision.

Results are shown in Table I.

APPLICATIONS

Molecular weights

The precision with which the molecular weights of organic compounds can be measured by the apparatus can be seen from Table I. The mean value of the standard deviations is ±0·002 mole/kg and the experimental value for a substance of molecular weight of 1000 in 1-molal solution would be found to lie between 1004 and 996. If, however, the solution were 0·1 molal, the value would lie between 1040 and 960. It follows that within the bounds of ideality, the more concentrated the solutions the smaller the error. The samples in Table I included solutions up to 1·2 molal.

For a molal solution of a substance of molecular weight 10000, the limits would be 9960 and 10040,

TABLE I.—RESULTS OF MEASUREMENTS AND THEIR PRECISION

Solvent	Solutes	No. of results	Std. devn., *mole/kg*
Water	Sucrose, glucose, urea, catechol, resorcinol, hydroquinone, phenol, aniline, benzylamine	72	±0·0035
Benzene	Naphthalene, α-naphthol, catechol, benzil, fats and oils	65	±0·0016
Dioxan	Naphthalene, benzoic acid, 1,5-, 1,6-, 1,3-, 1,4-, 1,7-, 2,3-, 2,7-dihydroxynaphthalenes, methyl salicylate, nitrobenzene, pyrogallol, catechol, fats and oils	105	±0·0021
Nitrobenzene	Naphthalene, coumarin	20	±0·0015

but it often becomes more difficult to make such a concentrated solution as the molecular weight rises, It would seem unwise to claim that it is possible to extrapolate the readings to high molecular weights. *i.e.*, in excess of 10000, as is sometimes done.

Purity

Taking the mean standard deviation as 0·002 mole/kg and assuming that twice this value is needed for detection, then the minimum amount of impurity that could be detected in organic materials soluble in any of the four solvents suitable, would be 0·0004 mole % if a 1-molal solution were used.

Other uses

It is possible to examine self-associated species in benzene and nitrobenzene[3] and weak complexes in an inert solvent.[4] The number of particles present under certain experimental conditions can be determined and this might be useful in the study of reaction mechanisms.

The nature of the recorder traces enables a study to be made of the last stages of the melting of liquids and dilute solutions. Melting points can be determined and although it is not claimed that T_e is the physical melting point, it is based on theory and reproducible to within ±0·005°.

Department of Chemistry
The City University
St. John Street, London E.C.1.

R. F. GREENWOOD

Summary—An apparatus for the determination of the melting point of a partially frozen liquid is described. Thermal equilibrium is rapidly attained, largely because of the presence of glass balls in the experimental flask, and the method of agitation. The use of a thermistor and a recording potentiometer allows charting of the temperature changes with time. The melting point can be calculated from points on the trace. The apparatus has been used to study melting point depressions for solutions of hydrocarbons and phenols in benzene, nitrobenzene, water and dioxan.

Zusammenfassung—Ein Gerät zur Bestimmung des Schmelzpunktes einer teilweise gefrorenen Flüssigkeit wird beschrieben. Das thermische Gleichgewicht wird mit Hilfe eines Vorrats von Glaskugeln im Versuchskolben und eines besonderen Rührverfahren rasch erreicht. Ein Thermistor und ein Schreiber ermöglichen es, die zeitliche Änderung der Temperatur zu registrieren. Der Schmelzpunkt kann aus Punkten auf der Registrierspur berechnet werden. Mit dem Gerät sind Schmelzpunktenniedrigungen einiger Lösungen von Kohlenwasserstoffen und Phenolen in Benzol, Nitrobenzol, Wasser und Dioxan untersucht worden.

Résumé—On décrit un appareil pour la détermination du point de fusion d'un liquide partiellement congelé. L'équilibre thermique est rapidement atteint, essentiellement à cause de la présence de billes de verre dans la fiole d'expérimentation et de la méthode d'agitation. L'emploi d'un thermistor et d'un potentiométre enregistreur permet

l'enregistrement des variations de température en fonction du temps. Le point de fusion peut être calculé de points sur le tracé. On a utilisé l'appareil pour étudier les dépressions du point de fusion pour des solutions d'hydrocarbures et de phénols en benzène, nitrobenzene, eau et dioxane.

REFERENCES

1. C. A. Kraus and R. A. Vingee *J. Am. Chem. Soc.* 1934, **56**, 511.
2. N. E. Smidt, Y. A. Buslaew, U. G. Murator and L. D. Kulikovskaya, *Zh. Fiz. Khim.*, 1968, **42,** 2354.
3. R. V. Huggett, *Student project*, The City University, London, 1969.
4. R. F. Greenwood, *Ph.D. Thesis*, University of London, 1967.

Talanta, 1970, Vol. 17, pp. 1003 to 1006. Pergamon Press. Printed in Northern Ireland

A silver electrode in the potentiometric titration of thiols*†

(*Received* 26 *July* 1969. *Revised* 20 *January* 1970. *Accepted* 11 *March* 1970)

THE AMPEROMETRIC method of Benesch *et al.*[1] using silver as the titrant has been used extensively for measuring thiols. Kolthoff and co-workers[2] have made a critical study of the method and discussed the merits of several titrants. We had difficulty in locating the end-point in amperometric titrations, so we tried potentiometry. We have found that simply immersing a piece of silver wire in a solution of a thiol for a short time produces an electrode responsive to thiol concentration. Cecil and McPhee[3] had earlier used a silver–silver sulphide electrode prepared by an involved procedure and the restrictive conditions they reported may have discouraged extensive use of their method.

Since the electrode follows the thiol level, any thiol reagent should be satisfactory as titrant, and the reagent forming the most stable compound should give the sharpest end-point. Mercury(II) salts, monosubstituted organo-mercuric salts and silver nitrate have been used successfully.

The operating procedure was designed to accommodate the slow electrode response, and a simple treatment prior to each titration eliminated the reduction in electrode response that occurred with continued use.

The response of the electrode would be expected to arise from

$$\mathrm{RSH} \rightleftharpoons \mathrm{RS^-} + \mathrm{H^+}; \qquad [\mathrm{RS^-}] = K_1\frac{[\mathrm{RSH}]}{[\mathrm{H^+}]}$$

$$\mathrm{Ag(s)} + \mathrm{RS^-} \rightleftharpoons \mathrm{AgRS(s)} + e$$

$$E = E^\circ - 0{\cdot}059 \log \frac{1}{[\mathrm{RS^-}]}$$

$$= E^{\circ\prime} + 0{\cdot}059 \log [\mathrm{RSH}] \text{ (at constant pH)}$$

The electrode potentials for three different levels of cysteine at pH 7·0, measured with two electrodes (the first a silver wire immersed in the solution until a steady potential was attained, the second deliberately coated with a heavy silver sulphide layer) gave slopes of 0·054 and 0·057 V, confirming the proposed mechanism, though the E° values were different.

EXPERIMENTAL

Preparation of electrode

Coil 0·15 m of 1·27-mm diameter silver wire for several turns round a 4-mm tube. The first time the electrode is used, immerse it briefly in ammonia solution (1 + 3), rinse with demineralized water, immerse it in dilute nitric acid (1 + 3) for 2 min and rinse with demineralized water.

---

* This work was supported in part by a USPHS Grant No. 1T1 DE175 and in part by the United States Atomic Energ yCommission, Contract No. W-7401-Eng-49 and has been assigned Report No UR-49-960.

† Thiols are generally referred to as "sulfhydryls" in American and biochemical terminology.

The electrode must be cleaned after each titration; otherwise the potential change at the end-point decreases considerably. Immerse the electrode in ammonia solution (1 + 3) for 1 min (after titration of simple systems; 3–5 min after protein titration) then wash with demineralized water. If the electrode has not been used for a long time, immersion for about an hour is advisable.

Titration assembly

A saturated potassium chloride salt bridge is constructed from borosilicate glass 20 mm in diameter drawn down to a 4-mm tube with a porous piece of carborundum sealed into its end. A silver-silver chloride reference electrode is placed in the salt bridge and the silver wire electrode is placed round the 4-mm tube. A microsyringe readable to 0·1 μl and a multirange millivoltmeter complete the assembly. The burette and potentiometer can be coupled to a recorder for automatic plotting of the titration curve.

Titrants

Mercury(II) chloride, 0·005*M*. Standardized against pure glutathione.

p-*Chloromercuriphenyl sulphonate* (*PCMPS*) *solution*. Standardized with glutathione.

Silver nitrate solution. Standardized by adding an excess of standard sodium chloride solution and measuring the excess by an instrumental method.

Titration

Because of the slowness of electrode response, continuous titration is impossible. However, most of the potential change after addition of an increment of titrant occurs within 30 sec, and $>90\%$ within 60 sec; no further change occurs after 2 min. A heavily coated sulphide electrode has an even slower response; if the reading at the end of 3 min is used as reference standard, 50–60% of the increase occurs during the first minute, about 30% within the second minute and the rest during the third; longer intervals produce further small changes.

If successive equal additions of titrant are made at equal time intervals, the end-point lies within the increment that gives the greatest potential change. Figure 1 shows two typical titration curves, one for a simple thiol, the other for a complex one.

Only the portion of the titration curve near the end-point need be plotted. The end-point can usually be located within a 2-μl increment, though the electrode will respond to an addition of <1 μl.

Titrations with all three titrants gave curves of the same shape, but with different sizes of potential

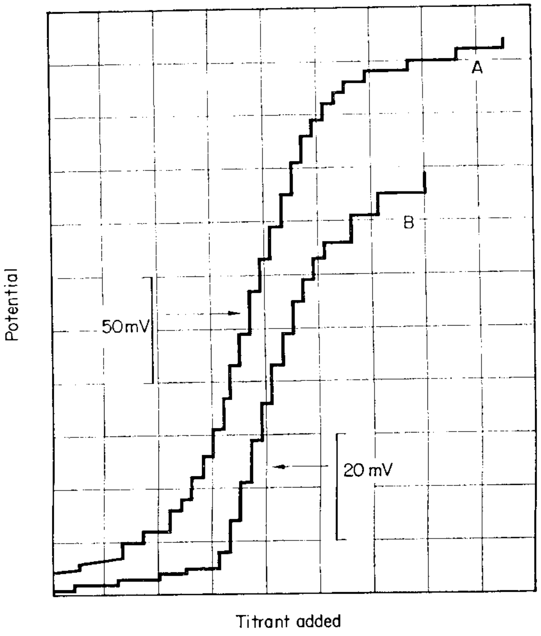


FIG. 1.—Titration curves. A—cysteine; B—albumin.

break, and the conditions for titration differed. Mercury(II) chloride is satisfactory as a titrant at pH 4·5–9·5, PCMPS at pH 7–9·5, and silver nitrate only at pH 9·5 (performance at pH values outside the range 4·5–9·5 was not tested).

Procedure

Place 2 ml of 5% albumin solution and 4 ml of 0·1*M* tris buffer, pH 7·0, in a 10-ml beaker with a small stirring bar. Immerse the electrode just to clear the stirring bar, and place the burette tip just below the surface of the liquid. Add the titrant in increments which decrease as the expected equivalence point is approached. When the potential definitely starts to rise, add increments of exactly 0·002 ml at 2-min intervals.

RESULTS

Titration of cysteine

Although titrations of cysteine solutions gave very sharp end-points at the three pH values studied, only at pH 4·5 were the results consistent when an air atmosphere was used. At pH 7 and 9·5 the results were lower and somewhat erratic until the solutions were freed from oxygen and a nitrogen atmosphere was maintained during titration. Table I shows the results obtained with two different solutions.

TABLE I.—TITRATION OF CYSTEINE WITH MERCURIC CHLORIDE

	Titre, *ml*	
pH	1	2
4·5	0·1841	0·1940
	0·1800	0·1960
7·0	0·1801	0·1960
	0·1822	0·1901
9·5	0·1820	0·1941
		0·1941
		0·1960

Titration of albumin

Albumin solution kept in a refrigerator for a month showed no change in thiol content, and a nitrogen atmosphere was required only for titration at pH 9. Table II shows the results obtained with different titrants and, for comparison, the results obtained amperometrically.

TABLE II.—TITRATION OF ALBUMIN

Method	Titrant	No. of detns.	SH, *μmole/g*
Potentiometric	$HgCl_2$	21	8·32 ± 0·09
Potentiometric	PCMPS	9	8·65 ± 0·21
Potentiometric	$AgNO_3$	10	8·18 ± 0·09
Amperometric	$HgCl_2$	4	8·26 ± 0·16

Since urea is commonly used to denature proteins, its effect on the titration of albumin was determined. It was necessary to purify reagent grade urea by passing its solution through a mixed-bed ion-exchange resin. When a nitrogen atmosphere was used the same titre was obtained with or without urea present. In an air atmosphere at pH 7, the solution containing urea gave a lower titre.

DISCUSSION

It was thought desirable to carry out titrations near pH 7 in order to maintain conditions as close to physiological ones as possible. Cecil and McPhee[2] found that glutathione could only be titrated in the pH range 1·8–2·2 and cysteine in the range 3·5–7·5 with silver nitrate and their sulphide electrode. In the present work, identical results were obtained with mercury(II) chloride at pH 4·5, 7·0 and 9·5 for simple thiols and albumin provided that a nitrogen atmosphere was maintained.

Mercury(II) chloride is preferred as titrant because it gives the largest potential change at the end-point.

The use of silver as titrant was of special interest. Some doubt has been cast upon the validity of titration with silver in the amperometric methods,[2,4] in which positive errors were attributed to reactions with groups other than thiol. Since the electrode used in the present study responds directly to the thiol level, it is apparent from the results in Table II that silver gives correct results.

Department of Radiation Biology and Biophysics
University of Rochester School of Medicine and Dentistry
Rochester, New York 14620, *U.S.A.*

TAFT Y. TORIBARA
LARYSA KOVAL

Summary—A silver wire immersed in a thiol solution gives a potential responsive to the thiol concentration, and is a sensitive indicator electrode in the potentiometric titration of thiols with mercury(II) chloride, *p*-chloromercuryphenyl sulphonate, and silver nitrate at pH 4·5–9·5, 7–9·5 and 9·5 respectively. Titrations of simple thiols such as cysteine or a protein such as albumin are equally successful, but the potential break was smaller for the protein. The end-point could be determined within an increment of titrant equal to 5 nmole of thiol. An inert atmosphere is needed for titration at $\text{pH} \geqslant 7$.

Zusammenfassung—Ein in eine Thiollösung tauchender Silberdraht gibt ein Potential, das ein Maß für die Thiolkonzentration darstellt. Der Draht ist eine empfindliche Indikatorelektrode bei der potentiometrischen Titration von Thiolen mit Quecksilber(II)chlorid, *p*-Chlormercuriphenylsulfonat und Silbernitrat bei pH 4,5–9,5: 7–9,5 bzw. 9,5. Titrationen einfacher Thiole wie Cystein oder eines Proteins wie Albumin sind gleichermaßen möglich; der Potentialsprung war jedoch beim Protein kleiner. Der Endpunkt ließ sich innerhalb einer Zugabe von Titrant feststellen, die 5 nMol Thiol entspricht. Bei Titrationen bei $\text{pH} \geqslant 7$ benötigt man eine inerte Atmosphäre.

Résumé—Un fil d'argent immergé dans une solution de thiol donne un potentiel sensible à a concentration en thiol, et est une électrode indicatrice sensible dans le titrage potentiométrique des thiols par le chlorure de mercure(II), le *p*-chloromercuriphényl sulfonate et le nitrate d'argent à pH 4,5–9,5, 7–9,5 et 9,5 respectivement. Les titrages de thiols simples tels que la cystéine ou d'une protéine telle que l'albumine sont également couronnés de succés, mais la cassure de potentiel est plus petite pour la protéine. Le point de fin de dosage peut être déterminé avec un incrément d'agent de titrage égal à 5 nmole de thiol. Une atmosphère inerte est nécessaire pour le titrage à $\text{pH} \geqslant 7$.

REFERENCES

1. R. Benesch and R. E. Benesch, *Arch. Biochem.*, 1948, **19**, 35.
2. I. M. Kolthoff, W. S. Shore, B. H. Tan and M. Matsuoka, *Anal. Biochem.*, 1965, **12**, 497.
3. R. Cecil and J. R. McPhee, *Biochem. J.*, 1955, **59**, 234.
4. A. C. Allison and R. Cecil, *ibid.*, 1958, **69**, 27.

