ANALYTICA CHIMICA ACTA

International monthly devoted to all branches of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 39, No. 1, 1–140, September 1967

ANALYTICA CHIMICA ACTA

GENERAL INFORMATION

Languages

Papers will be published in English, French or German.

Submission of papers

Papers should be sent to: Prof. Philip W. West, Coates Chemical Laboratories, College of Chemistry and Physics, Louisiana State University, Baton Rouge 3, La. 70803 (U.S.A.) or to

Dr. A. M. G. Macdonald, Department of Chemistry, The University, P.O. Box 363, Birmingham 15 (Great Britain)

Manuscripts

Authors should submit two copies in double-spaced type with adequate margins on pages of uniform size. Acknowledgements, summary and references should be placed at the end of the paper.

Tables should be typed on separate pages and numbered in Roman numerals in the order in which they are mentioned in the text. All Tables should have descriptive titles. The use of chemical formulae and conventional abbreviations is encouraged in Tables and Figures but chemical formulae should not be used in the text unless they are necessary for clarity. Units of weight, volume, etc., when used with numerals should be abbreviated and unpunctuated (*e.g.*, 2%, 2 ml, 2 g, 2 µl, 2 µg, 2 ng, 2 cm, 200 mµ).

Figures should be drawn in Indian ink on drawing or tracing paper with all lettering in **thin** pencil. Standard symbols should be used in line drawings; the following are available to the printers:

▼ ▽ ■ □ ● ◎ ■ ◘ ⊖ ▣ ▪ + ×

Photographs should be submitted as clear black and white glossy prints. Figures and photographs should be of the same size as the typed pages. Legends for figures should be **typed on a separate page**. Figures should be numbered in Arabic numerals in the order in which they are mentioned in the text.

References should be given at the end of the paper and should be numbered in the order of their appearance in the text (**not** arranged alphabetically). Abbreviations of journal titles should conform to those adopted by the *Chemical Abstracts List of Periodicals*, 1961 Edition and supplements. The recommended form for references to journal papers and books is as follows:

1. J. J. Lingane and A. M. Hartley, *Anal. Chim. Acta*, 11 (1954) 475.
2. F. Feigl, *Spot Tests in Organic Analysis*, 7th Ed., Elsevier, Amsterdam, 1966, p. 516.

For multi-author references, **all** authors must be named, and initials given, in the reference list, although the use of, for example, Smith *et al.*, is desirable in the text.

Summaries are published in English, French and German; authors must always provide a summary in the language of the paper, and are encouraged to supply translations where convenient. No summaries are needed for Short Communications.

Reprints

Fifty reprints will be supplied free of charge. Additional reprints (minimum 100) can be ordered at quoted prices. They must be ordered on order forms which are sent together with the proofs.

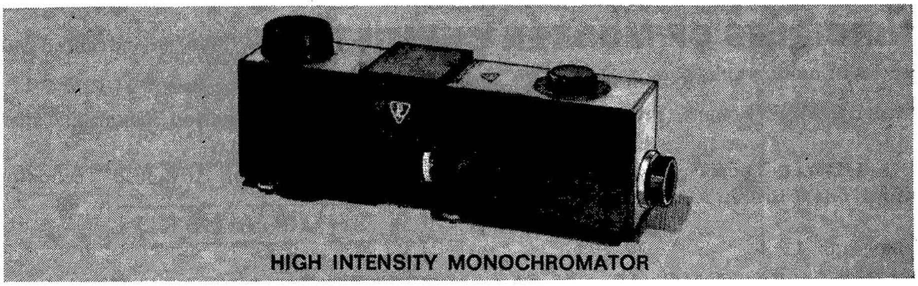
Publication

In 1968, Analytica Chimica Acta will have three issues to the volume, and four volumes will appear. Subscription prices: $ 17.50 or £ 6.6.— or Dfl. 63.— per volume; $70.00 or £ 25.4.0 or Dfl. 252.— per year, plus postage. Additional cost for copies by airmail available on request. For advertising rates apply to the publishers.

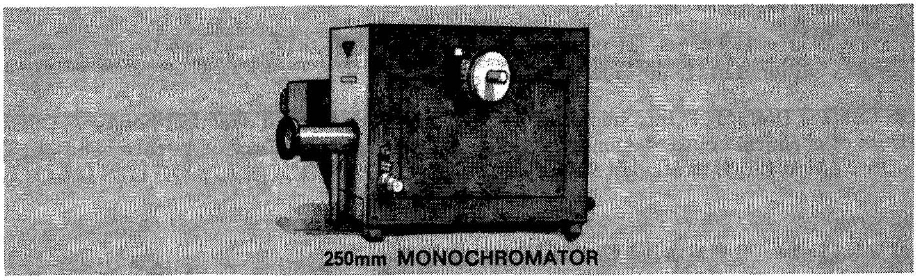
Subscriptions

Subscriptions should be sent to:

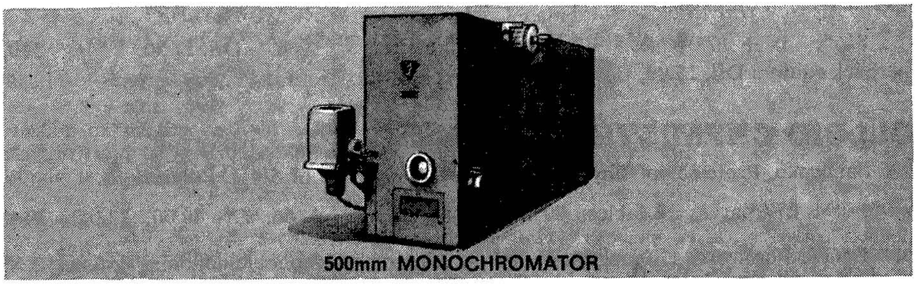
ELSEVIER PUBLISHING COMPANY, P.O. Box 211, Amsterdam, The Netherlands



HIGH INTENSITY MONOCHROMATOR



250mm MONOCHROMATOR



500mm MONOCHROMATOR

Elsevier teaching texts

FUNDAMENTAL PRINCIPLES OF CHEMICAL ANALYSIS

by W. F. PICKERING, Professor of Chemistry, University of Newcastle, N.S.W., Australia

5½ x 8½″, ix + 270 pages, 3 tables, 64 illus., 149 lit. refs., 1966, Dfl. 30.00, 60s. $10.00

CONTENTS: 1. Introduction. 2. Determinations based on phase separations. 3. Electrical transformations. 4. Ionic equilibria in solution. 5. Energy transitions. 6. Physical properties of matter. 7. Statistics, sampling and solution of samples. 8. Selective chemical reactions. 9. Heterogeneous equilibrium reactions. 10. Chromatographic separations. 11. Selection of analytical methods. 12. Tutorial problems. Index.