Talanta, 1970, Vol. 17, pp. 1006 to 1009. Pergamon Press. Printed in Northern Ireland

Amperometric complex-formation titration of traces of alkaline earths

(*Received* 17 *February* 1970. *Accepted* 17 *April* 1970)

IN A PREVIOUS communication[1] the principles of the amperometric complex-formation titration of metal ions with indication by following the anodic wave of the excess of ligand, have been presented. The work of Campbell and Reilley,[2] who used a dropping mercury electrode, could be extended to a higher sensitivity by using a rotating mercury electrode as the indicator electrode. The criterion for a sharp end-point of a complexometric titration curve appeared to be

$$K'c \geq 2 \times 10^3$$

where K' is the conditional stability constant of the metal complex involved and c is the original concentration of the metal ion. When errors of 1% or slightly more are tolerable values of $K'c$ of 10^3 or even 10^2 can be used.

In the present paper the determination of the alkaline earth metals with EDTA, EGTA and DTPA as chelating agents* is described. A prediction of the limit of determination can easily be made by means of the sharpness criterion mentioned above. In Table I the conditional stability constants of the various complexes are given for a pH-value of 10. The Table shows that the determination of the alkaline earths should be possible at the $10^{-5}M$-concentration level, when the appropriate chelating agent is used, *i.e.*, any of the three for calcium, EDTA or DTPA for magnesium, DTPA or EGTA for strontium or barium. When errors of about 1% are admissible determinations at the $10^{-6}M$-level should be possible.

TABLE I.—VALUES OF log K'_{MY} AT pH 10

Metal	EDTA	EGTA	DTPA
Ca	10·2	10·9	9·9
Mg	8·2	5·1	8·6
Sr	8·1	8·4	9·0
Ba	7·3	8·3	8·1

As the titration cell is constructed for determinations in a volume of 10 ml the minimum amount of these metals that can be determined should be about 10 nmole, which corresponds to about 0·2–1·4 μg, depending on the metal.

EXPERIMENTAL

Apparatus

The titration cell has a volume of 10 ml. It is connected by means of fritted glass discs on the one side with a saturated calomel electrode and on the other side with a compartment containing an auxiliary tungsten electrode. All three compartments of the titration cell are filled with the same supporting electrolyte solution. The rotating mercury electrode (600 rpm) used as the indicator electrode was described in the previous paper. The Beckmann Electroscan 30 supplied the voltage for the cell and also served for the measurement of the current. Titrations were carried out by adding the titrant solution from a 1-ml syringe microburette.

Selection of the potential

The selection of the potential to be applied to the indicator electrode is very important. The most favourable potential depends on the concentration of the metal ion to be titrated and on the condition of the electrode. The correct selection of the potential can be made by recording polarograms with the indicator electrode of solutions containing the supporting electrolyte solution and small but different amounts of the titrant.

Reagents

Potassium nitrate (10 g) and ammonium nitrate (8 g) were dissolved in 1 litre of distilled water. The pH was adjusted to 10 by addition of potassium hydroxide to give a $0{\cdot}1M$ buffer solution. A $0{\cdot}001M$ buffer solution was prepared in a similar way.

Stock solutions of the alkaline-earth metals were prepared from the chemically pure nitrates or sulphates and were standardized complexometrically.

Solutions of EDTA, DTPA, and EGTA were standardized against calcium carbonate.

Procedure

The sample, containing 1–100 μg of the alkaline earth metal, is dissolved in 10 ml of $0{\cdot}001M$–$0{\cdot}1M$ buffer solution. The solution is put in the titration cell and titrated with a 10^{-4}–$10^{-2}M$ solution of the appropriate complexing agent; the titration graph is recorded on the Electroscan. In order to avoid too large an iR-drop across the cell, the titration is stopped when a 20% excess of the titrant has been added. The end-point is obtained as the point of intersection of the two straight parts of the curve.

* EDTA = ethylenediaminetetra-acetic acid.
EGTA = ethyleneglycol bis(β-aminoethyl ether)-N,N,N',N'-tetra-acetic acid.
DTPA = diethylenetriaminepenta-acetic acid.

RESULTS

In Table II some typical results are given for determinations in the 100-μg range, and in Table III for the 1-μg range.

It can be seen from Table III that $10^{-6}M$ solutions of the alkaline earth metals can be titrated with fair accuracy. The time required for a titration is between 3 and 5 min.

TABLE II.—DETERMINATIONS OF ALKALINE EARTH METALS IN THE 100-μg RANGE AT pH 10

Metal, μg		Error, %	Std. devn., % (no. of detns.)	Titrant
taken	found			
48·7 Mg	47·7	−2	0·5 (4)	EDTA
48·7 Mg	47·8	−2	0·6 (4)	DTPA
59·3 Ca	58·8	−0·8	0·5 (5)	EGTA
79·0 Ca	77·1	−2·2	1·2 (5)	DTPA
128·8 Sr	128·4	−0·3	2·0 (5)	EDTA
128·8 Sr	127·0	−1·4	2·2 (5)	EGTA
128·8 Sr	128·8	—	1·6 (5)	DTPA
269·7 Ba	261·3	−3	5·2 (4)	EGTA
202·4 Ba	201·3	−0·5	3·7 (5)	DTPA

TABLE III.—DETERMINATION OF THE ALKALINE EARTH METALS IN THE 1-μg RANGE AT pH 10

Metal, μg		Error, %	Std. devn., % (5 variates)	Titrant
taken	found			
0·365 Mg	0·371	+1·6	4·1	DTPA
0·365 Mg	0·374	+2·4	2·3	EDTA
0·395 Ca	0·416	+5	3·1	EDTA
0·790 Ca	0·830	+7	2·3	EDTA
1·58 Ca	1·60	+1·2	1·3	EDTA
1·29 Sr	1·29	—	3·5	EGTA
1·29 Sr	1·37	+6	2·0	DTPA
2·02 Ba	2·04	+1	3·2	EGTA
2·02 Ba	2·05	+1·5	5·6	DTPA

Determination of calcium in the presence of magnesium

The investigations have been extended to include the determination of calcium with EGTA in the presence of magnesium. The maximum admissible concentration of magnesium can be found from the sensitivity condition mentioned in the previous paper [equation (19′)]:[1]

$$K'_{Mg}c_{Mg} < (n - 1)$$

where n is the factor by which the sensitivity may be reduced. The determination of $1{\cdot}5 \times 10^{-6}M$ calcium has been carried out in the presence of a 100-fold and a 1000-fold amount of magnesium. A considerable decrease in the slope of the titration curve after the equivalence point and thus a considerable decrease in sensitivity was to be expected in these cases. The experimental results agree reasonably with the predictions, but as the decrease of linearity observed was smaller than predicted,

TABLE IV.—DETERMINATIONS OF CALCIUM WITH EGTA IN THE PRESENCE OF MAGNESIUM

Calcium, μg		Magnesium μg	Error, %	Std. devn., % (no. of detns.)
present	found			
0·596	0·581	37·6	−2·5	5·8 (6)
0·596	0·589	364	−1·2	4·9 (9)

the experiments turned out to be better than expected. An exact agreement could not be expected as the stability constants used in the calculations were determined under conditions other than the actual experimental conditions. The analytical results are given in Table IV.

Although a great number of complexometric titrations of the alkaline earth metals have been described, the amperometric indication of the excess of ligand with a rotating mercury electrode would seem to offer improvements in sensitivity and speed. Only a few minutes are required for each titration.

Laboratory for Analytical Chemistry
University of Amsterdam
Nieuwe Achtergracht 125
Amsterdam-C

G. DEN BOEF
F. FREESE
M. M. P. F. KRAMER
H. POPPE

Summary—Alkaline earth metals were determined in microgram quantities by complexometric titration with EDTA, EGTA and DTPA. The end-point was detected by following the anodic wave of the chelating agent at the rotating mercury electrode. All the alkaline earths can be titrated at the microgram level with reasonable accuracy, and calcium may be titrated with EGTA in the presence of a 1000-fold excess of magnesium.

Résumé—On a dosé les métaux alcalino-terreux en quantités de l'ordre du microgramme par titrage complexométrique avec EDTA, EGTA et DTPA. Le point de fin de dosage est détecté en suivant la vague anodique de l'agent chélatant sur l'électrode de mercure rotative. Tous les alcalino-terreux peuvent être titrés à l'échelle du microgramme avec une precision raisonnable, et l'on peut titrer le calcium à l'EGTA en la présence d'un excès 1000 fois plus grand de magnésium.

Zusammenfassung—Erdalkalimetalle wurden in Mikrogrammengen durch komplexometrische Titration mit EDTA, EGTA und DTPA bestimmt. Der Endpunkt wurde durch Beobachtung der anodischen Stufe des Chelatbildners an der rotierenden Quecksilberelektrode ermittelt. Alle Erdalkalien lassen sich im Mikrogrammbereich ausreichend genau bestimmen; Calcium kann in Gegenwart eines 1000-fachen Überschusses von Magnesium mit EGTA titriert werden.

REFERENCES

1. F. Freese, H. J. Jasper and G. den Boef, *Talanta*, 1970, **17**, 945.
2. R. T. Campbell and C. N. Reilley, *ibid.*, 1962, **9**, 153.

Talanta, 1970, Vol. 17, pp. 1009 to 1013. Pergamon Press. Printed in Northern Ireland

A microwave-excited emissive detector for gas chromatography

Further studies with sulphur compounds

(*Received* 19 *March* 1970. *Accepted* 12 *April* 1970)

THIS communication describes some improvements to a microwave-excited emissive detector for gas chromatographic detection of some sulphur compounds. The system previously described[1] has been modified by restricting the volume occupied by the discharge, using a catalyst to aid the thermal degradation of the sulphur compounds, using all of the sample eluted from the gas chromatograph, and stabilizing the vacuum in the detector tube.

These modifications have led to an overall improvement in this type of detection technique and have yielded superior detection limits, particularly for those sulphur compounds of relatively low volatility or high thermal stability.

EXPERIMENTAL

Restriction of the discharge

The detector tube used (Fig. 1) was fabricated from 8 mm internal diameter transparent silica tubing with two constrictions, *ca.* 2 mm diameter, such that a bulb *ca.* 30 mm in length was formed. The bulb could be situated almost entirely within the microwave field of either a quarter-wave foreshortened radial line cavity or a quarter-wave Evenson type of cavity, thus maintaining the discharge within the bulb. Under these conditions the plasma was found to be quite stable. Stability was increased further by the use of a large (*ca.* 50 l.) ballast tank in the vacuum line, downstream from the detector, which smoothed out the previously observed fluctuations due to the exhaust action of the vacuum pump.

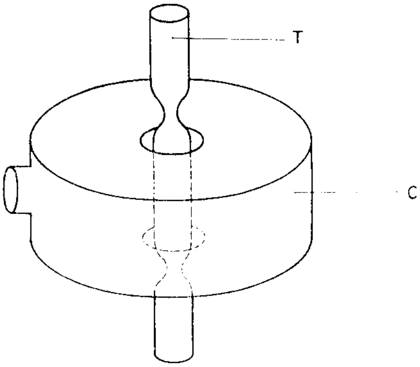


FIG. 1.—Microwave cavity and detector tube.
T—detector tube.
C—quarter-wave foreshortened radial line resonant cavity.

Use of platinum catalyst

A difficulty frequently associated with low-pressure microwave-excited plasmas is the inability to supply sufficient energy to break down relatively stable compounds completely. It was found, however, that a loop of 0·35 mm diameter platinum wire placed in the bulb of the detector tube greatly increased the detection limit of the compounds thiophen, dimethyl sulphoxide and thioglycollic acid. One probable reason for this action is that at the temperature of the discharge the platinum partially vaporizes (substantiated by the presence of platinum atomic emission at 265·9 and 306·6 nm) and aids the fragmentation process. The use of the Evenson quarter-wave cavity also gives increased fragmentation in comparison to the quarter-wave foreshortened radial line cavity.

The physical effects observed with the platinum loop in the bulb of the detector were a concentration of the discharge around the platinum loop, diminution of short-term background noise of the discharge by approximately one half and initiation of the discharge without the use of a "Tesla" vacuum tester at an applied microwave power of 50 W.

Use of total sample

In the present arrangement all of the sample eluted from the column was utilized for microwave detection, by means of the gas chromatographic oven circuit shown in Fig. 2. The outlet from the sample side of the katharometer detector passes back inside the oven and a needle valve is incorporated in the line also within the oven. On the upstream side of this, a T-joint connects the microwave detector and the flow meter into the line. The pipework outside the oven is kept to the minimum consistent with the experimental layout, and is heated to approximately 200° with an electrically heated wire to prevent sample condensation.

Maximum peak height was recorded when the sample was eluted from the gas chromatographic column in the shortest possible time, preferably in less than 90 sec. Long elution times caused the peak to become less well-defined because any tailing or peak broadening in the gas chromatographic system was magnified in the microwave detection unit by the extra pipework involved. However, there must be sufficient resolution of the sample from air and water (which appear as trace impurities) and also from the solvent employed. It was found in our arrangement that a suitable retention time for the sample was between 30 and 80 sec, whilst that of the solvent should exceed this by at least 40 sec.

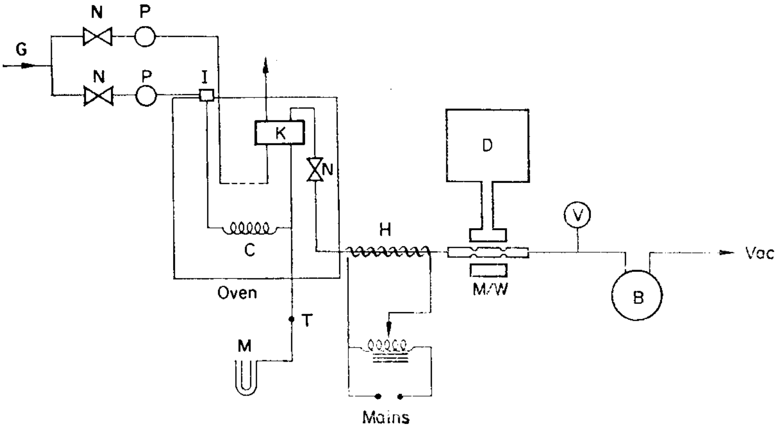


FIG. 2.—Experimental arrangement.

G—carrier gas inlet; *N*—needle valves; *P*—pressure gauges (0–30 psi); *I*—GLC injection block; *K*—katharometer detector; *C*—GLC column; *H*—heating wire (at *ca.* 200°); *D*—detecting and recording system; *M*/*W*—microwave system (see Fig. 1); *V*—vacuum gauge (0–50 mbar); *B*—ballast for vacuum pump; *M*—flow-meter; *T*—on-off tap.

Separation and detection of samples

The general apparatus used in the investigation was the same as that described previously[1] with the exception of the monochromator, which was an Optica CP4 grating instrument.

The carrier gas flow through the column and reference arm of the katharometer detector was first optimized. The tap *T* to the flow-meter was then opened and the needle valve adjusted to register zero flow through the flow-meter. In this way all of the sample eluting from the column passed through the needle valve and was accommodated by the pumping rate of the vacuum pump. Thus, the requisite carrier gas pressure was maintained upstream of the needle valve and maximum vacuum (approximately 4 mbar) downstream. Prior to any determination the tap *T* was closed in order to reduce the "dead" and unswept volumes of the apparatus.

The optimized experimental conditions for the detection of carbon disulphide and thiophen involved the use of a 0·6-m long 6-mm diameter Porapak "P" column, an oven temperature of 200°, benzyl alcohol as solvent and a helium carrier-gas flow-rate of 2 l./hr (producing a pressure of *ca.* 4 mbar in the detector tube). For the detection of dimethyl sulphoxide and thioglycollic acid a 0·6-m, 3-mm diameter Porapak "Q" column was used and a helium carrier-gas flow-rate of 6 l./hr (producing a pressure of *ca.* 8 mbar in the detector tube).

In all instances both the CS bandhead at 257·6 nm and the carbon atomic line at 247·9 nm were monitored, with a photomultiplier voltage of 950 V and monochromator entrance and exit slits of 0·2 mm. Table I shows the relevant retention data obtained under these conditions.

Table II summarizes the detection limits (for a signal to noise ratio of 2) obtained for the sulphur compounds in the quarter-wave foreshortened and quarter-wave Evenson cavities (Electro-Medical

TABLE I.—RETENTION DATA

	Retention time, *sec*	
	Porapak P (helium 2 l./hr)	Porapak Q (helium 6 l./hr)
Gas hold-up time	13	2
Water	17	4
Benzyl alcohol	>150	>150
Carbon disulphide	47	12
Thiophen	85	24
Dimethyl sulphoxide	>150	54
Thioglycollic acid	>150	72

Supplies, Parts Nos. 211L and 214L respectively) with and without the presence of platinum. The detection limits are obtained from the maximum peak height as measured on a chart recorder and refer to a 1-μl sample injection. In this arrangement the detection limit is eventually set by the response time and characteristics of the read-out system. A better method of measurement would be peak integration, probably *via* photon counting, which would not be so dependent on the column characteristics and retention times.

TABLE II.—DETECTION LIMITS FOR SOME SULPHUR COMPOUNDS

		Detection limit, *ng* of sulphur*							
Wavelength of measurement, *nm*	Catalyst	Carbon disulphide 211L†	Carbon disulphide 214L‡	Thiophen 211L†	Thiophen 214L‡	Dimethyl sulphoxide 211L†	Dimethyl sulphoxide 214L‡	Thioglycollic acid 211L†	Thioglycollic acid 214L‡
257·6	None	0·84§		0·67#		30·0		¶	¶
(CS)	Pt	0·15	0·187	0·114	0·071	8·65	4·33	28·7	9·6
247·9	None	1·96						¶	¶
(atomic C)	Pt	0·39	0·15	0·39	0·097	34·6	6·3	¶	¶

* 1-μl injection, measured at maximum peak height, detection limit taken as signal to noise ratio of 2:1.
† Quarter-wave foreshortened radial line cavity.
‡ Quarter-wave cavity (Everson).
§ Previous detection limit 0·2 ng of sulphur.
# Previous detection limit 1000 ng of sulphur.
¶ Not detected at 1000 ng of sulphur.

For carbon disulphide, placing platinum in the quarter-wave foreshortened cavity area produces an increase (*ca.* 5-fold) in peak height at both 247·9 and 257·6 nm, but a decrease (by about a quarter) at 257·6 nm for the quarter-wave Evenson cavity; this trend indicates breakdown to atomic species. In all other instances platinum enhances the breakdown (4–5-fold) of the material and the more efficient Evenson quarter-wave resonant cavity yields the most favourable detection limits. Previously[1] thiophen could only be detected at the 1-μg of sulphur level and dimethyl sulphoxide and thioglycollic acid could not even be detected at this level.

CONCLUSIONS

The oven circuit, described above, allows all of the sample eluted from the gas chromatograph to be passed into the gas discharge, which leads to a considerable improvement in the sensitivity achieved by the system. The use of the constricted detector tube restricts the plasma within the bulb of the tube and results in an intense plasma of increased stability which completely fills the entrance slit of the monochromator. Further plasma stability is achieved by using a ballast to smooth out small fluctuations in the pumping rate of the vacuum pump. Lastly, the inclusion of a platinum catalyst in the gas discharge area, and the use of the Evenson type of quarter-wave cavity results in a greater degree of sample degradation.

In summary, for these sulphur compounds of high thermal stability (*i.e.*, thiophen, dimethyl sulphoxide and thioglycollic acid) greatly improved limits of detection may be obtained by using these modifications.

Acknowledgements—We are grateful to the Science Research Council for financial aid and for the provision of a research studentship to one of us (S. J. P.) under the Co-operative Award in Pure Science scheme. We also thank the Heavy Organic Chemicals Division of I.C.I. (Billingham) for the loan of apparatus and the Central Research Fund of the University of London for the provision of part of the apparatus.

Chemistry Department
Imperial College
London, S.W.7.

R. M. DAGNALL
S. J. PRATT
T. S. WEST

H.O.C. Division, I.C.I. Ltd.
Billingham, Teeside, U.K.

D. R. DEANS

Summary—Improvements in the design and operation of the microwave excited detector for gas chromatography have led to an increase in the sensitivity and a lowering of detection limits for sulphur compounds.

Zusammenfassung—Verbesserungen in Konstruktion und Betrieb des Mikrowellenantegungsdetektors in der Gaschromatographie führten zu Empfindlichkeitserhöhung und zur Senkung der Nachweisgrenzen für Schwefelverbindungen.

Résumé—Des améliorations dans la conception et le travail du détecteur à excitation microonde pour chromatographie en phase vapeur ont mené à un accroissement dans la sensibilité et un abaissement des limites de détection pour les composés du soufre.

REFERENCE

1. R. M. Dagnall, D. R. Deans, S. J. Pratt and T. S. West, *Talanta*, 1969, **16**, 797.

Talanta, 1970, Vol. 17, pp. 1013 to 1014. Pergamon Press. Printed in Northern Ireland

Potentiometric determination of lead with DTPA in the presence of large amounts of aluminium

(*Received* 6 *October* 1969. *Accepted* 2 *April* 1970)

MOLLENHOWER[1] has described a direct gravimetric procedure for the determination of lead in glasses by an electrolytic procedure which is very exact. The method proposed here uses diethylenetriaminepenta-acetic acid (DTPA) to determine lead in lead glasses which are high in aluminium and silicon, with ease, speed and accuracy. DTPA forms a relatively weak complex with aluminium,[2] and hence can be used for this titration. Štráfelda[3] has used a silver-EDTA electrode for complexometric titration, and a silver-DTPA electrode was used in the present work.

EXPERIMENTAL

Reagents

DTPA solution, 0·1*M*. Dissolve 39·5 g of DTPA in about a litre of water with addition of sodium hydroxide to adjust the pH to 8·5. Standardize by potentiometric titration with lead nitrate solution. Dilute to 0·05 or 0·01*M* for use in titrations.

Silver nitrate solution, 0·0002*M*

Borate buffer, 0·5*M*. Dissolve 61·83 g of boric acid and 20·0 g of sodium hydroxide in 2 l. of water. The pH should be 9·0–9·5.

Procedure

Weigh 0·5000 g of lead glass or lead silicate into a platinum dish, add hydrofluoric and perchloric acids and when the sample has dissolved completely, or nearly so, heat to dryness. Then add 15 ml of water and 2 ml of concentrated nitric acid. Evaporate to dryness then add 15 ml of water and 2 ml of nitric acid. Boil the solution and add 3–4 drops of 30% hydrogen peroxide. Continue boiling for 15 min to remove excess of peroxide.

Dilute the solution to 100 ml and add 2 g of sodium tartrate. Then, using phenolphthalein as indicator, add sodium hydroxide until the colour changes. Buffer the solution to pH 9 ± 0·1 with the borate buffer, measured by pH-meter as the pH is critical. Add one drop of 0·0002*M* silver nitrate, insert glass and silver electrodes, and titrate the solution with 0·05*M* DTPA until the potential break is reached.

RESULTS

Typical results showed 100·0 ± 0·1% recovery of 9 mg of lead in the presence of 5–50 mg of aluminium. Two glasses, one of composition SiO_2 41·4%; Al_2O_3 17·9% and PbO 40·7% and the other SiO_2 25·7%; Al_2O_2 20·1%; B_2O_3, 18·6% and PbO 35·6% were analysed, and gave PbO 40·7% and 35·6% respectively.

Owens-Illinois Technical Center
1700 N. Westwood
Toledo, Ohio 43607, U.S.A.

JOHN P. CUMMINGS

Summary—Lead can be titrated accurately in the presence of aluminium with diethylenetriaminepenta-acetic acid, with a silver electrode system for detection of the end-point. The method is very suitable for analysis of lead glasses.

Zusammenfassung—Blei kann in Gegenwart von Aluminium mit Diäthylentriaminpentaessigsäure genau titriert werden; ein Silberelektrodensystem dient zur Endpunktsbestimmung. Die Methode ist zur Analyse von Bleigläsern sehr gut geeignet.

Résumé—On peut titrer le plomb avec précision en la présence d'aluminium au moyen d'acide diéthylènetriaminopentacétique, avec un système d'électrode d'argent pour la détection du point de fin de dosage. La méthode convient très bien à l'analyse de verres au plomb.

REFERENCES

1. H. P. Mollenhower, *J. Soc. Glass Technol.*, 1950, **34,** 254.
2. R. Přibil and J. Horáček, *Talanta*, 1969, **16,** 750.
3. F. Štráfelda, *Collection Czech. Chem. Comm.*, 1965, **30,** 2320.

Talanta, 1970, Vol. 17, pp. 1014 to 1018. Pergamon Press. Printed in Northern Ireland

Optimum physical and chemical conditions for the Methylene Blue method of estimating gaseous sulphide in the environment

(*Received* 24 *June* 1969. *Revised* 4 *February* 1970. *Accepted* 29 *April* 1970)

THE METHYLENE BLUE method for gaseous sulphide estimation is fairly simple and straightforward, but despite its age[1] has not been very systematically studied, and numerous variants exist.[2-10] Perhaps the only fairly detailed study was made by Gustafsson[2] in 1960.

Besides the absorption peak at about 670 nm, another peak at around 740 nm has been reported.[2-5,11] Hardly anyone has used the latter peak for the sulphide estimation although it has been reported as the more sensitive of the two.[4] We now report an examination of this peak and of the optimum physical and chemical conditions for the determination.

EXPERIMENTAL

Chemical aspects

The various methods in the literature are summarized in Table I. The influence of each reagent was studied in turn.

Cadmium hydroxide suspension. An aqueous suspension of cadmium hydroxide in a bubbler was used to absorb gaseous sulphide, since it has been shown to be an efficient retainer of gaseous sulphide[12] even at comparatively high flow-rates of about 3 l./min. Zinc acetate has been used by others but there is no experimental evidence with regard to its efficiency at higher flow-rates. We have found it unnecessary to wash the cadmium hydroxide free from the sodium chloride (or sulphate) which is formed as a by-product.[6] For normal operation a volume of about 25 ml of suspension containing 200–250 mg of cadmium hydroxide is found to be satisfactory.

Concentration of the dye. Only the sulphuric acid concentration was found to have a significant influence on the optimum amount of *p*-aminodimethylaniline required. We find that the absorbance (for up to 120 μg of sulphide) is maximal and constant at dye concentrations above 0·007% w/v in the final solution, for 1·5*M* sulphuric acid medium. We therefore suggest 4 mg of dye per 50 ml for routine work. If smaller amounts of dye are used as in nos. 2, 4 and 8 of Table I, and the sulphide

TABLE I.

Method No.	Reference	Final volume, *ml*	Amount of dye used, *mg/50 ml*	Final acidity, *N*	Amount of iron(III), *mg/50 ml*	Acidity of $FeCl_3$, *N*	Remarks
1	3	50	5·0	2·4	5·5	5·0	H_2SO_4 used
2	6	50	2·25	0·22	6·1	0	H_2SO_4 used
3	7	100	7·2	1·0	16·1	0	H_2SO_4 used
4	8, 9	500	1·0	0·2	0·55	0·5	HCl used in the dye solution
5	4	10	12·5	3·6	71·5	2·25	Iron(III) ammonium sulphate and H_2SO_4 used
6	5	250	5·0	0·55	1·2	1·20	HCl used
7	2	100	3·4–6·8	0·6	13·0	0·5	H_2SO_4 and iron(III) ammonium sulphate used
8	10	50–100	1·2–2·5	0·32–0·66	14·7	0	H_2SO_4 used
9	Present work	50	4·0	3·0	10·0	0·5	H_2SO_4 used

concentrations are relatively high, departure from Beer's law is not surprising (*cf.* Johnson and Nishita[13]) although acid concentration also affects adherence to Beer's law.

Sulphuric acid concentration. It is well known that the absorbance of Methylene Blue is pH-dependent, but most studies have been confined to acid concentrations $<0{\cdot}7M$.

We have found that if the acid concentration is not changed between reaction and measurement, only the 675-nm peak is observed for low acidity. With increasing acidity this peak grows and reaches a maximum at a sulphuric acid concentration of about $0{\cdot}4M$. At the same time the 749-nm peak appears and grows in intensity with sulphuric acid concentration up to about $1{\cdot}4M$, at which it becomes constant and about 20% more than the maximum of the 675-nm peak. At higher acidity the 675-nm peak gradually decreases.

The absorbance at 675 nm is dependent on the sulphuric acid concentration both at the time of reaction and at the time of measurement, especially at the lower concentrations. When the reaction and measurement concentrations are both above $1{\cdot}0M$, there is little variation of the absorbance at 675 nm. On the other hand, the absorbance at 749 nm is entirely dependent on the acid concentration at measurement, if the reaction is performed in sulphuric acid $\geqslant 0{\cdot}7M$. The absorbance at 749 nm also shows dependence on the acid concentration at reaction if this is $<0{\cdot}7M$. There is no appreciable increase in the absorbance at 749 nm if the sulphuric acid concentration at measurement is about $1{\cdot}5M$, and the absorbance is then about 20% higher than the maximum at 675 nm.

We propose that the absorbance at 749 nm or the sum of the intensities at both 675 and 749 nm be used to measure the sulphide concentration (the arithmetic sum of the two remains more steady than the separate values when the acid concentration is varied) and that for both reaction and measurement the sulphuric acid concentration be $\sim 1{\cdot}5M$.

Repetition with hydrochloric in place of sulphuric acid yielded similar results with a slightly different value for the optimum concentration.

Hofmann and Hamm[10] have suggested that the 749-nm peak is due to the interaction of Methylene Blue with a chloroferrate(III) complex, for which an excess of iron(III) is necessary, but our observations show that the 749-nm peak is dependent mainly on the acid concentration.

Beer's law is very closely followed only at higher acid concentrations. If sufficient dye is used, this may account for the deviations reported by earlier investigators, most of whom used low acid concentrations.

We find that too low an iron(III) concentration lowers the absorbance. For $<200\ \mu g$ of sulphide, absorbance is maximal with 8 mg or more of iron(III)/50 ml (if the iron concentration is reduced to 2 mg/50 ml, the absorbance decreases by about 15% at both peaks). The acidity of the iron(III) solution needs only to be the minimum needed to keep the solution clear,[14] whether the chloride or the sulphate is used.

Physical conditions

Temperature. Some workers[2,5,15] have studied the effect of temperature on the absorbance of Methylene Blue, and some have reported that the temperature should be controlled within ±2°.

We find that at normal laboratory temperatures there is hardly any variation in the absorbance with temperature between 10° and 25°. However, when a dye solution containing sulphuric acid is used it is advisable to precool the solutions to around 10° so that on dilution the temperature does not exceed 25°. As discussed later, reaction at 10–15° minimizes gas-phase loss of hydrogen sulphide.

Exposure to light. Some investigators[2,5] have reported that exposure to light adversely affects the absorbance and have recommended shielding from direct light, but have not stated at which point of the procedure the effect occurs.

We find that under normal lighting or in daylight there is no detectable effect on the Methylene Blue during or after the reaction, but that both zinc and cadmium sulphides undergo photodecomposition. This observation is substantiated by the work of Lahman and Prescher.[16] The effect is less on the zinc sulphide, but we prefer to use the cadmium sulphide suspension (200–250 mg of hydroxide in 20–25 ml of water) because of its efficiency for sulphide retention.[12]

The sulphide sampler should be shielded from light during sampling and the sample should be kept in the dark until analysis, especially for sampling of low concentrations of hydrogen sulphide

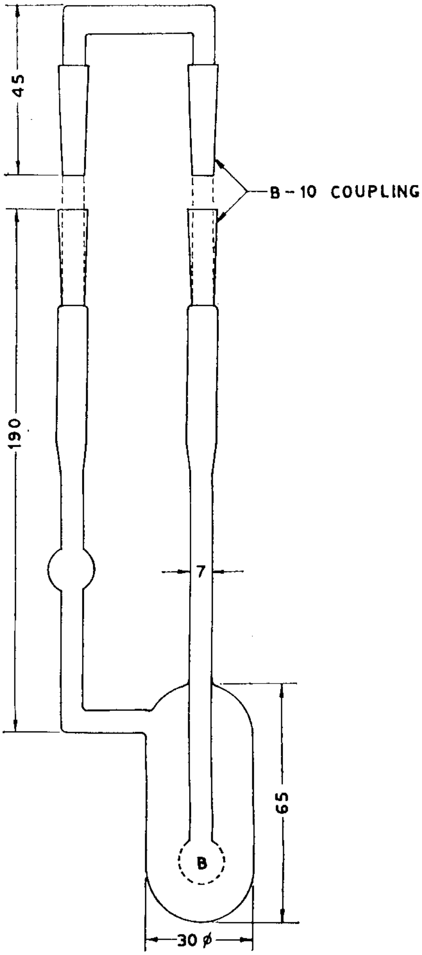


FIG. 1.—Bubbler for hydrogen sulphide sampling. Dimensions in mm.

er extended periods of time. During and after the reaction, protection from light is not necessary.