PRINCIPLES OF MODERN CHEMISTRY A guide to advanced study

A series of monographs

edited by W. F. FORBES, Professor of Chemistry, University of Waterloo, Ontario, Canada; and
W. J. ORVILLE–THOMAS, Professor of Chemistry, Royal College of Advanced Technology, Salford, Great Britain

Monograph 1

THE STRUCTURE OF SMALL MOLECULES

by W. J. ORVILLE–THOMAS

5½ x 8½″, ix + 189 pages, 31 tables, 55 illus., 1966, Dfl. 26.00, 52s., $9.50
Paperback edition: Dfl. 15.00, 30s., $5.00

CONTENTS: Preface. 1. Introductory survey. 2. The formation of chemical bonds. 3. Characteristics of chemical bonds. 4. Quantum theory. 5. The stereochemistry of valence bonds. 6. The structure of individual molecules. Subject index.

Monograph 2

PHYSICAL ORGANIC CHEMISTRY

by OWEN H. WHEELER, Department of Chemistry and Puerto Rico Nuclear Center, University of Puerto Rico at Mayaguez

5½ x 8½″, ix + 172 pages, 42 tables, 51 lit. refs., 1966, Dfl. 27.50, 55s. $10.00
Paperback edition: Dfl. 15.00, 30s., $5.00

COLLOID CHEMISTRY

by A. SHELUDKO, Professor of Physical Chemistry, University of Sofia, Bulgaria

6 x 9″, x + 277 pages, 12 tables, 70 illus., 288 lit. refs., 1966, Dfl. 40.00, £4.0.0., $14.50

CONTENTS: Foreword. 1. Preparation and purification of lyophobic colloidal systems. 2. The optical properties of colloids. 3. The molecular kinetic properties of colloidal solutions. 4. Physical chemistry of surfaces. 5. Electrokinetic phenomena. 6. Thin layers. 7. Stability of lyophobic sols. 8. Foams and emulsions. Index.

ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK

283 E

HAMILTON

PB 600 REPEATING DISPENSER
(attachment to syringe)

- **discharges 1/50th of the syringe's capacity each time you push the button**
- **for a wide variety of applications, including thin-layer chromatography.**

PB 600-1 for use with all Hamilton syringes from 25 ul through 2,5 milliliter capacity

PB 600-10 for use with all Hamilton syringes from 5-10 milliliter capacity

For information please write to the European distributors

MICROMESURE N.V.

P.O. BOX 205 - THE HAGUE (THE NETHERLANDS)
Telephone: 18.07.26 — Cables: MICROMES

505

Fundamental Aspects of Petroleum Geochemistry

edited by

B. NAGY, Department of Chemistry, University of California at San Diego, La Jolla, Calif., (U.S.A.), and

U. COLOMBO, Department of Geochemistry, Istituto di Recerche "G. Donegani", Montecatini-Edison, Novara (Italy)

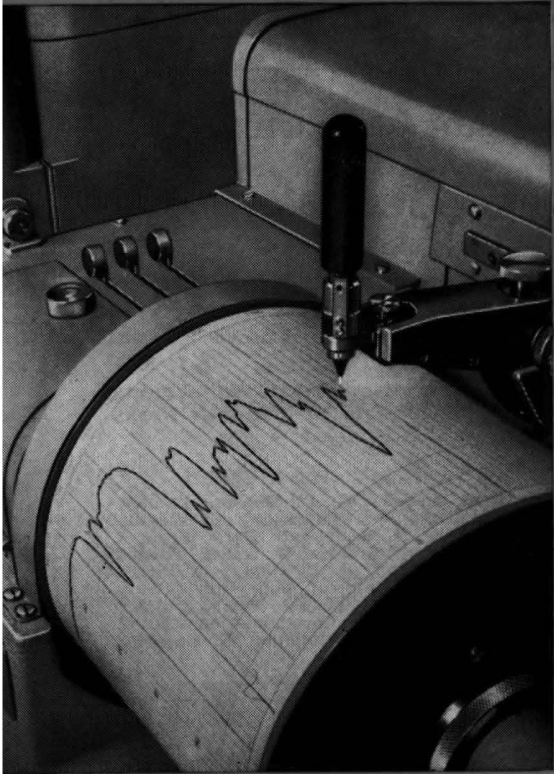
6 x 9", vii + 380 pages, 75 tables, 125 illustrations, 1967

A number of active and authoritative research workers review significant subjects within the field of petroleum geochemistry, bringing together recent and older works in proper perspective.

CONTENTS: 1. Oil and gas accumulations, and some allied deposits (G. D. Hobson, London, Great Britain). 2. The significance of clay minerals in sediments (C. E. Weaver, Atlanta, Ga., U.S.A.). 3. Petroleum hydrocarbons (M. A. Bestougeff, Paris, France). 4. Non-hydrocarbon compounds in petroleum (G. Costantinides, G. Arich, Trieste, Italy). 5. Geochemistry of porphyrins (G. W. Hodgson, B. L. Baker, E. Peake, Edmonton, Alta., Canada). 6. The asphaltic components of petroleum (P. A. Witherspoon, Berkeley, Calif., U.S.A. and R. S. Winniford, Spokane, Wash., U.S.A.). 7. A geochemical evaluation of petroleum migration and accumulation (E. G. Baker, Linden, N.J., U.S.A.). 8. Origin and evolution of petroleum (U. Colombo, Novara, Italy). Index.

ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK

602 E



SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 39, No. 1, September 1967

A PRECISE CONSTANT-CURRENT COULOMETER

A precise constant-current coulometer is described suitable for manual or automatic coulometric titrations. The apparatus provides 11 increments of current in the range 250 μA to 200 mA and gives a standard deviation of better than 30 p.p.m. for the total measurement of coulombs.

J. A. Pike and G. C. Goode,
Anal. Chim. Acta, 39 (1967) 1–6

THE DETERMINATION OF SMALL AMOUNTS OF LONG-CHAIN TERTIARY ALKYLAMINES AND QUARTERNARY AMMONIUM SALTS

Bromocresol green has been investigated as an alternative to ammonium erdmannate for the absorptiometric determination of small amounts of long-chain alkylamines and quaternary ammonium salts in aqueous solution in a solvent extraction procedure. The molecular absorption coefficient of the reagent at 615 nm is about 3 times that of the erdmannate ion at 353 nm; visual methods of comparison are simplified by the blue colour of the bromocresol green anion. The sensitivity of both the bromocresol green and the erdmannate method may be increased by stripping the coloured reagents into a small volume of aqueous solution. Both methods are free of interference from iron, but the present procedure has the disadvantage of a blank which depends both on the pH and on the concentration of excess reagent.

H. M. N. H. Irving and J. J. Markham,
Anal. Chim. Acta, 39 (1967) 7–12

CATION ANALYSIS BY THIN-LAYER CHROMATOGRAPHY AND REFLECTANCE SPECTROSCOPY

PART I. THE RAPID IDENTIFICATION OF CATIONS RESOLVED ON THIN-LAYER PLATES

A rapid method has been devised whereby 14 cations — Al^{3+}, Bi^{3+}, Cd^{2+}, Cr^{3+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Mn^{2+}, Hg^{2+}, Ni^{2+}, Ag^{+}, Sn^{2+} and Zn^{2+} — can be separated on one-dimensional, cellulose thin-layer plates and then identified by means of their reflectance spectra. The procedure requires micro-amounts of sample and only one spray reagent.