Gas-phase losses of sulphide. On addition of the acidic dye solution to the mixture of cadmium droxide and sulphide, the hydrogen sulphide evolved immediately reacts with the dye in the presence iron(III). If, however, the container has an appreciably larger volume than the liquid contents, me of the hydrogen sulphide escapes into the space above the liquid and may not react, thus leading a negative error.[4,5] This loss can be minimized by performing the reaction in a 50-ml standard sk, but there may be loss of material during transfer from the sampling bubbler. We have therefore veloped a special sampling bubbler (Fig. 1), with a total volume of slightly less than 50 ml. The bbler is shielded from light during sampling and until the reaction is performed in it.

The bubbler is marked at a level corresponding to its capacity minus the volumes of dye and n(III) solutions to be added (we propose these to be 1 ml of 3% w/v solution of iron(III) chloride eCl$_3$ or equivalent amount of FeNH$_4$(SO$_4$)$_2$] in 0·5*M* hydrochloric acid and 10 ml of 0·04% w/v lution of *p*-aminodimethylaniline in 7·5*M* sulphuric acid).

About 20 ml of hydroxide suspension are used for sampling and are diluted to the reference ark with distilled water, the dye and the iron solutions are added in quick succession and the bubbler closed with the link stopper and then shaken briskly. The link is the only gas space.

Capture of hydrogen sulphide is quantitative in this bubbler for concentrations up to 200 μg/m^3 air at bubbling rates below 3 l./min. At higher bubbling rates there is a proportionate loss.

alibration curve

Detailed procedures have been suggested for preparing standard sulphide solutions, and these are ten lengthy and need care.[3] It is possible to avoid this problem by determining the average degree of nversion of sulphide into Methylene Blue (by comparing the theoretical amount of the latter with at actually obtained from standards) and then using a standard solution of Methylene Blue and the covery factor for calibration purposes. Of course, the purity of the Methylene Blue used must be own, especially its degree of hydration, which appears to be variable from source to source of the estuff.

cknowledgement—The authors express their grateful thanks to Dr. K. G. Vohra for his continued terest and encouragement.

ir Monitoring Section
ealth Physics Division
habha Atomic Research Centre
rombay, Bombay, India

P. K. Zutshi
T. N. Mahadevan

Summary—The sensitivity and reproducibility of the Methylene Blue method for gaseous sulphide estimation have been investigated with respect to physical conditions and the concentrations of the reagents, especially sulphuric acid. A new design of absorber is proposed to minimize gas-phase loss of the sulphide in the final stage of the procedure.

Zusammenfassung—Die Empfindlichkeit und Reproduzierbarkeit der Bestimmung von Sulfid in der Gasphase mit Methylenblau wurden im Hinblick auf die physikalischen Versuchsbedingungen und auf die Konzentration der Reagentien, speziell der Schwefelsäure, untersucht. Ein neukonstruierter Absorber wird vorgeschlagen, um den Verlust von Sulfid in der Gasphase bei der Endstufe des Verfahrens möglichst klein zu halten.

Résumé—On a étudié la sensibilité et la reproductibilité de la méthode au bleu de méthylène pour le dosage du sulfure gazeux par rapport aux conditions physiques et aux concentrations des réactifs, spécialement l'acide sulfurique. Une nouvelle conception de l'absorbeur est proposée pour minimiser la perte en phase gazeuse du sulfure dans le stade final de la technique.

REFERENCES

1. E. Fischer, *Ber.*, 1883, **16**, 2234.
2. L. Gustafsson, *Talanta*, 1960, **4**, 227.

3. M. W. Brenner, J. L. Owades and R. Colyzniak, *Am. Soc. Brewing Chemists Ann. Meeting*, p. 83, 1953.
4. S. Patel and C. P. Spencer, *Anal. Chim. Acta*, 1962, **27**, 278.
5. J. K. Fogo and M. Popowsky, *Anal. Chem.*, 1949, **21**, 732.
6. M. B. Jacobs, M. M. Braverman and S. Hochheiser, *ibid.*, 1957, **29**, 1349.
7. K. E. Prescher and E. Lahman, *Gesundh. Ing.*, 1966, **87**, 12, 351.
8. L. H. Almy, *J. Am. Chem. Soc.*, 1925, **47**, 1381.
9. W. Mecklenburg and F. Rosenkränzer, *Z. Anorg. Allgem. Chem.*, 1914, **86**, 143.
10. K. Kuratomi, K. Ohno and S. Akabori, *J. Biochem. (Tokyo)*, 1957, **44**, 183.
11. K. K. Hofmann and R. Hamm, *Z. anal. Chem.*, 1967, **232**, 167.
12. C. E. Bostroem, *Intern. J. Air Water Pollution*, 1966, **10**, 435.
13. C. M. Johnson and H. Nishita, *Anal. Chem.*, 1952, **24**, 736.
14. H. Demus and H. Liebert, *Faserforsch. Textiltech.*, 1966, **17**, 422.
15. H. T. Badings and J. J. G. Van der Pol, *Neth. Milk Dairy J.*, 1965, **19**, 283.
16. E. Lahman and K. E. Prescher, *Staub*, 1965, **25**, 527.
17. I. St. Lorant, *Z. Physiol. Chem.*, 1929, **185**, 245.

Talanta, 1970, Vol. 17, pp. 1018 to 1020. Pergamon Press. Printed in Northern Ireland

Determination of platinum, palladium and silver in geological materials and their concentrates by fire assay and emission spectrography

(*Received* 19 *November* 1969. *Accepted* 19 *May* 1970)

PLATINUM, palladium and silver are determined by fire-assay preconcentration and the graphite arc. A measured volume of the assay-bead solution is evaporated to dryness on the surface of two flat-top graphite electrodes and the dry residue excited according to the modified method of Zilberstein.[1]

EXPERIMENTAL

Fire assay

A mixture of 65 g of sodium carbonate, 17 g of potassium carbonate, 17 g of fused borax, 38 g of lead oxide and 13 g of starch is used as flux; 100–150 g of the mixture are placed in a 750-ml fireclay crucible, then 50 or 150 g of sample are added and the contents thoroughly mixed; some flux is added to cover the mixture. The crucible is placed in the muffle of a fire assay furnace preheated to 850–950°, and the temperature is raised to 1000–1100° over a period of 40–50 min. The crucible is then removed and the molten charge is poured into an iron mould and allowed to cool. The slag is carefully chipped and worked away from the lead with a hammer and brush and the lead is tapped into a cube, producing the lead button. The lead of the button is separated from its noble metal content by cupellation.

Typical sample contents were gold from 1 to 3 g/ton and silver from 15 to 20 g/ton. The weights of the beads ranged from 0·5 to 4 mg.

Dissolution of the bead, and spectrographic analysis

The bead is transferred to a 25-ml crucible, 0·8 ml of nitric acid (sp.gr. 1·44) is added and the crucible covered with a watch-glass. The contents are heated slowly and carefully to prevent or to minimise the powdering of the insoluble residue. Palladium and silver are dissolved by the nitric acid and the remaining platinum metals and gold remain undissolved in the form of a black porous mass. The nitric acid solution is transferred quantitatively to another 25-ml crucible and evaporated to a moist residue, which is treated with 5 ml of distilled water and evaporated to moistness again, this water/evaporation step being repeated thrice more. Finally the residue is dissolved with 1 ml of distilled water, from which three aliquot portions of 0·1 ml each are transferred by means of a micropipette to each of two flat-top graphite electrodes previously waterproofed with a 0·5% petroleum ether solution of Apiezon grease "N". The electrodes are dried at 110°, then 0·5 ml of a 1-ppm solution of molybdenum and 1 drop of the mixed buffer (0·25% sodium chloride and 0·5% potassium chloride) are transferred to the same electrodes. The electrodes are kept in the drying room until placed in the arc stand. The apparatus and operating conditions are listed below. When silver is to be determined in ores, 0·5 ml of the nitric acid solution is diluted to volume in a 100-ml volumetric flask and this solution is used for analysis.

Twelve drops of *aqua regia* are added to the residue to dissolve platinum. The mixture is heated slightly to hasten dissolution. The solution is evaporated to dryness and 4 drops of hydrochloric acid are added and the solution again evaporated to remove the remaining nitric acid. A fourfold evaporation with 5 ml of distilled water is again used. As the concentration of platinum in the samples is very low, the moist residue is mixed with 0·3 ml of distilled water and the entire solution is added to the two electrodes. Consequently only a single result for platinum is obtained. The analytical lines used are given in Table I.

TABLE I.—ANALYTICAL LINES USED IN DETERMINATION OF PLATINUM, PALLADIUM AND SILVER

Element	Analytical line *nm*	Concentration range based on analytical curve, *μg*
Pt	306·471	0·01–0·1
Pd	324·270	0·005–0·15
Ag	328·068	0·00001–0·1

The Mo 317·035 nm lines was used as internal standard throughout.[2]

Apparatus and spectrographic operating conditions

A quartz spectrograph [ISP-28 (USSR)], with a mean reciprocal linear dispersion of approximately 1·6 nm/mm in the working range, was used with a three-lens system. The operating conditions were as follows: slit height 3·2 mm; analytical gap 2 mm; slitwidth 0·020 mm for Pd and Ag and 0·018 mm for Pt; arc generator DB-6 (East Germany) or DG-2 (USSR); current 8 A; microphotometer, Carl Zeiss (Jena) type II, with a slitwidth of 0·015 mm; exposure 30 sec; spectral plates ORWO–WU2; electrodes EKL type T3 (East Germany) and type C3 (USSR).

The concentrations of the elements in the unknown samples are obtained from analytical curves established by plotting the ratio of the intensities of the analytical and internal standard lines minus the background intensities (ordinate) *vs.* log concentration (abscissa).[3] Transmittance measurements are made with a microphotometer.

Preparation of standards

Stock solutions of the elements, 0·1% w/v, are made by dissolving palladium(II) chloride and hexachloroplatinic acid in 0·2*M* hydrochloric acid, and silver nitrate in distilled water. These stock solutions are then diluted with the solvent to give 100, 10, 1, 0·1, 0·01 ppm of palladium and platinum, and 100, 10, 1, 0·1, 0·01, 0·001, 0·0001 ppm of silver. The 1-ppm molybdenum solution is made by appropriate dilution of an ammonium molybdate solution in distilled water.

The standards for determination of each element are made separately by transferring 0·1 ml of each standard solution to each of two flat-top graphite electrodes. After drying, the standards are run by the method described. The concentration of silver in the samples is generally about 100 times that of the palladium. For this reason 0·1 ml of the silver solution (0·1% w/v) is added to the palladium standard electrodes.

RESULTS AND DISCUSSION

The precision of the method is illustrated by the results obtained in 20 replicate determinations. The standard deviations were 10, 4 and 11 ng for 79 ng of platinum, 55 ng of palladium and 81 ng of silver respectively. To illustrate the accuracy of the method, aliquots of palladium and platinum standards were added to 25 and 50 g of copper ore; the material was dried at 110° and analysed according to the method described. The recoveries were 89–92% for 1 μg of platinum and 97–105% for 1 μg of palladium.

Best results with regard to the intensity of the spectral lines were obtained when the acidity of the solutions was maintained at a pH of about 4. At a low pH (0·8) the sensitivity for platinum decreases to 0·1 μg, for palladium to 7 ng, and for silver to 0·5 ng. Excluding the influence of anion content on sensitivity, it was found that when the solutions were at pH 4 there was little or no loss of residue during the arcing process, thus providing good sensitivity.

It was found that a large excess of platinum and palladium does not influence the intensity of the silver line. Hence the method can be used for the determination of silver in platinum or palladium metal. When silver is 100 times greater in concentration than the other two metals, the intensity of the palladium line used is increased, while that of the platinum line is unchanged. When the silver is present in greater excess than this, the sensitivity decreases to 0·1 μg for platinum and 10 ng for palladium and the results are very erratic. This can best be explained in terms of the maximum quantity of dry residue permitted on the surface of the electrodes. Silver enhances the intensity of the molybdenum line and may be used to increase the sensitivity for that element (1 ng) when it is to be determined.

The determination of palladium is not influenced by an excess of platinum and therefore the method can be used for the determination of palladium in platinum metal. When the concentration of palladium is high, the Pd 306·531 nm line interferes with the Pt 306·471 nm line. The platinum 265·945 nm line could then be used, but this has not been investigated experimentally. Gold does not interfere.

Faculty of Chemistry
State University of Sofia
1 *Anton Ivanov Avenue*
Sofia 26, *Bulgaria*

E. G. Koleva
S. H. Arpadjian

Summary—A method is described for the determination of platinum down to 10 ng, palladium to 5 ng and silver to 10 pg in 50 or 100 g of sample. Fire-assay techniques are used to preconcentrate these metals into a bead which is first treated with nitric acid to dissolve palladium and silver and then with *aqua regia* to dissolve platinum. Both solutions are diluted and adjusted to pH 4, then analysed by optical emission spectrography of the residue from a measured volume evaporated on a pair of flat-top graphite electrodes. This method requires much less sample handling than most published methods for these elements.

Zusammenfassung—Ein Verfahren zur Bestimmung von Platin bis herunter zu 10 ng, Palladium bis 5 ng und Silber bis 10 pg in 50 oder 100 g Probe wird beschrieben. Zur Anreicherung dieser Metalle werden sie in eine Perle geschmolzen; diese wird zuerst mit Salpetersäure behandelt, um Palladium und Silber zu lösen, dann mit Königswasser zur Auflösung von Platin. Beide Lösungen werden verdünnt und auf pH 4 eingestellt; dann wird ein abgemessenes Volumen auf einem Paar flacher Graphitelektroden eingedampft und durch optische Emissionsspektrographie analysiert. Dieses Verfahren erfordert weit weniger Operationen mit der Probe als die meisten bekannten Analysenmethoden für diese Elemente.

Résumé—On décrit une méthode pour la détermination du platine descendant jusqu'à 10 ng, du palladium jusqu'à 5 ng et de l'argent jusqu'à 10 pg dans 50 ou 100 g d'échantillon. Des techniques par voie sèche sont utilisées pour la préconcentration de ces métaux dans une perle qui est d'abord traitée á l'acide nitrique pour dissoudre le palladium et l'argent puis à l'eau régale pour dissoudre le platine. Les deux solutions sont diluées et ajustées à pH 4, puis analysées par spectrographie d'émission optique du résidu d'un volume mesuré évaporé sur une paire d'électrodes en graphite à partie supérieure plane. La méthode nécessite beaucoup moins de manipulation d'échantillon que la plupart des méthodes publiées pour ces éléments.

REFERENCES

1. Kh. I. Zilberstein, *Zh. Tekh. Fiz.*, 1955, **25**, 1491.
2. J. Haffty and L. B. Riley, *Talanta*, 1968, **15**, 111.
3. N. Jordanov and Ch. Sheitanov, *Physical Methods of Analytical Chemistry*, Sofia, 1965.

Talanta, 1970, Vol. 17, pp. 1021 to 1023. Pergamon Press. Printed in Northern Ireland

Theoretical considerations on the estimation of sample matrix effects in analytical chemistry

(*Received* 19 *March* 1970. *Accepted* 1 *May* 1970)

SEVERAL methods in analytical chemistry are used to determine concentration by means of a linear equation of the form

$$R = kC_X + R_{C_X=0} \qquad (1)$$

where R is the reading of some instrument, C_X is the concentration of some substance X, k is a proportionality constant (for a given set of conditions), and $R_{C_X=0}$ represents R for a sample identical with that to be analysed except that $C_X = 0$. Thus $R_{C_X=0}$ represents an effect caused by the matrix in which X is to be determined. Examples are photometric determination (where R can be absorbance or emission) and polarography (where R is the current).

The assumption that in equation (1) $R_{C_X=0} = 0$ is usually either stated explicitly, assumed implicitly, or ignored. It can, however, be unjustified and so affect considerably the results obtained through the use of equation (1).

It should be noted that equation (1) states that R is directly proportional to C_X only for a given set of conditions. Thus a change of the concentration C_X effected through a change of the amount of the substance X (m_X) is not equivalent to a change of concentration effected through a change in the volume (V_S) of the pure solvent used—unless the original sample consisted only of the pure solvent and the substance X.

As an example we can consider a volume V_X of some biological fluid, in which m_X represents m moles of calcium. On doubling m_X the term $R - R_{C_X=0}$ will be doubled. However on doubling V by the addition of pure solvent (say water) of volume $V_S = V_X$ the term $R - R_{C_X=0}$ will not necessarily decrease by a factor of 2, as the dilution of the biological fluid can (and generally will) affect the value of both k and $R_{C_X=0}$. Thus the methods based on equation (1) have to take into account the behaviour of both k and $R_{C_X=0}$ on the determination of m_X. The implications of the argument above have already been considered in some detail in a study of the flame photometry of calcium in the presence of strongly interfering substances.[1,2]

It has been shown that k can easily be obtained experimentally. The effect of $R_{C_X=0}$, which is identified with a contribution due to interference, R_I, is more difficult to assess. It has been suggested that some convenient parameter out of the many parameters affecting R could be utilized for the detection and evaluation of R_I. Such utilization of dilution as the changing parameter has been treated theoretically and experimentally,[1,2] but it was shown that dilution is not an ideal parameter for this purpose. In photometry a promising parameter appears to be the wavelength λ. The possible use of this parameter is discussed below.

Let us assume that the instrument (equipped with a monochromator precise within ±0·05 nm)[3] is set initially to the wavelength suitable to the element concerned, *e.g.*, for calcium to 422·7 nm., At this wavelength λ^0 the reading for the unknown mixture will be $R_M{}^0$, and we assume that it is due to the contribution $R_X{}^0$ of the element to be determined, and the contribution $R_I{}^0$ of some interference. On altering λ we shall get a new reading $R_M(\lambda)$, composed similarly:

$$R_M(\lambda) = R_X(\lambda) + R_I(\lambda). \qquad (2)$$

At any λ the value R_M is assumed to be directly proportional to the quantity of the substance X, so that at any λ, according to equation (1),

$$k(\lambda) = \left(\frac{\partial R_M(\lambda)}{\partial m_X}\right)_\lambda \qquad (3)$$

and

$$R_M(\lambda) = k(\lambda)m_X + R_I(\lambda). \qquad (4)$$

To obtain m_X from equation (4) it is necessary to have some information on $R_I(\lambda)$ in addition to the experimentally obtainable $R_M(\lambda)$ and $k(\lambda)$. The simplest assumption is that $R_I = 0$. In such a case $R_M(\lambda)$ plotted against $k(\lambda)$ should give a straight line passing through the origin of the co-ordinates. A more direct indication, without the necessity of measuring the k's, would be the shape of $R_M(\lambda)$ plotted against λ: with $R_I = 0$ the tails should taper to zero on both sides of λ^0. The next simplest assumption is that R_I is a constant independent of λ. The possibility of the evaluation of m_X in such a simple case is discussed by Herrmann and Alkemade.[4] Following our previous argument, in this case a plot of $R_M(\lambda)$ against $k(\lambda)$ would again yield a straight line, but the intercept would now be not zero but R_I. The plot of $R_M(\lambda)$ against λ would show tails maintaining a constant value on both sides of λ^0. However both $R_I = 0$ and $R_I =$ constant represent only special cases. In general $R_I(\lambda)$ *will* exist, and will *not* be constant. A more reasonable approximation appears to be that $R_I(\lambda)$ can be expressed by a linear function, *e.g.*,

$$R_I(\lambda) = R_I{}^0 + A(\lambda - \lambda^0). \tag{5}$$

Such a situation is described in Fig. 1, assuming a Gaussian line for the element X.

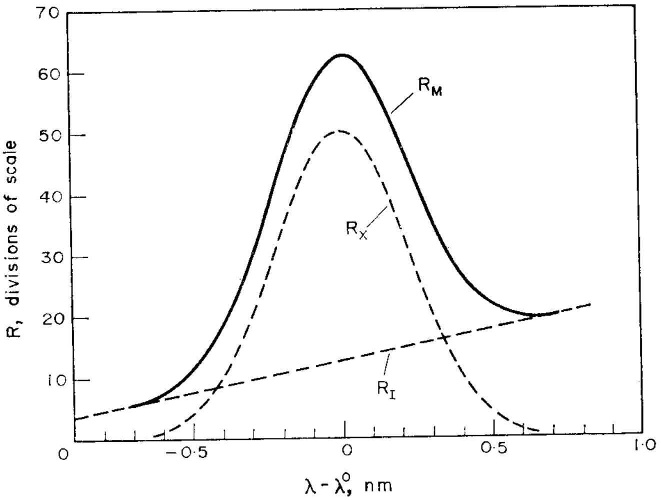


FIG. 1.—R as a function of wavelength, assuming that $R_M = R_X + R_I$ while $R_X = 50 \exp \{-1(\lambda - 422{\cdot}7)^2\}$ and $R_I = 12{\cdot}5 + 10(\lambda - 422{\cdot}7)$.

The numerical values presented in Fig. 1 were obtained from:

$$R_X = 50\, e^{-1(\gamma-422.7)^2} \tag{6}$$

and

$$R_I = 12{\cdot}5 + 10(\lambda - 422{\cdot}7) \tag{7}$$

These values are in line with the $R_X{}^0$ and $R_I{}^0$ obtained previously,[1] and with the spectrum of calcium obtained by Watanabe and Kendall.[3] It is probable that a system of water, lanthanum chloride, calcium chloride and hydrochloric acid follows approximately the behaviour described in Fig. 1.

It can be seen that the experimentally obtained behaviour of $R_M(\lambda)$ can be used to evaluate $R_I(\lambda)$ graphically from the limiting slope of the tails. Introduction of $R_I{}^0$ so obtained into equation (4), with $R_M{}^0$ and k^0 determined experimentally, yields m_X directly. In this case the exact shape of $R_X(\lambda)$ is irrelevant—as long as it approaches zero asymptotically on both sides and not too far from λ^0.

If the linearity of the tails is less obvious, and $R_I(\lambda)$ cannot be deduced directly from the graph, it can still be possible to utilize the experimental values of $R_M(\lambda)$ and $k(\lambda)$ to obtain $R_I{}^0$ and m_X. Theoretically, three experiments should be sufficient to obtain the constants m_X, $R_I{}^0$ and A from equations (4) and (5). In our example, with R_M precise to within ±1 %, three measurements at λ's not further than 0·3 nm from λ^0 would already yield m_X with an error of only about 3 %. A greater accuracy could be obtained by conducting a larger number of experiments, and determining the constants by least squares. It should be noted that here again the form of R_X need not be Gaussian.

Finally, an approximation can be used to avoid the laborious determination of $k(\lambda)$. If a Gaussian form is assumed for $R_X(\lambda)$, it is easily seen that $k(\lambda)$ must also have a Gaussian form with the same exponent. Thus equation (4) assumes the form:

$$R_M = k^0 e^{-B(\gamma-\gamma^0)^2} m_X + R_I{}^0 + A(\lambda - \lambda^0). \tag{8}$$

Theoretically, five determinations of $R_M(\lambda)$ without any other measurements should suffice to determine the constants k^0, A, B, $R_I{}^0$ and m_X. In practice, at least k^0 would be determined experimentally, and a larger number of $R_X(\lambda)$ would be available to obtain reasonable results.

In the last method the function $R_X(\lambda)$ had to be introduced explicitly, to obtain $k(\lambda)$. The assumption that $R_X(\lambda)$ is a Gaussian curve can easily be wrong, as the exact function is determined by many unknown experimental factors. Possibly a Lorentzian shape would be a closer approximation, in which case instead of equation (8) one could use equation (9):

$$R_M = \frac{k^0 m_X}{1 + B(\lambda - \lambda^0)^2} + R_I{}^0 + A(\lambda - \lambda^0). \tag{9}$$

Thus an independent study of $R_X(\lambda)$ would be a prerequisite for the use of the last (approximate) method.

The discussion above demonstrates how the method of the changing parameter introduced in reference (1) can be applied to photometry, with λ used as the changing parameter. It can be seen that while the basic principle is the same as that applied in the case of dilution,[1,2] the functions R_M, R_I and k are completely different in the two cases. Similar analyses would have to be carried out in the case of any changing parameter applied to any analytical method based on equation (1). It would be of interest to test experimentally the conclusions reached above—unfortunately commercial atomic absorption flame photometers are unsuitable for such measurements. It would also be of interest to apply the method to other systems employing equation (1).

Polymer Department
Weizmann Institute of Science
Rehovot, Israel

ADAM SHATKAY

Summary—Methods are suggested for evaluating the magnitude of matrix effects on the results of analysis.

Zusammenfassung—Methoden zur Berechnung der Größe des Einflusses der Matrix auf Analysenergebnisse werden vorgeschlagen.

Résumé—On suggère des méthodes pour évaluer la grandeur des influences de gangue sur les résultats d'analyse.

REFERENCES

1. A. Shatkay, *Anal. Chem.*, 1968, **40**, 2097.
2. *Idem*, *Appl. Spectr.*, 1970, **24**, 14.
3. H. Watanabe and K. K. Kendall Jr., *ibid.*, 1955, **9**, 132.
4. R. Herrmann and C. T. J. Alkemade, *Chemical Analysis by Flame Photometry*, 2nd Rev. Ed., p. 322. Interscience, New York, 1965.

Talanta, 1970, Vol. 17, pp. 1025 to 1028. Pergamon Press. Printed in Northern Ireland

ANNOTATION

Behaviour of dilute solutions of mercury*

(*Received* 10 *February* 1970. *Accepted* 31 *March* 1970)

IN STUDIES on the separation of submicrogram quantities of mercury, many of the steps were followed by using the radioisotope ^{203}Hg. When vials containing the sample were left uncapped, it was noticed that activity was lost.[1] This observation was somewhat surprising in that solutions of ionic mercury are not ordinarily considered to lose appreciable amounts of the element by volatilization at room temperature.

There is ample documentation of the movement of mercury in and out of solutions under a variety of conditions. Magos[2] has shown that rapid isotope exchange occurs when air containing mercury vapour is passed through a ^{203}Hg-labelled mercury(II) acetate solution. Clarkson *et al.*[3,4] have demonstrated the ready movement of mercury from biological systems to air, both *in vitro* and *in vivo*. In one experiment they showed that all the radioactivity in a serum sample appeared in an adjacent mercury pool within a short period of time in a closed Warburg flask. In another they showed that in a serum sample exposed to air or oxygen saturated with mercury vapour there was a continuous uptake of mercury, but in a similar experiment using a 95% nitrogen–5% carbon dioxide atmosphere saturated with mercury vapour there was barely significant uptake, if any. Magos *et al.*[5] reported that micro-organisms normally present in the laboratory and the laboratory water supply were capable of rapidly volatilizing mercury as the metallic vapour from solutions of mercury(II) salts in plasma, broth or urine. They also showed that mercury would volatilize from solutions of mercury(II) chloride after the addition of vitamin C.

In previous reports on the loss of mercury the existence of reducing agents within the system permitted the postulation that reduction to metallic mercury occurred with subsequent volatilization. The present studies were undertaken in order to elucidate the mechanism by which mercury moved from dilute inorganic solutions to which no reducing substances were added.

EXPERIMENTAL

Materials

All solutions were made with reagent grade chemicals and demineralized water. Carrier-free ^{203}Hg was added to the desired quantities of mercury(II) chloride solutions.

Apparatus

For initial studies Warburg flasks were used, but the ease with which separated solutions could mix led to the design of a container, in essence a modified Conway unit, in which the solutions should not accidentally mix and several different solutions could be placed in the same atmosphere to compete for the radioactivity from a single solution. An inverted plastic Petri dish (100 × 20 mm) was fitted into a groove cut into a 10-mm thick "Lucite" sheet. The groove was filled with stop-cock grease. The cups ($<$40 mm diameter) were made from commercially obtainable polyethylene stoppers.

Procedure

In the Warburg flask, 3 ml of mercury(II) chloride solution in $\sim$0·1*M* hydrochloric acid were placed in the main portion, and 1 ml of trapping solution was placed in the side-arm. In some experiments a drop of metallic mercury was covered with the trapping solution, and in others was left uncovered in a separate side-arm. In the special apparatus, equal volumes of original solution and trapping solution were used. The vial containing the trapping solution was placed in a polyethylene bag before insertion into the well of the radioactivity counter.

In the competition experiments and for studying the effect of potassium permanganate on the escape of mercury, the multicup arrangement was used, with 3 ml of trapping solution in each cup, except for metallic mercury which was limited to 2 drops. Experiments were carried out at room temperature with no attempt at accurate temperature control. Gentle mixing was provided by placing the flasks on a gyratory platform shaker.

---

* This work was supported in part by a USPHS Grant No. 1T1 DE175 and in part by the United States Atomic Energy Commission, Contract No. W-7401-Eng-49 and has been assigned Report No. UR-49-1226.

RESULTS

In the initial experiments an attempt was made, based on observations already reported in the literature,[4] to determine the conditions under which mercury would move. Accordingly, the atmosphere was varied and metallic mercury was introduced in several ways. The results are summarized in Table I. There was insignificant movement of the isotope except when metallic mercury was in open contact with the atmosphere of the flask. The multicup unit was then used so that several different solutions could be used in competition under various conditions. The results summarized in Table II show that only solutions containing some mercury salts absorb radioactivity. Experiment 3 shows this effect rather strikingly since a potassium nitrate solution without mercury has gained no radioactivity whereas a solution with mercury has gained a sizable fraction of the original activity.

TABLE I.—MOVEMENT OF MERCURY TO VARIOUS TRAPPING SOLUTIONS IN ONE DAY

Activity remaining, *cpm*	Trapping solution	Metallic mercury	Atmosphere	Activity in trap, *cpm*
88100	0·1*M* HCl	none	O_2	0
87600	0·1*M* HCl	none	N_2	0
15	0·1*M* HCl, 0·2*M* KBr	separate	O_2	0
80300	0·1*M* HCl, 0·2*M* KBr	in trap	O_2	434
11	0·1*M* HCl, 0·2*M* KBr	separate	N_2	0
89545	0·1*M* HCl, 0·2*M* KBr	in trap	N_2	62

Original solutions had an activity of 87400 cpm; when metallic mercury was used separated from the trapping solution, all the activity was transferred to the mercury.

TABLE II.—EFFECT OF VARIOUS COMPOUNDS ON MOVEMENT OF RADIOACTIVE MERCURY

Experiment	Dish	Initial composition of liquid in dish	Fraction of original activity, found in dish, %	
1	1	30 μg of Hg + ^{203}Hg	57·7 (1 day)	54·7 (4 days)
	2	10 μg of Hg in HCl + KBr	18·2	22·2
	3	10 μg of Hg in HCl + NH_4Cl	18·0	17·8
	4	10 μg of Hg in NaOH	2·8	1·2
2	1	30 μg of Hg + ^{203}Hg	104 (5 days)	
	2	0 μg of Hg in HCl + KBr	0	
	3	0 μg of Hg in HCl + NH_4Cl	0	
	4	0 μg of Hg in NaOH	0	
3	1	30 μg of Hg + ^{203}Hg	72 (4 days)	
	2	0 μg of Hg + NH_4OH	0	
	3	0 μg of Hg + KNO_3	0	
	4	10 μg of Hg + KNO_3	18	
4	1	30 μg of Hg + ^{203}Hg + $KMnO_4$	100·2 (3 days)	
	2	30 μg of Hg in HCl	0	
	3	10 μg of Hg in HCl + KBr	0	
	4	10 μg of Hg in HCl + KNO_3	0	
5	1	30 μg of Hg + ^{203}Hg + $KMnO_4$	99 (1 day)	
	2	2 drops of mercury	0	
6	1	30 μg of Hg + ^{203}Hg + $KMnO_4$	144 (1 day)	
	2	30 μg of Hg + ^{203}Hg	17·2	
	3	2 drops of mercury	not measured	
7	1	30 μg of Hg + ^{203}Hg + $KmnO_4$	103 (3 days)	
	2	30 μg of Hg + ^{203}Hg	99	

Experiment 1 shows that some differences occur in the ability of various salt solutions to absorb the radioactivity when equal amounts of mercury salts are present. The reasons for this were not pursued.

Table II also summarizes the effects of adding a small quantity of potassium permanganate to the solution initially containing all the radioactivity, or (experiments 6 and 7) to one of the solutions initially containing equal amounts of radioactivity.

The presence of the strongly oxidizing potassium permanganate is shown to prevent movement of radioactivity out of the solution even when liquid mercury is present elsewhere in the system. Other experiments (Table I) had shown that radioactive mercury moved rapidly to a metallic mercury trap. Experiments 6 and 7 (Table II) show that a solution containing permanganate successfully competed with the liquid mercury drops for the radioactivity escaping to a saturated mercury atmosphere from a solution containing no oxidizing agent.