D. F. Zaye, R. W. Frei and M. M. Frodyma,
Anal. Chim. Acta, 39 (1967) 13–18

A BASIC STUDY OF COLUMN ADSORPTION CHROMATOGRAPHY

PART I. STANDARDIZATION OF ADSORBENT

The method of measuring f(1) values is proposed as a measure of the adsorption capacity of adsorbents. The f(1) value, a characteristic figure for a particular system, can be obtained chromatographically by measuring the progression rate of zone and the degree of packing of the column. For a system involving a unit concentration of *trans-p*-methoxyazobenzene in benzene as standard solution and alumina as adsorbent, optimum conditions for the measurement of f(1) were established. The effects of daylight, pretreatment of column, temperature, flow rate of solution, amount of adsorbent and degree and mode of packing were studied. Under optimum conditions, the value of f(1) was reproducible within ± 2%.

T. NOMURA AND K. TAKAOKA,
Anal. Chim. Acta, 39 (1967) 19–29

A BASIC STUDY OF COLUMN ADSORPTION CHROMATOGRAPHY

PART II. RELATION BETWEEN CHROMATOGRAPHIC AND BATCH-WISE ADSORPTION

The adsorption isotherm for the alumina–3-nitro-*o*-toluidine–benzene system was measured by the chromatographic and the batch methods. The chromatographic method gave a much higher value for the amount of solute adsorbed than the batch method. The isotherm of the alumina–*trans-p*-methoxyazobenzene–benzene system was also measured chromatographically; it was confirmed that this isotherm is concave to the *C*-axis. The proposed f(1) method for standardizing adsorbents was thus confirmed.

T. NOMURA, K. TAKAOKA AND G. KURATA,
Anal. Chim. Acta, 39 (1967) 31–35

THIAZOLYLAZO DYESTUFFS AS COORDINATING LIGANDS

PART I. THE STABILITY CONSTANTS FOR 4-(2-THIAZOLYLAZO)-RESORCINOL AND RELATED COMPOUNDS

The complex forming properties of the thiazole azo dyestuffs and related compounds have been studied in order to try to ascertain the role of importance of the donor atoms present in thiazolylazo-resorcinol. Potentiometric titrations were employed for these determinations, although in many cases meaningful stability constants could not be obtained because of reagent instability or insolubility of the complexes formed on chelation.

G. NICKLESS, (the late) F. H. POLLARD AND T. J. SAMUELSON,
Anal. Chim. Acta, 39 (1967) 37–46

SEPARATION OF INDIUM AND TIN IN THE PRESENCE OF EDTA

(in French)

Tin can be precipitated from weakly ammoniacal solutions in the presence of EDTA. Indium, in mg- or μg-amounts, remains almost completely in solution, together with 1–2% of the tin. The separation was checked with radioactive indium and tin.

G. LANFRANCO AND F. CERRATO,
Anal. Chim. Acta, 39 (1967) 47–50

THE SPECTROPHOTOMETRIC DETERMINATION OF ANIONS BY SOLVENT EXTRACTION WITH METAL CHELATE CATIONS. PART XX. TRICHLOROACETIC ACID WITH TRIS(1,10-PHENANTHROLINE)IRON(II) CHELATE

Trichloroacetic acid can be extracted from an aqueous solution by nitrobenzene with tris(1,10-phenanthroline)iron(II) chelate, and can be determined spectrophotometrically by measuring the extract at 516 nm. The extracted species is probably $[Fe(phen)_3]\cdot(CCl_3COO)_2$. Beer's law is obeyed over the concentration range $1.0\cdot10^{-5}$–$1.0\cdot10^{-4}M$ trichloroacetic acid in aqueous solution. Large amounts of phosphate and sulfate and moderate amounts of chloride, acetic acid, and monochloroacetic acid do not interfere; equal amounts of dichloroacetic acid give a slight positive error.

Y. Yamamoto, T. Kumamaru and Y. Uemura,
Anal. Chim. Acta, 39 (1967) 51–56

EXTRACTION OF LANTHANIDES AND ACTINIDES BY ALKYLPHOSPHINE OXIDES

PART III. EXTRACTION OF NITRIC ACID BY SOME DIPHOSPHINE OXIDES

(in French)

The distribution of nitric acid between an aqueous phase of constant or variable ionic strength and a benzene solution of diphosphine dioxide can be explained by the following reactions

$$H_a^+ + NO_{3_a}^- + DiPO_0 \rightleftharpoons DiPO\cdot HNO_{3_0}$$

$$H_a^+ + NO_{3_a}^- + DiPO\cdot HNO_{3_0} \rightleftharpoons DiPO\cdot 2\ HNO_{3_0}$$

At constant ionic strength, the stability constants K_I'' were determined for the complexes 1,1-DiPO·HNO_3 (9.8 ± 0.1 $(M)^{-1}$), 1,4-DiPO·HNO_3 (44 ± 3 $(M)^{-1}$) and 1,5-DiPO·HNO_3 (51 ± 1 $(M)^{-1}$). The constants K_{II}'' for the complexes 1,1-DiPO·2 HNO_3 and 1,5-DiPO·2 HNO_3 are respectively 0.35 ± 0.01 $(M)^{-1}$ and 6.2 ± 0.05 $(M)^{-1}$ at 25°. With an aqueous phase of variable ionic strength, values of $K_I' = 54 \pm 7$ $(M)^{-2}$ for 1,5-DiPO·HNO_3 and $K_{II}' = 6.5 \pm 0.4$ $(M)^{-2}$ for 1,5-DiPO·2 HNO_3 were obtained.

J. Goffart and G. Duyckaerts,
Anal. Chim. Acta, 39 (1967) 57–71

DETERMINATION OF PLUTONIUM IN Pu–Al ALLOYS BY X-RAY FLUORESCENCE

(in French)

An X-ray fluorescence method is described for the determination of plutonium in Pu–Al alloys. In order to obtain satisfactory reproducibility, the alloy is first dissolved in a nitric acid–mercury(II) nitrate mixture. The $L\alpha$ emission of plutonium is measured; to eliminate matrix effects, an internal standard with a wavelength near that of the Pu emission is used. Equipment and sample preparation are described. Extension of the method to other determinations is discussed.

M. Ganivet and T. Arnal,
Anal. Chim. Acta, 39 (1967) 73–80

THE DETERMINATION OF ALUMINUM AND BERYLLIUM BY ATOMIC ABSORPTION SPECTROSCOPY

The use of atomic absorption spectroscopy for the determination of aluminum and beryllium has been studied. The nitrous oxide–acetylene flame was found to be useful for the determination of trace amounts of either aluminum or beryllium. Beryllium can also be determined in an oxy–acetylene flame at the 1 p.p.m. level and upwards if the aqueous solution contains 10% of diethylene glycol diethyl ether. The determinations were essentially free from interferences.

T. V. Ramakrishna, P. W. West and J. W. Robinson,
Anal. Chim. Acta, 39 (1967) 81–87

THE DETERMINATION OF TRACES OF IRIDIUM IN RHODIUM BY NEUTRON ACTIVATION ANALYSIS

Iridium traces were determined in rhodium by thermal neutron activation for 2 days at a flux of $4 \cdot 10^{11}$ n$\cdot$cm$^{-2}\cdot$sec^{-1}. After cooling for at least 1 week, the samples were analysed by γ-spectrometry. No radiochemical separations were required. Special attention was paid to self-absorption phenomena in the rhodium samples.