DISCUSSION

The published work on loss of mercury from solutions containing trace quantities has involved either biological solutions or solutions containing a reducing agent. Here it seemed very likely that the mercury escaped as the metallic vapour. However, when movement occurred from inorganic solutions containing no added reducing agents, there was the possibility that a volatile compound of mercury might be involved. The experimental evidence does not support this possibility, and thermodynamic considerations indicate that the mechanism is reduction of mercury(II) to mercury(I) which then disproportionates into mercury(II) and metallic mercury.

Consider the volatilities of mercury and mercury(II) chloride. At 26°, the vapour pressure of mercury is 2·66 μbar,[6] and the solubility in water at 20° is 0·02 μg/ml.[7] The complete reduction of only 1% of a $10^{-5}M$ mercury(II) chloride solution would saturate the solution with mercury, and the gas-phase mercury content would be 23 ng/ml. It is easy to see how a solution containing μg quantities of mercury could exchange its contents rapidly in a process involving metallic mercury.

The vapour pressure of mercury(II) chloride at 26° is 0·1 μbar,[6] which is about 5% that of metallic mercury. However, its partial pressure in a $10^{-5}M$ solution would be only 0·02 pbar, and the gas phase would contain 2×10^{-4} pg/ml. Such small quantities make it unlikely that mercury(II) chloride vapour plays an appreciable role in the movement of the mercury activity out of solution. This conclusion was experimentally verified by showing that increasing the amount of mercury(II) chloride in the initial solution reduced the amount of radioactivity escaping.

The rapid escape of activity from solution when a mercury pool was present and the necessity of having mercury(II) salts in the trapping solution show that an exchange process involving mercury vapour is involved. In order to account for the movement when no mercury vapour is deliberately supplied, we must postulate that a small amount of reducing material is introduced with the various reagents used. A possible mechanism may be proposed, based on the mercury(I) disproportionation equilibrium.[8]

$$Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg(l)\ E = 0{\cdot}065\ V$$

At equilibrium the ratio $[Hg^{2+}]/[Hg_2^{2+}]$ is 6×10^{-3}, so further reduction of $[Hg^{2+}]$ would permit spontaneous disproportionation and the metallic mercury formed would easily escape from the solution. Such an extensive reduction of the $[Hg^{2+}]$ levels would not be necessary at room temperature because collisions of molecules could provide about a fifth of the 12 kJ/mole free energy change.

The actual quantities of free mercury(II) and mercury(I) ions in solution are far less than the total amount of mercury(II) salt in solution, as may be determined from the stability constants and solubility products. The solutions used in this study were usually $\sim 0{\cdot}1M$ chloride solutions. The predominant mercury(II) complex is probably $HgCl_4^{2-}$, and its stability constant[8] is $1{\cdot}2 \times 10^{15}$.

If the mercury(II) in solution is $10^{-5}M$ and the chloride is $0{\cdot}1M$, $[Hg^{2+}] = 8{\cdot}3 \times 10^{-17}M$. The solubility product of Hg_2Cl_2 is given as $1{\cdot}1 \times 10^{-18}$; in a $0{\cdot}1M$ chloride solution $[Hg_2^{2+}] = 1{\cdot}1 \times 10^{-16}M$. It may be seen that only a small quantity of mercury(II) need be reduced to give a saturated solution of the mercury(I) ion, which then would remain at a constant level. Furthermore, with smaller quantities of mercuric salts in solution the quantity of mercury(II) ion would decrease whereas that of mercury(I) ion would remain constant. Thus, the disproportionation would be favoured by smaller amounts of the mercury(II) salt in solution. The stability of dilute solutions of mercuric salts thus becomes a question of the quantity of mercury in solution.

The high oxidation potential of the Hg(II)/Hg(I) couple indicates a high probability of reduction by almost any reducing substance. The extreme insolubility of mercury(I) chloride also indicates that a very small quantity of a reducing agent would provide a saturated solution ($1{\cdot}1 \times 10^{-16}M$). The introduction of such low levels of reducing substances through the reagents or even the demineralized water is almost inevitable but difficult to quantitate. However, the postulation is supported by the fact that small amounts of potassium permanganate (Table II) added to solutions containing radioactive mercury effectively prevent the loss of any radioactivity.

A crucial experiment (Table II, No. 6) is that in which equal amounts of mercury(II) salts and of radioactivity are contained in two solutions, but some potassium permanganate has been added to one. A saturated mercury vapour atmosphere is provided by placing 2 drops of liquid mercury in a third dish. Here it is shown that in one day there has been movement out of only one solution, and also substantial increase in activity in the other, which shows that oxidation of the mercury vapour by the permanganate has occurred. A contrasting experiment (No. 7) in which no mercury vapour is provided shows the much slower movement of the radioactivity in the absence of a saturated mercury atmosphere.

CONCLUSIONS

Thermodynamic considerations show that the loss of mercury from a solution which contains the element in the mercury(I) form may occur readily through disproportionation and subsequent loss of metallic mercury. Because of the high oxidation potential of the mercury(II)-mercury(I) system almost any reducing substance can convert some mercury(II) into mercury(I).

Because of the near impossibility of preventing introduction of small amounts of reducing substances by the reagents, the more dilute mercury(II) solutions would be less stable and lose mercury more readily. The only practical method for stabilization would be to add a small excess of an oxidizing substance (such as permanganate) which has a higher oxidation potential than the mercury(II)-mercury(I) system.

Department of Radiation Biology
and Biophysics
University of Rochester School of
Medicine and Dentistry
Rochester, New York 14620, *U.S.A.*

T. Y. Toribara
C. P. Shields
Larysa Koval

Summary—It is shown that loss of radioactivity from labelled mercury(II) solutions is due to reduction of some mercury(II) by reductants adventitiously introduced, followed by disproportionation of mercury(I) and loss of metallic mercury in the gas phase. The loss can be prevented by addition of a small excess of an oxidant such as permanganate.

Zusammenfassung—Es wird gezeigt, daß der Aktivitätsverlust von markierten Quecksilber(II)-Lösungen auf Reduktion von etwas Quecksilber(II) durch zufällig eingeschleppte Reduktionsmittel beruht. Das Quecksilber(I) disproportioniert dann und metallisches Quecksilber geht in die Gasphase verloren. Der Verlust kann durch Zugabe eines kleinen Überschusses eines Oxidationsmittels wie Permanganat verhindert werden.

Résumé—On montre qu'une perte de radioactivité de solutions de mercure(II) marqué est due à la réduction d'une partie du mercure(II) par des réducteurs introduits accidentellement, suivie par la dismutation du mercure(I) et la perte de mercure métallique dans la phase gazeuse. On peut prévenir la perte par addition d'un petit excès d'un oxydant tel que le permanganate.

REFERENCES

1. T. Y. Toribara and C. P. Shields, *Am. Industr. Hyg. Assoc. J.*, 1968, **29**, 92.
2. L. Magos, *Brit. J. Industr. Med.*, 1966, **23**, 230.
3. T. Clarkson and A. Rothstein, *Health Physics*, 1964, **10**, 1115.
4. T. W. Clarkson, J. Gatzy and C. Dalton, *University of Rochester Atomic Energy Project Rept.* UR-582 (1960).
5. L. Magos, A. A. Tuffery and T. W. Clarkson, *Brit. J. Industr. Med.*, 1964, **21**, 294.
6. N. A. Lange, *Handbook of Chemistry*, Revised 10th Ed., p. 1443. McGraw-Hill, New York, 1967.
7. N. V. Sidgwick, *The Chemical Elements and Their Compounds*, p. 287. Clarendon Press, Oxford, 1950.
8. W. M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd Ed., pp. 177–181. Prentice-Hall, New York, 1952.

Talanta, 1970, Vol. 17, pp. i to ii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Determination of fluoride in oxides by means of the fluoride ionactivity electrode: M. A. PETERS and D. M. LADD. (22 *June* 1970)

Chelatbidende Austauscherharze XI. Abtrennung des Be(II) vom Al(III) am Chelatustauscher auf der Basis von *o*-(2-Hydroxy-phenylazo)benzosäure: E. BLASIUS, K.-P. JANZEN and W. FALLOT-BURGHARDT. (17 *July* 1970)

Polarographische Be(III)-Bestimmung mit *o*-(2-Hydroxy-5-methyl-phenylazo)benzosäure: E. BLASIUS. K.-P. JANZEN and W FALLOT-BURGHARDT. (17 *July* 1970)

Rapid polarographic method for the microdetermination of organically-bound phosphorus: S. W. BISHARA and M. E. ATTIA. (22 *July* 1970)

Cation-exchange behaviour of several elements in formic acid solutions: MOHSIN QURESHI and WAQIF HUSAIN. (22 *July* 1970)

Spectrophotometric studies on the complexes of vanadium(V) with some *N*-arylhydroxamic acids: J. P. SHUKLA and S. G. TANDON. (23 *July* 1970)

A borax fusion technique for quantitative X-ray fluorescence analysis: J. H. H. G. VAN WILLIGEN, H. KRUIDHOF and E. A. M. F. DAHMEN. (23 *July* 1970)

Zur Elementaranalyse des Schwefels im Nanogramm-Bereich: ADOLF GRÜNERT and GÜNTHER TÖLG (23 *July* 1970)

Spectrophotometric determination of cadmium in nuclear-grade Zircaloy-2 after selective extraction with a liquid anion-exchanger: G. GHERSINI and S. MARIOTTINI. (30 *July* 1970)

Photometric complex-formation titration of submicromolar amounts of metal—II: J. KRAGTEN. (30 *July* 1970)

Determination of nanogram amounts of nickel by flameless atomic-absorption spectroscopy: S. DIPIERRO and G. TESSARI. (5 *August* 1970)

Purification and characterizing properties of the analytical reagent quinizarin-2-sulphonic acid and its sodium salt: J. A. THOMSON and G. F. ATKINSON. (7 *August* 1970)

Spectrophotometric investigations of lanthanon(III) complexes with oximidobenzotetronic acid: G. S. MANKU, A. N. BHAT and B. D. JAIN. (7 *August* 1970)

Potentiometric titration of cerium and manganese at room temperature—I. Determination of formal redox potential of Mn^{7+}/Mn^{3+}, Ce^{4+}/Ce^{3+} and Mn^{3+}/Mn^{2+} in condensed phosphoric acid: P. P. NAIDU and G. G. RAO. (14 *August* 1970)

Potentiometric titration of cerium and manganese at room temperature—II. Analysis of steels, alloys ores, rocks and minerals: P. P. NAIDU and G. G. RAO. (14 *August* 1970)

Detection and identification of cannabis constituents by luminescence spectrophotometry: A. BOWD, P. BYROM, J. B. HUDSON and J. H. TURNBULL. (14 *August* 1970)

Potentiometric titrations with a mercury–mercury sulphide electrode: T. R. WILLIAMS, S. PIEKARSKI and C. MANNING. (14 *August* 1970)

Uranium(VI) complexes of oxine and its derivatives: A. CORSINI, J. ABRAHAM and M. THOMPSON. (14 *August* 1970)

Spectrophotometric determination of lanthanum, thorium and iron(III) with chromotropic acid azo dyes of the pyridine series: A. K. MAJUMDAR, and A. B. CHATTERJEE. (21 *August* 1970)

Synergistic effects in the solvent extraction of zinc with salicylaldoxime: A. P. RAO and S. P. DUBEY (21 *August* 1970)

Determination of chloride by displacement of hydrogen cyanide from mercuric cyanide: M. K. BHATTY and P. C. UDEN. (21 *August* 1970)

Analytical application of the urease method for determination of biuret: P. BOZADZIEV, E. BALABANOVA and L. ILCHEVA. (25 *August* 1970)

The effect of orthophosphate on the gravimetric determination of pyrophosphate: P. BOZADZIEV, M. GEORGIEVA and L. ILCHEVA. (25 *August* 1970)

Resin beads as indicators in precipitation titrations: MOHSIN QURESHI, SAIDUL ZAFAR QURESHI and NIGHAT ZEHRA. (25 *August* 1970)

Spectrophotometric determination of germanium with Cathechol Violet and cetyltrimethylammonium bromide: C. L. LEONG. (25 *August* 1970)

Talanta, 1970, Vol. 17, p. iii. Pergamon Press. Printed in Northern Ireland

NOTICES

SOCIETY FOR APPLIED SPECTROSCOPY

The 10th National Meeting of the Society for Applied Spectroscopy (also the XXII Mid-America Symposium on Spectroscopy) will be held at Stouffer's Riverfront Inn in St. Louis, Missouri, 18–22 October 1971. Original papers are invited for general sessions on spectroscopy (including X-ray, emission, atomic absorption, flame emission, atomic fluorescence, absorption, electron, resonance, mass and nuclear) and gas chromatography. Papers are also invited for symposia on use of computers and new frontiers in spectroscopy, literature and data retrieval, and spectroscopy in environmental control, biomedicine, space and oceanography.

Titles and abstracts (on 215 × 280 mm paper and within an area of 150 × 250 mm) should be sent to Dr. E. F. Kaelble, Monsanto Company, Inorganic Research Department, 800 North Lindbergh Blvd., St. Louis, Missouri 63166, U.S.A., by 15 April 1971.

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

7s 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

SUMMARIES FOR CARD INDEXES

Quantitative analysis in pharmacy and pharmaceutical chemistry by nuclear magnetic resonance spectroscopy: D. M. RACKHAM, *Talanta*, 1970, **17**, 895. (Analytical Department, Lilly Research Centre Ltd., Erl Wood Manor, Windlesham, Surrey.)

Summary—The applications of n.m.r. to the quantitative analysis of pharmaceutical formulations and products of interest to the pharmacist and pharmaceutical analyst are reviewed. Special attention is paid to the accuracy of the method, the coefficients of variation being quoted (or calculated from data in the original paper) where possible. An elementary knowledge of n.m.r. is assumed.

Thermometric titration studies of mixed ligand complexes of thorium: G. C. KUGLER and G. H. CAREY, *Talanta*, 1970, **17**, 907. (U.S. Army Materials and Mechanics Research Center, Watertown, Mass., U.S.A.)

Summary—Mixed-ligand chelates consisting of two different multidentate ligands linked to a central thorium(IV) ion have been prepared in aqueous solution and their heats of formation studied thermometrically. Pyrocatechol, tiron, chromotropic acid, potassium hydrogen phthalate, 8-hydroxyquinoline-5-sulphonic acid, iminoacetic acid, 5-sulphosalicylic acid and salicylic acid were used as the secondary ligands, while ethylenediaminetetra-acetate and 1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetra-acetate were used as primary ligands. ΔH values for the overall reactions are given, and where possible, the ΔH and ΔS values for the specific secondary ligand addition were calculated. The overall stability of the mixed-ligand chelates and the enhanced stability of EDTA mixed chelates relative to the analogous DCTA chelates were found to be due to entropy rather than enthalpy effects.

Verwendung von Alkylphosphorsäuren in der analytischen Chemie. Extraktion von Gallium(III) aus Lösungen sauerstoffhaltiger Säuren mit Lösungsmittelgemischen: I. S. LEVIN und N. A. BALAKIREVA, *Talanta*, 1970, **17**, 915. (Institut für physikalisch-chemische Grundlagen der Aufarbeitung von Mineralstoffen, Novosibirsk, Derzhavina 18, U.S.S.R.)

Summary—Gallium(III) can be separated from aluminium in sulphuric or hydrobromic acid medium by synergic extraction with a combination of mono(2-ethylhexyl)phosphoric acid and tributyl phosphate, or of mono(2-ethylhexyl)phosphoric acid with hexyl methyl ketone. All other metals extracted are removed by selective stripping reactions.

ПРИМЕНЕНИЕ КОЛИЧЕСТВЕННОГО АНАЛИЗА МЕТОДОМ ЯДЕРНОГО ПАРАМАГНИТНОГО РЕЗОНАНСА В ФАРМАЦИИ И ФАРМАЦЕВТИЧЕСКОЙ ХИМИИ:

D. M. Rackham, *Talanta*, 1970, **17**, 895.

Резюме—Приведен обзор применения ЯМР в количественном анализе фармацевтических рецептур и продуктов интересных для фармацевта и фармацевтического аналитика. Особенное внимание уделено точности метода; в многих случаях приведены коэффициенты вариации или вычислены из данных оригинальной стати. Предполагается основное познавание метода ЯМР.

ИЗУЧЕНИЕ КОМПЛЕКСОВ ТОРИЯ С СМЕШАННЫМИ ЛИГАНДАМИ МЕТОДОМ ТЕРМОМЕТРИЧЕСКОЙ ТИТРАЦИИ:

G. C. Kugler and G. H. Carey, *Talanta*, 1970, **17**, 907.

Резюме—Приготовлены хелаты с смешанными лигандами, представляющими собой два различных мултидентатных лиганда связанных с центральным ионом тория(IV), в водном растворе и их теплоты образования изучены термометрическим методом. Пирокатехин, тирон, хромотроповая кислота, кислий фталат калия, 5-сульфосалициловая кислота и салициловая кислота использованы в качестве вторичного лиганда, а этилендиаминтетраацетат и 1,2-диаминоциклогексан-N,N,N',N'-тетраацетат в качестве первичноголиганда. Приведены значения ΔH для общих реакций и, если возможно, вычислены значения ΔH и ΔS для специфического присоединения вторичного лиганда. Обнаружено что общая стабильность хелатов с смешанными лигандами и повышенная стабильность смешанных хелатов с ЭДТА в сравнении с аналогическими хелатами ДЦТА являются результатом эффектов энтропии лучше чем эффектов ентальпии.

ПРИМЕНЕНИЕ АЛКИЛФОСФОРНЫХ КИСЛОТ Ъ АНАЛИТИЧЕСКОЙ ХИМИИ: ЭКСТРАГИРОВАНИЕ ГАЛЛИЯ(III) ИЗ РАСТВОРОВ КИСЛОРОДСОДЕРЖАЩИХ КИСЛОТ СМЕСЯМИ РАСТВОРИТЕЛЕЙ:

I. S. Levin and N. A. Balakireva, *Talanta*, 1970, **17**, 915.

Резюме—Галлий(III) отделяют от алюминия в сернокислой или бромистоводородной среде синэнергетическим экстрагированием комбинацией моно(2-этилгексил)фосфорной кислоты и трибутилфосфата, или моно(2-этилгексил)фосфорной кислоты и гексилметилкетона. Все другие экстрагированные металлы удаляют селективными стриппинг реакциями.

Photochemical precipitation of thorium and cerium and their separation from other ions in aqueous solution: M. DAS, ARNO H. A. HEYN, MORTON Z. HOFFMAN and R. P. AGARWAL, *Talanta*, 1970, **17**, 925. (Department of Chemistry, Boston University, Boston, Massachusetts 02215, U.S.A.)

Summary—Thorium was precipitated from homogeneous solution by exposing solutions of thorium and periodate in dilute perchloric acid to 253·7 nm radiation from a low-pressure mercury lamp. Periodate is reduced photochemically to iodate which causes the formation of a dense precipitate of the basic iodate of thorium(IV). The precipitate was redissolved, the iodate reduced, the thorium precipitated first as the hydroxide, then as the oxalate and ignited to the dioxide for weighing. Thorium(IV) solutions containing 8–200 mg of ThO_2 gave quantitative results with a standard deviation (s) of 0·2 mg Separations from 25 mg each of iron, calcium, magnesium, 50 mg of yttrium and up to 500 mg of uranium(VI) were quantitative (s = 0·25 mg). Separations from rare earths, except cerium, were accomplished by using hexamethylenetetramine rather than ammonia for the precipitation of the hydroxide. Cerium(III) was similarly precipitated and converted into CeO_2 for weighing. Quantitative results were obtained for 13–150 mg of CeO_2 with a standard deviation of 0·2 mg. Separations from 200 mg of uranium were quantitative. Other rare earths and yttrium interfered seriously. The precipitates of the basic cerium(IV) and thorium iodates obtained are more compact than those obtained by direct precipitation and can be handled easily. Attempts to duplicate Suzuki's method for separating cerium from neodymium and yttium were not successful.

Coulometric determination of uranium with a platinum working electrode: W. DAVIES, W. GRAY and K. C. MCLEOD, *Talanta*, 1970, **17**, 937. (United Kingdom Atomic Energy Authority (Reactor Group), Dounreay Experimental Reactor Establishment, Thurso, Caithness, Scotland.)

Summary—Experimental conditions have been established which enable uranium to be determined coulometrically by the reduction of uranium(VI) to uranium(IV) at a platinum working electrode, by controlled-potential or controlled-potential-limit techniques. The procedure has been used successfully as a subsidiary method in the routine determination of uranium in pure uranyl nitrate solutions. The platinum electrode has several important practical advantages over the well established mercury-pool electrode for the coulometric determination of uranium. The consecutive determination of iron(III) and uranium(VI), or plutonium(IV) and uranium(VI) can be carried out with the same working electrode in the same solution and the coulometric oxidation of uranium(IV) to uranium(VI) is practicable. The rate of stirring of the cell liquor is much less critical in the case of the platinum electrode. Two main problems had to be overcome before a practical procedure could be achieved; hydrogen evolution during the uranium(VI)–(IV) reduction had to be eliminated so that 100% current efficiency could be obtained for the desired reaction and electrode-surface poisoning phenomena had to be controlled so that reaction times could be kept reasonably short. It was found that selection of a hydrochloric acid base solution containing a small amount of bismuth(III) enabled hydrogen evolution to be avoided: also electrode-surface poisoning with this base solution was not particularly serious and could be maintained at a satisfactorily low level by occasionally anodizing the electrode in dilute sulphuric acid. Bismuth(III) forms a complex with chloride ions and its presence increases the hydrogen overvoltage at the working electrode: no visible deposit of bismuth metal forms on the electrode during the uranium reduction. Samples containing nitrate can be analysed provided sulphamic acid is added to this hydrochoric acid base solution.

ФОТОХИМИЧЕСКОЕ ОСАЖДЕНИЕ ТОРИЯ И ЦЕРИЯ И ИХ ОТДЕЛЕНИЕ ОТ ДРУГИХ ИОНОВ В ВОДНОМ РАСТВОРЕ:

M. DAS, ARNO H. A. HEYN, MORTON Z. HOFFMAN and R. P. AGARWAL, *Talanta*, 1970, **17**, 92 5.

Резюме—Торий осаждали из гомогенного раствора выдержкой растворов тория и периодата в разбавленной хлорной кислоте в радиации 253,7 нм ртутной лампы низкого давления. Периодат восстанавливается фотохимическим путем в иодат который вызивает образование плотного осадка основного иодата тория(IV). Осадок растворяли, восстанавливали иодат, затем осаждали торий в форме гидроокиси, потом в форме оксалата и обзоливали до двуокиси дия взвешивания. Растворы тория(IV) содержащие 8–200 мг $\mathrm{Th\ O_2}$ дали количественные резултаты с стандартной ошибкой (*s*) 0,2 мг. Получены количественные отделения от 25 мг железа, кальция и магния, от 50 мг иттрия и от 500 мг урана(VI) (*s* = 0,25 мг). Отделение от редкоземельных элементов за исключением церия получено с использованием гексаметилентетрамина вместо аммиака для осаждения гидроокиси. На подобный начин осаждали церий(III) и превращали в $\mathrm{CeO_2}$ для взвешивания. Получены количественные результаты для 13–150 мг $\mathrm{CeO_2}$ с стандартной ошибкой 0,2 мг. Получено количественное отделение от 200 мг урана. Обнаружено серьёзное влияние других редкоземельных элементов и иттрия. Полученные осадки основного иодата церия(IV) и тория более плотны чем полученные непосредственным осаждением осадки и легко фильтрируются. Не удалось отделит церий от неодима и иттрия методом Сузуки.

КУЛОНОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ УРАНА С ПЛАТИНОВЫМ РАБОЧИМ ЭЛЕКТРОДОМ:

W. DAVIES, W. GRAY and K. C. MCLEOD, *Talanta*, 1970, 937.

Резюме—Определены опытные условия для кулонометрического определения урана восстановлением урана(VI) в уран(IV) на платиновом рабочем электроде, с использованием методов регулированного напряжения или регулированной граници напряжения. Метод успешно применен в качестве вспомогательного метода в серийном определении урана в чистых растворах нитрата уранила. Платиновый электрод имеет несколько важных практических преимуществ над обыкновенным ртутным электродом в кулонометрическом определении урана. Последующее определение железа(III) и урана(VI), или плутония(IV) и урана(VI) можно выполнять с тем же рабочим электродом в тем же растворе, а кулонометрическое окисление |урана(IV) в уран(VI) также проведимо. Скорость перемешивания раствора в ячейке менее критически влияет на определение в случае платинового электрода. Было нужно преодолеть две главных проблемы в разработке метода применимого в практике: исключить выделение водорода в течение восстановления урана(VI) в уран(IV) с целью получить 100% эффективность тока для реакции восстановления и предупредить затравливание поверхности электрода с целью достичь довольно короткое течение реакции. Выделение водорода избегнуто использованием раствора на основе соляной кислоты, содержащего небольшое количество висмута(III). Затравливание поверхности электрода в этом фоне было незначительно и выдержано на этом уровне периодичёким анодированием электрода в разбавленной серной кислоте. Висмут(III) образует комплек эс хлоридионами и его присутствие повышает наднапряжение водорода на рабочем электроде. Видимая пленка металлического висмута не образуется на электроде в течение восстановления урана. Удается анализировать нитратсодержащие образци если добавлять сульфаминовую кислоту этом солянокислом фону.

Amperometric complex-formation titrations of traces of copper: F. FREESE, H. J. JASPER and G. DEN BOEF, *Talanta*, 1970, **17**, 945. (Laboratory for Analytical Chemistry, University of Amsterdam, The Netherlands.)

Summary—Copper has been determined in the submicrogram range by means of a complexometric titration with triethylenetetramine (TRIEN), the end-point being detected by following the anodic wave of the chelating agent at a rotating mercury electrode. The influence of the presence of other metals has been investigated both from the theoretical and the experimental point of view. Because of its higher selectivity TRIEN is preferred to other reagents of the EDTA group. The results show that copper can be determined in the presence of large amounts of most other metals.

Silica gel as a support for inorganic ion-exchangers for the determination of caesium-137 in natural waters: KIKUO TERADA, HIRONOBU HAYAKAWA, KIYOSHI SAWADA and TOSHIYASU KIBA, *Talanta*, 1970, **17**, 955. (Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa, Japan.)

Summary—The preparation and characteristics of ammonium molybdophosphate and potassium or ammonium hexacyanocobalt ferrate supported in silica gel, and their application to the determination of ^{137}Cs in natural waters are described. Use of columns of these materials gives better recovery of ^{137}Cs from natural waters (in comparison with co-precipitation with ammonium molybdophosphate), requires less exchanger, so raising the γ-counting efficiency of ^{137}Cs, and permits elimination of other radionuclides by washing with hydrofluoric acid.

Atomic-fluorescence characteristics and analytical determination of manganese in an air–acetylene flame: L. EBDON, G. F. KIRKBRIGHT and T. S. WEST, *Talanta*, 1970, **17**, 965. (Chemistry Department, Imperial College, London, S.W.7., U.K.)

Summary—The atomic-fluorescence characteristics of manganese atoms in a premixed nitrogen-shielded air–acetylene flame are described. Excitation is obtained at 280 nm from a microwave-excited electrodeless discharge tube. A detection limit of 0·001 ppm for the determination of manganese by atomic-fluorescence spectroscopy is obtained by measurement of the resonance fluorescence observed at this wavelength. In addition to several other weaker atomic-fluorescence signals observed from manganese atoms in the flame, weak resonance fluorescence at 258 and 260 nm from manganese ions stimulated by ion line-emission from the source has been recorded. Linear calibration graphs for atomic-fluorescence measurement at 280 nm are obtained over the range 0·0025–10 ppm of manganese in aqueous solution. Of 26 foreign anions and cations examined for interference at the 1000-fold excess level only four produced interference. Large amounts of Si, Th and V interfere by scattering of the incident radiation, while Mg causes depression of the atomic fluorescence by a chemical effect.

АМПЕРОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ СЛЕДОВ МЕДИ НА ОСНОВЕ КОМПЛЕКСООБРАЗОВАНИЯ:

F. Freese, H. J. Jasper and G. den Boef *Talanta*, 1970, **17**, 945.

Резюме—Субмикрограммовые количества меди определены комплексонометрическим титрованием триэтилентетрамином (ТРИЭН). Конец титрования обнаружен следованием анодной волны хелатообразующего агента на вращающемся ртутном электроде. Изучено влияние других элементов с теоретической и экспериментальной точки зрения. Авторы предпочитают ТРИЭН другими реагентами группы ЭДТА из-за его лучшей селективности. Из результатов видно что медь можно определять в присутствии большинства других металлов.

СИЛИКАГЕЛЬ В КАЧЕСТВЕ НОСИТЕЛЯ ДЛЯ НЕОРГАНИЧЕСКИХ ИОНООБМЕННЫКОВ ДЛЯ ОПРЕДЕЛЕНИЯ ЦЕЗИЯ-137 В ПРИРОДНЫХ ВОДАХ:

Kikuo Terada, Hironobu Hayakawa, Kiyoshi Sawada and Toshiyasu Kiba, *Talanta*, 1970, **17**, 955.

Резюме—Описаны приготовление и характеристики молибдофосфата аммония и гексацианокобальтоферрата калия или аммония на силикагеле в качестве носителя, и их применение в определении ^{137}Cs в природных водах. Колонками этих материалов получаются лучшие выходы ^{137}Cs из природных вод (в сравнении с методом соосаждения молибдофосфатом аммония), потребуется менее ионообменныка, этим образом повышая эффективность считания гамма-лучей ^{137}Cs и позволяя удалять другие радионуклиды промыванием с фтороводородной кислотой.

АТОМНО-ФЛУОРЕСЦЕНТНЫЕ ХАРАКТЕРИСТИКИ И АНАЛИТИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МАРГАНЦА В ПЛАМЕНИ ВОЗДУХА И АЦЕТИЛЕНА:

L. Ebdon, G. F. Kirkbright and T. S. West, *Talanta*, 1970, **17**, 965.

Резюме—Описаны атомно-флуоресцентные характеристики атомов марганца в предварительно смешанной защищенной азотом пламени воздуха и ацетилена. Возбуждение получено при 280 нм с использованием возбужденной микроволнами безэлектродной разрядной трубки. Получена чувствительность 0,001 мкг/мл в определении марганца методом атомно-флуоресцентной спектроскопии, измерением резонансной флуоресценции при той же длины волн. Обнаружены слабые резонансные флуоресценции при 258 и 260 нм ионов марганца стимулированных ионной линейной эмиссией источника, кроме ряда других слабых атомно-флуоресцентных сигналов. Получены линейные калибрационные кривие для атомной флуоресценции при 280 нм в пределах 0,0025–10 мкг мл марганца в водном растворе. Только четыре мешают определению от 26 других анионов и катионов, присутствующих в 1000-кратном избытке. Большие количества Si, Th и V мешают, вызивая рассеяние падающей радиации, в то время как Mg вызывает депрессию атомной флуоресценции на основе химического эффекта.

Redoxaustauscher und ihre Anwendungen—XV. Reduktion von Eisen(III) an Redoxiten und anschließende oxydimetrische Bestimmung: Bruno Sansoni und Wolfgang Wiegand, *Talanta*, 1970, 17, 973. (Radiochemisch-analytische Abteilung im Institut für Strahlenschutz der Gesellschaft für Strahlenforschung mbH., 8042 Neuherberg bei München, und Chemisches Institut der Universität Marburg/Lahn.)

Summary—As an example of the reduction of cations on redox ion-exchangers, the reduction of 50–200 mg of iron(III) on Leucomethylene Blue- and ferrocene-resin of a polystyrene type, is described. The iron(II) was titrated potentiometrically with cerium(IV). Under optimum conditions, the standard deviation was 0·04–0·14 mg. In contrast to their behaviour on metal reductors, there is no interference from Cu^{2+}, Bi^{3+}, TiO^{2+}, Sn^{4+}, Ce^{4+} and AsO_4^{3-}. The method has been used for the direct determination of iron in ores, slags and special steels.

Redoxaustauscher und ihre Anwendungen—XVI. Entfernung von Wasserstoffperoxid aus wässeriger Lösung an Redox- und Ionenaustauschern: Bruno Sansoni und Elisabeth Bauer-Schreiber, *Talanta* 1970, **17**, 987. (Institut für Strahlenschutz der Gesellschaft für Strahlenforschung mbH., Radiochemisch-analytische Abteilung, 8042 Neuherberg bei München und Chemisches Institut der Universität Marburg/Lahn.)

Summary—Hydrogen peroxide can be removed semi-continuously from aqueous solution by reduction on an anion-exchange resin in the dithionite or sulphite form, or by catalytic decomposition on a resin in the OH^--form. Simple column arrangements suitable for this purpose providing for exclusion of air, and for quasi-column operation, when the resin is vigorously agitated by the evolution of considerable amounts of gas, are described.

Apparatus for the determination of melting points, molecular weights, freezing points and purity, and for the study of melting: R. F. Greenwood, *Talanta*, 1970, **17**, 999. (Department of Chemistry, The City University, St. John Street, London E.C.1.)