R. Gijbels and J. Hoste,
Anal. Chim. Acta, 39 (1967) 89–93

THE USE OF A DIGITAL COMPUTER FOR THE CALCULATION OF SUCCESSIVE COMPLEX FORMATION CONSTANTS

A simple digital computer technique is described for the calculation of the successive complex formation constants in systems in which only 2 types of complexes are formed. This method should prove useful for the calculation of equilibrium constants in more complicated systems.

E. A. Unwin, R. G. Beimer and Q. Fernando,
Anal. Chim. Acta, 39 (1967) 95–102

DETERMINATION OF TUNGSTEN IN SILICATES AND NATURAL WATERS

Coprecipitation with hydrous manganese dioxide is used for the concentration of tungsten from natural waters (including sea water) and from solutions prepared from silicate rocks and sediments by hydrofluoric acid attack. After dissolution of the hydrous manganese dioxide precipitate in acidified sulphur dioxide solution, cation exchange is used to separate tungsten and molybdenum from other coprecipitated elements, hydrogen peroxide being used as eluant. Molybdenum is separated from tungsten by extraction of its dithiol complex from 2.4 *N* hydrochloric acid medium containing citric acid and can be determined photometrically. After destruction of citric acid, tungsten is determined photometrically with dithiol. The overall chemical yield of the analytical process is $94 \pm 1\%$. The standard deviation of the method is ± 0.010 μg for sea water (0.116 μg W/l) and *ca.* 0.05 μg/g for siliceous sediments containing 0.5–1.0 μg W/g.

K. M. Chan and J. P. Riley,
Anal. Chim. Acta, 39 (1967) 103–113

1,1′-BIS(6-CHLOROANTHRAQUINONYL)AMINE AS A REAGENT FOR TRACE AMOUNTS OF BORON

A new reagent, 1,1′-bis(6-chloroanthraquinonyl)amine, has been synthesized and applied to the determination of trace amounts of boron. A blue complex is formed on heating with orthoboric acid in 96% sulfuric acid medium. Oxidizing agents and some cations interfere with the method; separation of the boron either by distillation of the methyl ester or by ion exchange removes such interferences. The method is very sensitive *i.e.*, 0.0005 μg B/cm^2, and can be used for the analyses of vegetation.

R. L. GROB, J. COGAN, J. J. MATHIAS, S. M. MAZZA AND A. P. PIECHOWSKI,
Anal. Chim. Acta, 39 (1967) 115–121

SPECTROPHOTOMETRIC DETERMINATION OF 2,5-HEXANEDIONE

(Short Communication)

C. L. DEASY AND A. E. STITZEL,
Anal. Chim. Acta, 39 (1967) 123–124

A TRANSISTORISED LINEAR-TO-LOGARITHMIC SIGNAL CONVERTER FOR USE WITH RECORDING SPECTROPHOTOMETERS

(Short Communication)

D. ALGER, G. F. KIRKBRIGHT, M. D. MAYHEW AND T. S. WEST,
Anal. Chim. Acta, 39 (1967) 125–128

OXIMIDOBENZOTETRONIC ACID: A NEW REAGENT FOR THE GRAVIMETRIC DETERMINATION OF COBALT

(Short Communication)

G. S. MANKU, A. N. BHAT AND B. D. JAIN,
Anal. Chim. Acta, 39 (1967) 128–131

NEUTRON ACTIVATION ANALYSIS FOR GOLD IN OSMIUM

(Short Communication)

R. GIJBELS AND J. HOSTE,
Anal. Chim. Acta, 39 (1967) 132–135

THE DETERMINATION OF DYSPROSIUM IN THE PRESENCE OF ALUMINUM

(Short Communication)

A. BRÜCK AND K. F. LAUER,
Anal. Chim. Actal, 39 (1967) 135–136

ANNOUNCEMENT
concerning the
JOURNAL OF ELECTROANALYTICAL CHEMISTRY

The boundaries between what are regarded as electroanalytical chemistry, electrochemistry and colloid chemistry are becoming increasingly diffuse. This has been reflected in the pages of the journal, where many of the papers published are of interest to chemists who consider themselves as falling under any of these three broad divisions.

The linking phenomena are those associated with the electrical double layer, and it is felt that it would be both useful and appropriate to acknowledge these broader interests by extending the scope of the journal to include all phenomena in which the electrical double layer plays an essential role.

These extend from applications in analytical chemistry through the fundamentals of electrode reactions, which are already the staple part of the journal, to studies of the double layer around colloidal particles, the stability of dispersions and electrokinetic phenomena as well as other surface chemical problems such as monolayers and soap films.

Since this broadening of the scope does not involve any change in the basic interests of the journal, the title has been only slightly modified. From January 1967 it has become:

JOURNAL OF ELECTROANALYTICAL CHEMISTRY AND INTERFACIAL ELECTROCHEMISTRY

An International Journal Devoted to All Aspects of Electroanalytical Chemistry, Double Layer Studies, Electrokinetics, Colloid Stability and Electrode Kinetics

Since the aim of a journal must be to publish papers rapidly, it has been decided that three volumes will be published in 1967. The delay in publication will thereby be reduced to a minimum level.

Dr. R. H. OTTEWILL of the University of Bristol has joined the board of Editors, and has special responsibility for the papers which fall within his field of interest.

Papers for publication should be sent to one of the following addresses:

Professor J. O'M. BOCKRIS, John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia 4, Pa. 19104, U.S.A.;

Dr. R. H. OTTEWILL, Department of Chemistry, The University, Bristol 8, England;

Dr. R. PARSONS, Department of Chemistry, The University, Bristol 8, England;
(Until July, 1967: Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, Calif. 91109, U.S.A.)

Professor C. N. REILLEY, Department of Chemistry, University of North Carolina, Chapel Hill, N.C. 27515, U.S.A.

A printed pamphlet "hints to authors" is available free of charge from the publishers, who will be glad to supply any further information to intending authors.

Subscription price for 1967: £18.18.0; US$52.50, Dfl. 189.00 plus postage 13s., US$1.80, Dfl. 6.50.

Orders may be placed with subscription agencies, booksellers or with

ELSEVIER PUBLISHING COMPANY

P.O. BOX 211 — AMSTERDAM — THE NETHERLANDS

DIFFRACTION OF X-RAYS BY CHAIN MOLECULES

by B. K. VAINSHTEIN

Foreword by M. F. PERUTZ

6 x 9″, xiii + 414 pages, 3 tables, 258 illus., 256 lit.refs.,
Dfl. 65.00, £6.10.0, $23.50

Contents: 1. Principles of the theory of X-ray diffraction. 2. Structures of chain molecules and assemblies. 3. Diffraction by an isolated chain molecule. 4. Scattering intensity and structure of object. 5. Properties of the distribution and interference functions. 6. Diffraction by assemblies of parallel chain molecules. 7. Diffraction by assemblies with nonparallel packing of chain molecules and by amorphous polymers. Subject index.

INFRA RED INSTRUMENTATION AND TECHNIQUES

by A. E. MARTIN

5½ x 8½″, x + 180 pages, 13 tables, 94 illus., 86 lit.refs., 1966,
Dfl. 32.50, 65s., $12.00

Contents: 1. Historical. 2. Modern infra-red spectrometers. 3. Miscellaneous instruments. 4. Interferometric spectrometers. 5. Accessories. 6. Experimental methods and techniques. Index.

ENERGY TRANSFER IN RADIATION PROCESSES

Chemical, Physical and Biological Aspects

Proceedings of the International Symposium held in Cardiff, 1965

edited by G. O. PHILLIPS

5½ x 8½″, xvi + 182 pages, 10 tables, 81 illus., 273 lit.refs., 1966,
Dfl. 32.50, 65s., $12.00

Contents: Introductions to the sections by F. S. Dainton, G. F. J. Garlick and Tikvah Alper. Invited papers by E. J. Bowen, Jett C. Arthur, N. Riehl, R. Mason. Contributed papers.

MASS SPECTROMETRIC ANALYSIS OF SOLIDS

edited by A. J. AHEARN

5½ x 8½″, viii + 167 pages, 13 tables, 46 illus., 242 lit.refs., 1966,
Dfl. 30.00, 60s., $10.75

Contents: 1. Introductory survey. 2. The production of ions from solids. 3. Photographic emulsions as ion detectors in quantitative mass spectrography. 4. Analysis of special samples. 5. Mass spectrographic microprobe analysis. Subject index.

RADIOCHEMICAL SURVEY OF THE ELEMENTS

Principal characteristics and applications of the elements and their isotopes

by M. HAISSINSKY
and
J.-P. ADLOFF

6 x 9″, ix + 177 pages, 1965, Dfl. 32.50, 65s., $12.00

Contents: Introduction. The elements in alphabetical order. Element 102. Element 104.

ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK

ANALYTICA CHIMICA ACTA

Vol. 39 (1967)

ANALYTICA CHIMICA ACTA

International monthly devoted to all branches of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 39 (1967)

PRINTED IN THE NETHERLANDS

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

A PRECISE CONSTANT-CURRENT COULOMETER

J. A. PIKE AND G. C. GOODE
Atomic Weapons Research Establishment, Aldermaston, Berkshire (Great Britain)

(Received February 4th, 1967)

In recent years constant-current coulometry has become established as a high-precision analytical technique by the pioneering work of TAYLOR and co-workers at the National Bureau of Standards[1-3] and others[4,5]. Standard deviations of the order of 50 p.p.m. have been attained for a variety of chemical systems and such results encourage the adoption of the technique for primary standardisation work using the coulomb as an independent physical standard. Acceptance of the technique requires the development of precise and reliable coulometers and although a number of instruments have been described capable of a precision of 500 p.p.m., few would be applicable to high-precision standardisation work.

Studies in this laboratory on high-precision analysis of nuclear materials[6,7] prompted the development of a high-precision constant-current coulometer and a detailed description of the instrument is given in this paper. During the preparation of this paper a coulometer of similar performance but differing somewhat in design has been described[8].

GENERAL DESIGN OF COULOMETER

In design considerations particular attention was paid to convenience for manual coulometric titrations and for provision of facilities for automated operation using an auto-titration switching unit such as that described by STEED AND FRANSMAN[9].

Experience in this laboratory with a simple microcoulometer[10] has shown that a Harwell-type 1350A timing unit provides an extremely convenient switching arrangement for coulometric titrations and this has been used in the instrument described. This unit enables the flow of current to be controlled by a relay-operated switch and simultaneously records the duration of current flow in minutes and seconds using a dekatron display. It also provides switching for pre-set time intervals (0.1, 1.0, 10, 120, 1200 sec), the shorter duration pulses being useful on approaching the end-point in a titration.

The stabilised supply provides 11 increments of current in the range 250 μA to 200 mA. Higher currents, often in excess of 1 A, have been used by other workers for precise standardisations, enabling large samples to be titrated and weighing errors to be reduced. In this laboratory, however, electrolysis currents of 100 mA or less have been used for up to 0.5 meq of sample, significant weighing errors being avoided by dispensing large weights of standard solution for titration. This approach was adopted, partly because of the nature of the materials concerned but also to avoid the difficul-

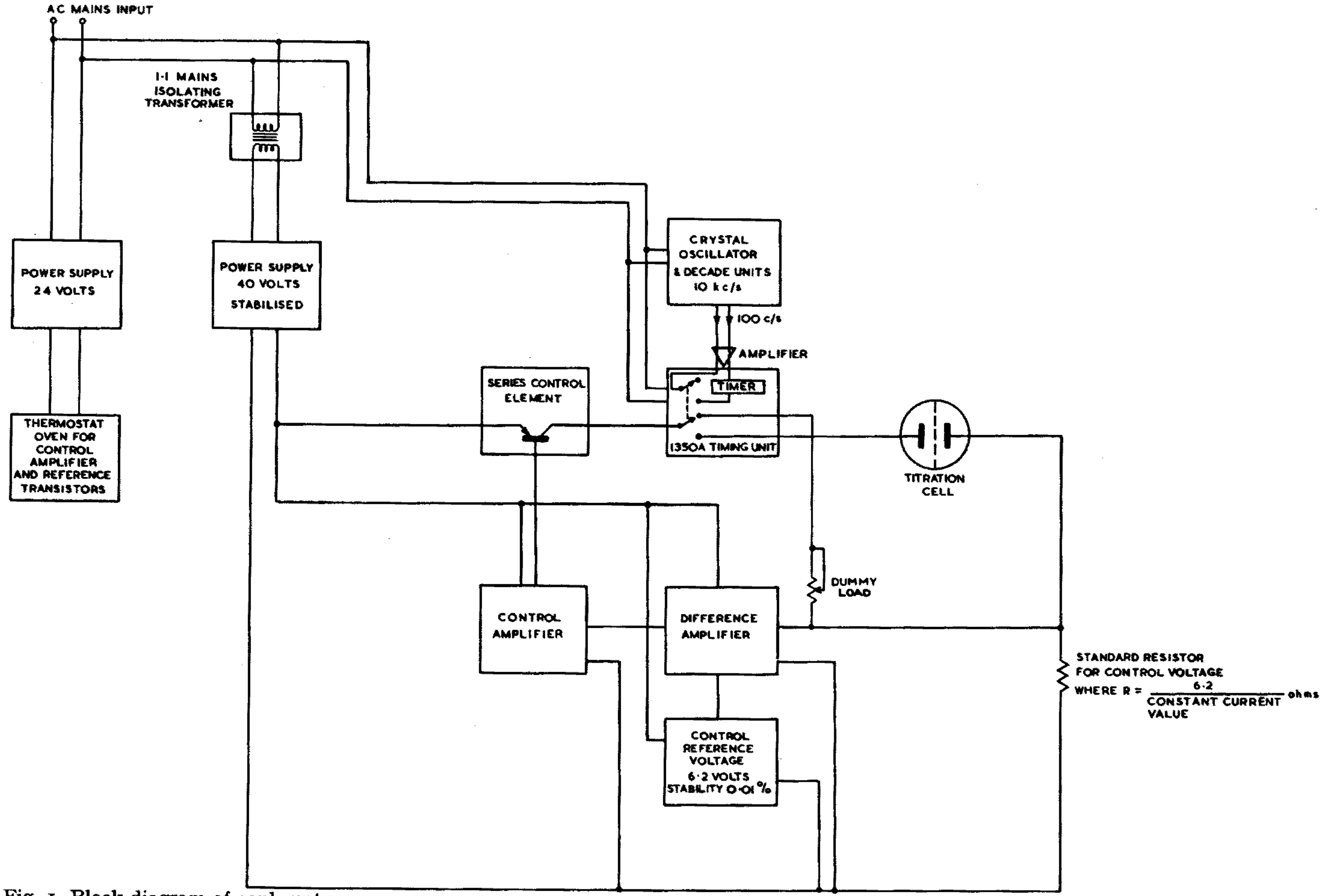


Fig. 1. Block diagram of coulometer.