Summary—An apparatus for the determination of the melting point of a partially frozen liquid is described. Thermal equilibrium is rapidly attained, largely because of the presence of glass balls in the experimental flask, and the method of agitation. The use of a thermistor and a recording potentiometer allows charting of the temperature changes with time. The melting point can be calculated from points on the trace. The apparatus has been used to study melting point depressions for solutions of hydrocarbons and phenols in benzene, nitrobenzene, water and dioxan.

ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНЫЕ ОБМЕННЫКИ И ИХ ПРИМЕНЕНИЕ—XV. ВОССТАНОВЛЕНИЕ ЖЕЛЕЗА(III) НА ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНЫХ ОБМЕННЫКАХ С ПОСЛЕДУЮЩИМ ОКСИДИМЕТРИЧЕСКИМ ОПРЕДЕЛЕНИЕМ:

BRUNO SANSONI and WOLFGANG WIEGAND, *Talanta*, 1970, **17**, 973.

Резюме—Описано восстановление 50–200 мг железа(III) на лейкометиленголубой и ферроценовой смоле типа полистирола, в качестве примера восстановления катионов на окислительно-восстановительных обменныках. Железо(II) титровали церием(IV) с использованием потенциометрического метода. В оптимальных условиях стандартная ошибка была 0,04–0,14 мг. Противно поведению на металлических восстановителях не обнаружено влияние Cu^{2+}, Bi^{3+}, ThO^{2+}, Sn^{4+}, Ce^{4+} и AsO_4^{3-}. Методом пользовались для непосредственного определения железа в рудах, шлаках и специальных сталях.

ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНЫЕ ОБМЕННЫКИ И ИХ ПРИМЕНЕНИЕ—XVI. УДАЛЕНИЕ ПЕРЕКИСИ ВОДОРОДА ИЗ ВОДНОГО РАСТВОРА ПРИ ПОМОЩИ ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНЫХ И ИОНООБМЕННЫКАХ:

BRUNO SANSONI and ELISABETH BAUER-SCHREIBER, *Talanta*, 1970, **17**, 987.

Резюме—Перекись водорода можно удалять полунепрерывным путем из водного раствора восстановлением на анионообменной смоле в форме дитионита или сульфита, или каталитическим разложением на смоле в OH-форме. Описаны несложные колонки для проведения этой реакции за исключением воздуха, и квазиколонки в которых смола энергично перемешивается значительными объемами газа выделяющегося в реакции.

ПРИБОР ДЛЯ ОПРЕДЕЛЕНИЯ ТЕМПЕРАТУРЫ ПЛАВЛЕНИЯ, МОЛЕКУЛЯРНОГО ВЕСА, ТЕМПЕРАТУРЫ ЗАСТЫВАНИЯ И ЧИСТОТЫ, И ДЛЯ ИЗУЧЕНИЯ ПЛАВЛЕНИЯ:

R. F. GREENWOOD, *Talanta*, 1970, **17**, 999.

Резюме—Описан прибор для определения температуры плавления частично застывшей жидкости. Быстро достигнуто термическое равновесие, главным образом вследствие присутствия стеклянных шаров в опытной колбе и примененного метода перемешивания. Использование термистора и самопишушчего потенциометра позволяет записывать перемены температуры с временем. Температура плавления вычисляется из точек на записанной крывой. Прибором пользовались для изучения снижения температуры плавления растворов углеводородов и фенолов в бензоле, нитробензоле, воде и диоксане.

A silver electrode in the potentiometric titration of thiols: TAFT Y. TORIBARA and LARYSA KOVAL, *Talanta*, 1970, **17**, 1003. (Department of Radiation Biology and Biophysics, University of Rochester School of Medicine and Dentistry, Rochester, New York 14620, U.S.A.)

Summary—A silver wire immersed in a thiol solution gives a potential responsive to the thiol concentration, and is a sensitive indicator electrode in the potentiometric titration of thiols with mercury(II) chloride, *p*-chloromercuryphenyl sulphonate, and silver nitrate at pH 4·5–9·5, 7–9·5, and 9·5 respectively. Titrations of simple thiols such as cysteine or a protein such as albumin are equally successful, but the potential break was smaller for the protein. The end-point could be determined within an increment of titrant equal to 5 nmole of thiol. An inert atmosphere is needed for titration at pH $\geqslant 7$.

Amperometric complex-formation titration of traces of alkaline earths: G. DEN BOEF, F. FREESE, M. M. P. F. KRAMER and H. POPPE, *Talanta*, 1970, **17**, 1006. (Laboratory for Analytical Chemistry, University of Amsterdam, Nieuwe Achtergracht 125, Amsterdam-C, The Netherlands.)

Summary—Alkaline earth metals were determined in microgram quantities by complexometric titration with EDTA, EGTA and DTPA. The end-point was detected by following the anodic wave of the chelating agent at the rotating mercury electrode. All the alkaline earths can be titrated at the microgram level with reasonable accuracy, and calcium may be titrated with EGTA in the presence of a 1000-fold excess of magnesium.

A microwave-excited emissive detector for gas chromatography. Further studies with sulphur compounds: R. M. DAGNALL, S. J. PRATT, T. S. WEST and D. R. DEANS, *Talanta*, 1970, **17**, 1009. (Chemistry Department, Imperial College, London, S.W.7., U.K.)

Summary—Improvements in the design and operation of the microwave excited detector for gas chromatography have led to an increase in the sensitivity and a lowering of detection limits for sulphur compounds.

ИСПОЛЬЗОВАНИЕ СЕРЕБРЯНОГО ЭЛЕКТРОДА ДЛЯ ПОТЕНЦИОМЕТРИЧЕСКОГО ТИТРОВАНИЯ ТИОЛОВ:

Taft Y. Toribara and Larysa Koval, *Talanta*, 1970, **17**, 1003.

Резюме—Проволока серебра погруженная в раствор тиола дает потенциал соответствующий концентрации тиола и представляет собой чувствительный индикаторный электрод для потенциометрического титрования тиолов хлоридом ртути(II), п-хлормеркурифенилсульфонатом и нитратом серебра при pH 4,5–9,5, 7–9,5 и 9,5, соответсвенно. Титрование несложных тиолов типа цистеина или протеина как на пример альбумина удается провести успешно, но скачок потенциала меньший в случае протеина. Удалось определить конец титрования добавлением объема титрованного раствора соответсвующего 5 нмоля тиола. Надо использовать инертную атмосферу для титрования при pH $\geqslant$ 7.

АМПЕРОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ СЛЕДОВ ЩЕЛОЧНОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ НА ОСНОВЕ КОМПЛЕКСООБРАЗОВАНИЯ:

G. den Boef, F. Freese, M. M. P. F. Kramer and H. Poppe, *Talanta*, 1970, **17**, 1006.

Резюме—Щелочноземельные элементы определены в микрограммовых количествах комплексонометрическим титрованием с ЭДТА, ЭГТА и ДТПА. Конец титрования определен обнаружением анодной волны хелатообразующего агента на вращающемся ртутном электроде. Все щелочноземельные элементы удаются титровать в микрограммовых количествах с довольном точностью, а кальций можно титровать с ЭГТА в присутствии 1000 кратного избытка магния.

ДАТЧИК НА ОСНОВЕ ЭМИССИИ МИКРОВОЛН ДЛЯ ГАЗОВОЙ ХРОМАТОГРАФИИ:

R. M. Dagnall, S. J. Pratt, T. S. West and D. R. Deans, *Talanta*, 1970, **17**, 1009.

Резюме—Улучшения в конструкции и работе возбужденного микроволнами датчика для газовой хроматографии привели повишению чувствительности и снижению пределов обнаружения сернистых соединений.

Potentiometric determination of lead with DTPA in the presence of large amounts of aluminium: John P. Cummings, *Talanta*, 1970, **17**, 1013. (Owens-Illinois Technical Center, 1700 N. Westwood, Toledo, Ohio 43607, U.S.A.)

Summary—Lead can be titrated accurately in the presence of aluminium with diethylenetriaminepenta-acetic acid, with a silver electrode system for detection of the end-point. The method is very suitable for analysis of lead glasses.

Optimum physical and chemical conditions for the Methylene Blue method of estimating gaseous sulphide in the environment: P. K. Zutshi and T. N. Mahadevan, *Talanta*, 1970, **17**, 1014. (Air Monitoring Section, Health Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay, India.)

Summary—The sensitivity and reproducibility of the Methylene Blue method for gaseous sulphide estimation have been investigated with respect to physical conditions and the concentrations of the reagents, especially sulphuric acid. A new design of absorber is proposed to minimize gas-phase loss of the sulphide in the final stage of the procedure.

Determination of platinum, palladium and silver in geological materials and their concentrates by fire assay and emission spectrography: E. G. Koleva and S. H. Arpadjian, *Talanta*, 1970, **17**, 1018. (Faculty of Chemistry, State University of Sofia, 1 Anton Ivanov Avenue, Sofia 26, Bulgaria.)

Summary—A method is described for the determination of platinum down to 10 ng, palladium to 5 ng and silver to 10 pg in 50 or 100 g of sample. Fire-assay techniques are used to preconcentrate these metals into a bead which is first treated with nitric acid to dissolve palladium and silver and then with *aqua regia* to dissolve platinum. Both solutions are diluted and adjusted to pH 4, then analysed by optical emission spectrography of the residue from a measured volume evaporated on a pair of flat-top graphite electrodes. This method requires much less sample handling than most published methods for these elements.

ПОТЕНЦИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СВИНЦА С ДТПА В ПРИСУТСТВИИ БОЛЬШИХ КОЛИЧЕСТВ АЛЮМИНИЯ:

John P. Cummings, *Talanta*, 1970, **17**, 1013.

Резюме—Можно провести аккуратное титрование свинца в присутствии алюминия диэтилентриаминпентауксусной кислотой, с использованием серебряного электрода для обнаружения конца титрования. Метод весьма полезен для анализа свинцовых стекол.

ОПТИМАЛЬНЫЕ ФИЗИКАЛЬНЫЕ И ХИМИЧЕСКИЕ УСЛОВИЯ ДЛЯ ОПРЕДЕЛЕНИЯ ГАЗООБРАЗНОГО СУЛЬФИДА В АТМОСФЕРЕ МЕТОДОМ МЕТИЛЕНОВОГО ГОЛУБОГО:

P. K. Zutshi and T. N. Mahadevan, *Talanta*, 1970, **17**, 1014.

Резюме—Изучены чувствительность и воспроизводимость метода метиленового голубого для определения газообразного сульфида учитивая физикальные условия и концентрации реагентов, особенно серной кислоты. Предложена новая конструкция абсорбера для уменьшения потерь сульфида в газовой фазе в конечной фазе процедуры.

ОПРЕДЕЛЕНИЕ ПЛАТИНЫ, ПАЛЛАДИЯ И СЕРЕБРА В ГЕОЛОГИЧЕСКИХ МАТЕРИАЛАХ И ИХ КОНЦЕНТРАТАХ СУХИМ ПУТЕМ И МЕТОДОМ ЭМИССИОННОЙ СПЕКТРОГРАФИИ:

E. G. Koleva and S. H. Arpadjian, *Talanta*, 1970, **17**, 1018.

Резюме—Описан метод определения платины до 10 нг, палладия до 5 нг и серебра до 10 пг в 50 или 100 г пробы. Использовано преконцентрирование сухим путем эттих металлов в королёк который затем обрабатывают азотной кислотой для растворения палладия и серебра, а затем царской водкой для растворения платины. Оба раствора разбавляют и приводят до pH 4 и анализируют методом эмиссионной спектрографии остатка, полученного выпариванием измеренного объема на пары графитовых электродов с плоским верхом. Этот метод требует гораздо менее манипулирования чем большинство опубликованных методов.

Theoretical considerations on the estimation of sample matrix effects in analytical chemistry: ADAM SHATKAY, *Talanta*, 1970, **17**, 1021. (Polymer Department, Weizmann Institute of Science, Rehovot, Israel.)

Summary—Methods are suggested for evaluating the magnitude of matrix effects on the results of analysis.

Behaviour of dilute solutions of mercury: T. Y. TORIBARA, C. P. SHIELDS and LARYSA KOVAL, *Talanta*, 1970, **17**, 1025. (Department of Radiation Biology and Biophysics, University of Rochester School of Medicine and Dentistry, Rochester, New York 14620, U.S.A.)

Summary—It is shown that loss of radioactivity from labelled mercury(II) solutions is due to reduction of some mercury(II) by reductants adventitiously introduced, followed by disproportionation of mercury(I) and loss of metallic mercury in the gas phase. The loss can be prevented by addition of a small excess of an oxidant such as permanganate.

ТЕОРЕТИЧЕСКИЕ РАССМОТРЕНИЯ ВЛИЯНИЯ МАТРИЦИ ОБРАЗЦА В АНАЛИТИЧЕСКОЙ ХИМИИ:

ADAM SHATKAY, *Talanta*, 1970, **17**, 1021.

Резюме—Предложены методы определения влияния матрици на результаты анализа.

ПОВЕДЕНИЕ РАЗБАВЛЕННЫХ РАСТВОРОВ РТУТИ:

T. Y. TORIBARA, C. P. SHIELDS and LARYSA KOVAL, *Talanta*, 1970, **17**, 1025.

Резюме—Показано что потеря радиоактивности в меченых растворах ртути(II) вызвана восстановлением части ртути(II) случайно введеными восстановителями, с последующим диспропорционированием ртути(I) и потерей металлической ртути в газовой фазе. Потерю можно предотвратить добавлением небольшого избытка окислителя, на пример перманганата.

This journal provides a medium of publication for original research in all facets of cosmetic chemistry at scientific and industrial levels. It reflects current work among cosmetic chemists throughout the world, and should, therefore, be available to all departments, institutions and libraries concerned with the subject.

The Journal of the Society of Cosmetic Chemists publishes original research papers and preliminary communications concerning cosmetic reactions on the skin, hair and teeth. the analysis, testing, processing and evaluation of materials, toxicology and industrial applications. Subject review articles which discuss new methods and techniques in cosmetic chemistry are also included from time to time, together with reviews of important books in the field.

PARTIAL CONTENTS OF A RECENT ISSUE

H. Baker MD MRCP Experimental studies on the influence of vehicles on percutaneous absorption

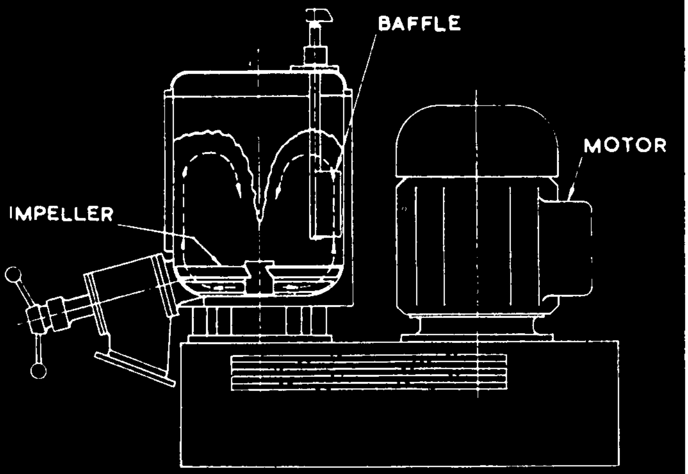
J. F. Corbett PhD ARIC *p*-Benzoquinonediimine – A vital intermediate in oxidative hair dyeing

P. R. Bunkall and M. Quinn Instrumental colour measurement and control

This journal is published every four weeks: five issues for the Society of Cosmetic Chemists of Great Britain by Pergamon Press. Six issues by the Society of Cosmetic Chemists Inc from 6220 Kansas Avenue NE Washington DC 20011 USA. And two issues for the Gesellschaft Deutscher Kosmetik Chemiker ev by Dr. Alfred Hüthig Verlag Wilkenstrasse 3-5 Heidelberg Germany.

Please write for free inspection copy of this journal

Journal of the Society of Cosmetic Chemists



Honorary Editor A. HERZKA BSc FRIC
Pressurized Packaging Consultants Ltd Alberon Gardens LONDON

13 issues per year

Pergamon Press

OXFORD · NEW YORK · LONDON · PARIS · SYDNEY

7/69

Volume 17, No. 10 October 1970

Contents

Short Communications

Annotation

Talanta Annual Subscription Rates (including postage)

$10 (£3.10.)—***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 $15 (£5.5.) per annum.

Printed in Northern Ireland at The Universities Press, Belfast