ties associated with the use of large currents. No attempt has been made to provide exactly known current values, or to attain long-term stability by manual adjustment of the reference potential but rather to minimise drift by thermal control of temperature-sensitive components and to achieve adequate stability for the period of the titration (up to 30 min).

For applications in which an earthed valve millivoltmeter is used for end-point detection, particularly with constant-current polarised electrodes, a high insulation to earth of both output terminals is essential. The use of a suitable 1:1 isolating transformer ensures that a resistance of at least 10^9 ohms is attained.

Current stabilisation

A conventional control system is employed in which the voltage developed across a precise resistor in series with the electrolysis cell is compared against a stable zener diode reference potential; the error voltage is amplified by a D.C. amplifier and used to control a series element, transistorised circuitry being employed. A block diagram of the coulometer is shown in Fig. 1. The D.C. amplifier and control element have sufficient current gain to present an output impedance of several megohms to the cell and enables precise stabilisation to be effected for changes in cell resistance of up to ±10%.

Time measurement

Precise timing is obtained by feeding the 1350A timing unit with an external 100 cycle per second signal from a Venner 10 kilocycle per second quartz crystal oscillator (type T.S.5) counted down through two decade selectors (type TS11). To operate the timing unit the 6-V pulses require amplification to 30 V and a single-stage transistor amplifier (not shown) is used for this purpose. The quartz crystal is not temperature-controlled but insignificant errors arise from normal changes in ambient temperature.

Circuit description

A detailed circuit diagram is shown in Fig. 2. Current for the electrolysis cell is provided by a 40-V supply PS1, stabilised to 0.02% via an appropriate bias resistor R_2 to R_{12}, milliammeter M2 and series control element VT5, and is controlled by a relay-operated start/stop switch on the timing unit. In the "Stop" position the circuit is completed by a variable resistor VR2 acting as a "dummy" cell. On "Start", current either flows through the electrolysis cell, or is controlled by the auto-titration switching unit depending on the position of the Manual/Auto switch S4. The resistor VR2 is adjusted to equal the cell resistance by depressing switch S2 and varying VR2 until the same voltage drop across the series element VT5 (meter M1) is obtained for both "Stop" and "Start" positions. This minimises the effects of switching transients and also indicates if the circuit is stabilising satisfactorily. A switch S3 enables a ballast resistor R31 to be included in the circuit if the cell resistance is less than 20 ohms. This is operated on high current ranges (100 mA and 200 mA) to prevent the series element VT5 from overheating.

Transistors VT3, VT4, VT7, VT8, VT9, zener diode D1 and resistors R13 to R23 are mounted in a block thermostatted at 40 ±0.5° and heated by an 8-ohm coil supplied from a 24-V supply PS2. The amplifier input transistors VT9, connected as a

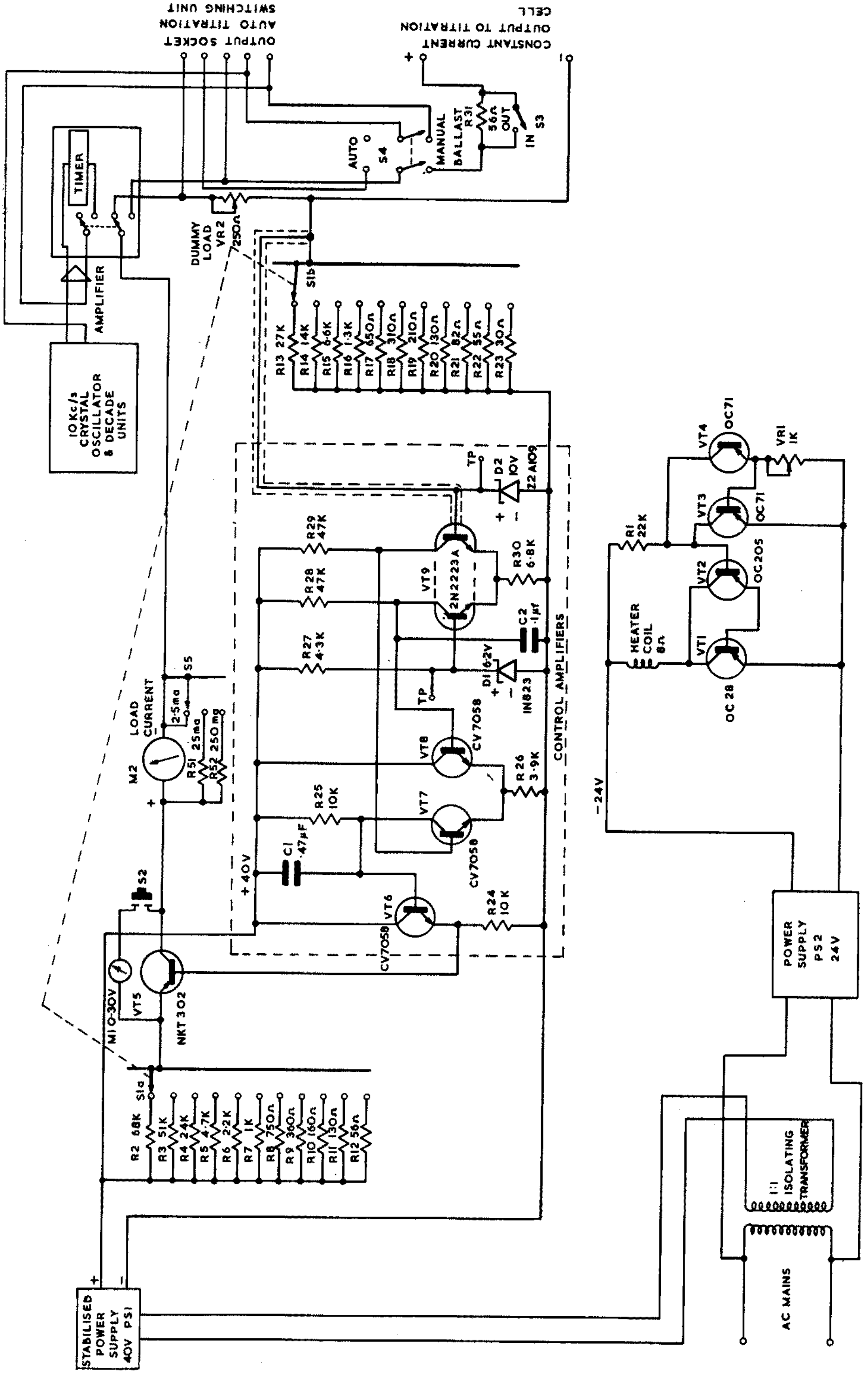


Fig. 2. Circuit diagram of coulometer. R1 to R4, ½-W resistors; R5 and R6, 3-W resistors; R7 to R12, 1½-W resistors. R13 to R23, Electrothermal Presistors, series G101 type 3505A; R13 to R18, ¼-W; R19, ½-W; R20 and R21, 1-W; R22 and R23, 2-W. R24 to R26, ½-W resistors; R27, 3-W resistors; R28 and R29, 1-W resistors; R30 and R31, 3-W resistors. VR1, VR2 and VR3, 1-W variable resistors. C1 and C2, Capacitors 125-V working. D1, Zener diode type IN823; D2, Zener diode type Z2A100; PS1, 40-V power supply unit, Coutant Electronics Ltd. Type D300/24; PS2, 24-V power supply unit Coutant Electronics Ltd. Type E50/40.

differential amplifier, form a matched pair (mounted in the same case to reduce further the effect of temperature changes) and are protected by zener diode D2. The potentials across the reference diode D1, and standard resistor R13 to R23 are taken to external test points.

Standards

Frequent current measurements are made during titrations by observing the voltage across a standard resistor in series with the electrolysis cell. Tinsley 4-terminal oil-filled standard resistors are used; these, though they nominally have an accuracy of only 300 p.p.m., have been calibrated against NPL class A resistors and have shown a stability of ±20 p.p.m. over periods of many months. Voltage measurements are made with a Cambridge "Vernier" potentiometer of 10 p.p.m. resolution which has been calibrated to 10 p.p.m. using a high-grade reference potentiometer. Saturated Weston cells are used for potentiometer reference potential; these are lagged to reduce temperature differentials and a correction for temperature coefficient is applied. Calibration against NPL standard cells has indicated a long-term stability of ±10 p.p.m.

The accuracy of the 10 kilocycles per second frequency standard has been shown to be better than 1 p.p.m. by calibration based on a standard broadcast frequency.

Calibrations for all electrical equipment have been made at regular intervals in the standards laboratory of this establishment and it is estimated that the overall error in absolute measurement of coulombs does not exceed 30 p.p.m., which is approximately the present error in the measurement of the Faraday.

PERFORMANCE

The instrument has functioned satisfactorily for some 18 months, and has been used both manually and in the automated mode. Figure 3 shows graphically typical changes of current for the 50-mA range over a period of approximately one month, the

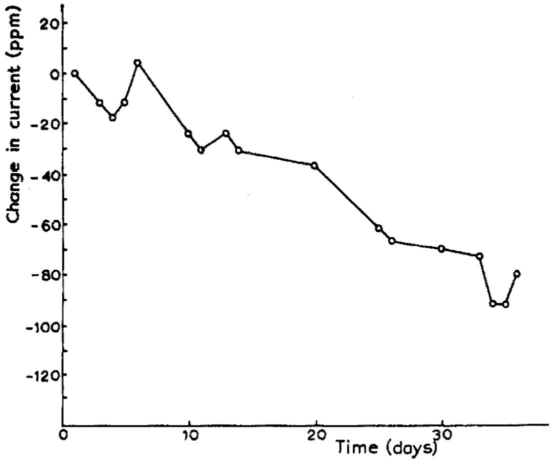


Fig. 3. Change of current with time for 50mA- range.

coulometer being switched on continuously, and changes in ambient temperature being less than 4°. It can be seen that a change in current of approximately 90 p.p.m. occurred during this period but day to day fluctuations did not exceed 20 p.p.m. For coulometric titrations of 30-min duration satisfactory precision is therefore obtained.

The precision and accuracy of the coulometer have been confirmed in coulometric titrations of standard uranium materials[6] for which a standard deviation of 20 p.p.m. was attained.

We thank Mr. K. C. STEED for much helpful discussion and Mr. K. A. HUGHES for advice on electrical standardisation problems.

SUMMARY

A precise constant-current coulometer is described suitable for manual or automatic coulometric titrations. The apparatus provides 11 increments of current in the range 250 μA to 200 mA and gives a standard deviation of better than 30 p.p.m. for the total measurement of coulombs.

RÉSUMÉ

On décrit un coulomètre à courant constant précis pour des titrages coulométriques manuels ou automatiques. Cet appareil peut fournir onze valeurs de courant de 250 μA à 200 mA, il donne une déviation standard de 30 p.p.m. au maximum pour la mesure totale des coulombs.

ZUSAMMENFASSUNG

Ein genaues Konstant-Strom-Coulometer wird beschrieben, welches für manuelle oder automatische coulometrische Titrationen geeignet ist. Die Apparatur sieht 11 Stromstufen im Bereich von 250 μA bis 200 mA vor und ergibt eine Standardabweichung von <30 p.p.m. in Bezug auf die gemessenen Coulombs.

REFERENCES

1 J. K. TAYLOR AND S. W. SMITH, *J. Res. Natl. Bur. Std.*, 63A (1959) 153.
2 G. MARINENKO AND J. K. TAYLOR, *J. Res. Natl. Bur. Std.*, 67A (1963) 31.
3 G. MARINENKO AND J. K. TAYLOR, *J. Res. Natl. Bur. Std.*, 67A (1963) 453.
4 E. L. ECKFELDT AND E. W. SHAFFER, *Anal. Chem.*, 37 (1965) 1534.
5 F. A. COOPER AND J. C. QUAYLE, *Analyst*, 91 (1966) 363.
6 G. C. GOODE, J. HERRINGTON AND W. T. JONES, *Anal. Chim. Acta*, 37 (1967) 445.
7 G. C. GOODE AND W. T. JONES, *Anal. Chim. Acta*, 38 (1967) 363.
8 J. C. QUAYLE AND F. A. COOPER, *Analyst*, 91 (1966) 355.
9 K. C. STEED AND F. FRANSMAN, *Anal. Chim. Acta*, 32 (1965) 472.
10 R. G. MONK AND K. C. STEED, *Anal. Chim. Acta*, 26 (1962) 305.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE DETERMINATION OF SMALL AMOUNTS OF LONG-CHAIN TERTIARY ALKYLAMINES AND QUARTERNARY AMMONIUM SALTS

H. M. N. H. IRVING AND J. J. MARKHAM*
School of Chemistry, The University, Leeds 2 (Great Britain)

(Received February 10th, 1967)

The determination of long-chain tertiary alkylamines and quarternary ammonium salts in water and in acidic raffinate solutions by the use of Erdmann's salt $(NH_4^+)[Co(NH_3)_2(NO_2)_4]^-$ has been described by IRVING AND DAMODARAN[1]. We have now examined the use of the more readily available sulphonphthalein indicator, bromocresol green, for the same purpose. Compared to the erdmannate method, the new procedure is found to have certain advantages, but there are disadvantages too.

Tetra-*n*-hexylammonium iodide has little tendency to dissolve in water but it is readily soluble in 1,2-dichloroethane. The same is true of tri-*n*-octylamine, and TRÉMILLON[2] has reported on the extraction of long-chain primary, secondary, and tertiary amines as their acid salts into various organic solvents. Extraction is a convenient and efficient way of collecting such compounds from quite dilute aqueous solutions.

In the erdmannate method the organic layer (1,2-dichloroethane), after being washed to remove excess of acid is equilibrated with a factitious excess of ammonium erdmannate dissolved in water. The erdmannate ion enters the organic phase in direct proportion to the concentration of tertiary amine salt or quaternary ammonium salt present:

$$(R_3NH^+X^-)_{org.} + E^- \rightleftarrows (R_3NH^+E^-)_{org.} + X^- \quad (1)$$

$$(R_4N^+X^-)_{org.} + E^- \rightleftarrows (R_4N^+E^-)_{org.} + X^- \quad (2)$$

Species present in the organic phase are distinguished by the subscript org. The erdmannate anion is represented by E^- and X^- represents the anion of the mineral acid used in the initial extraction. The organic layer is washed with water to remove any excess erdmannate, dried with anhydrous sodium sulphate and filtered into an optical cell. The absorbancy is measured at 353 nm against pure 1,2-dichloroethane. The calibration curve is a straight line passing through the origin. The erdmannate method is about 8 times as sensitive as the best previously reported method[3], with $\varepsilon = 1.4 \cdot 10^4$ against $\varepsilon = 1.7 \cdot 10^3$.

In contrast to the simplicity of the erdmannate method, the reactions that take place with bromocresol green are more complicated. Although the calibration curve is still linear, there is a blank and the concentration of reagent must be controlled.

Bromocresol green can be regarded as a diprotic acid H_2BCG and its successive

---

* Present address: Villanova University, Villanova, Pennsylvania (U.S.A.)

dissociations may be represented as:

$$H_2BCG \rightleftarrows H^+ + HBCG^- \qquad (3)$$

$$HBCG^- \rightleftarrows H^+ + BCG^{2-} \qquad (4)$$

Equation (4) represents the loss of the proton involved in the structural rearrangement responsible for the acid–base indicator properties of this dyestuff. The dissociation constant of $HBCG^-$ is given[4] by $pK_a = 4.7$.

In the proposed new method the layer of 1,2-dichloroethane containing the salts $R_3NH^+X^-$ or $R_4N^+X^-$ is equilibrated with an aqueous buffer which is $2 \cdot 10^{-6}$ *M* with respect to bromocresol green. The following reactions:

$$(R_3NH^+X^-)_{org.} + HBCG^- \rightleftarrows (R_3NH^+HBCG^-)_{org.} + X^- \qquad (5)$$

and

$$(R_4N^+X^-)_{org.} + HBCG^- \rightleftarrows (R_4N^+HBCG^-)_{org.} + X^- \qquad (6)$$

account for the passage of the bromocresol green anion into the organic layer in proportion to the amount of tertiary amine or quaternary ammonium salt present. The greater the tendency for reactions (5) and (6) to go to the right, the greater will be the slopes of the calibration curves. This would seem to call for an increase in the concentration of bromocresol green in the aqueous phase. However, there are two complications. In the first place, bromocresol green will partition into the organic phase in the form of undissociated H_2BCG; the lower the pH of the buffer, the larger the amount of indicator taken up in this form by the organic phase—and the larger the blank. On the other hand, there is a competing reaction due to the ion BCG^{2-} which produces a water-soluble complex, thus:

$$(R_3NH^+X^-)_{org.} + BCG^{2-} \rightleftarrows (R_3NH^+BCG^{2-}) + X^- \qquad (7)$$

$$(R_4N^+X^-)_{org.} + BCG^{2-} \rightleftarrows (R_4N^+BCG^{2-}) + X^- \qquad (8)$$

This competing reaction is easily demonstrated; for it is actually possible to "strip" a quaternary ammonium salt from an organic solvent by shaking with an alkaline solution of bromocresol green.

Clearly, in establishing optimum experimental conditions two factors must be carefully controlled, *viz.* (*a*) the total concentration of bromocresol green in the aqueous phase and (*b*) the pH of the solution. A value of $2 \cdot 10^{-6}$ *M* for the total concentration of bromocresol green in the aqueous layer is satisfactory and this may be easily checked by visual comparison with the contents of a separatory funnel (of the same shape and size as that used in the extraction) containing 1,2-dichloroethane and a buffer solution containing $2 \cdot 10^{-6}$ *M* bromocresol green in the same relative volumes as in the solutions under investigation. If after an initial equilibration it appears that the colour due to the bromocresol green left in the aqueous layer has decreased, more is added dropwise as a 10^{-4} *M* solution until the colour intensity again matches that in the comparison funnel. The solutions are again equilibrated and the procedure repeated, should it be necessary.

Clearly, it will be advisable to have the pH low so that tertiary amines will be present as R_3NH^+ rather than as R_3N. Low pH will also minimise the formation of the anion BCG^{2-}. On the other hand, as the pH decreases the blank due to the extraction of H_2BCG increases. The final pH is thus a compromise.

The indicator extracted into the organic phase as $R_3NH^+HBCG^-$ or $R_4N^+HBCG^-$ is not measured spectrophotometrically in this form. Instead, the combined organic extracts are shaken with exactly 10.0 ml of a solution that is 10^{-1} *M* with respect to sodium hydroxide and 10^{-3} *M* with respect to sodium perchlorate. With the tertiary amine this brings about the reaction:

$$\underset{\text{yellow}}{(R_3NH^+HBCG^-)_{org.}} + 2\,OH^- \rightarrow (R_3N)_{org.} + 2\,H_2O + \underset{\text{blue}}{BCG^{2-}} \tag{9}$$

while for the quaternary compounds we have:

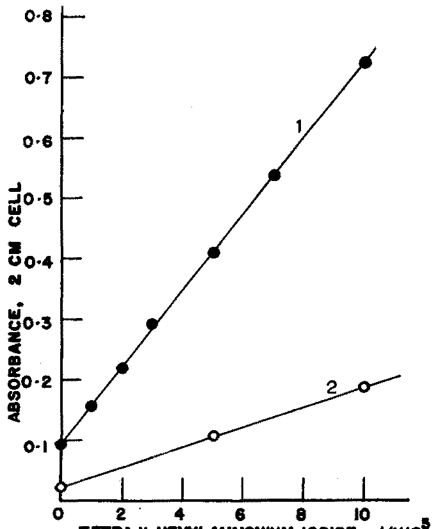
$$\underset{\text{yellow}}{(R_4N^+HBCG^-)_{org.}} + OH^- \rightarrow R_4N^+ + \underset{\text{blue}}{BCG^{2-}} + H_2O \tag{10}$$

and

$$\underset{\text{yellow}}{(R_4N^+HBCG^-)_{org.}} + ClO_4^- \rightarrow (R_4N^+ClO_4^-)_{org.} + \underset{\text{blue}}{BCG^{2-}} + H^+ \tag{11}$$

If perchlorate is not used there is considerable tendency for emulsion formation and the ion-pair $R_4N^+HBCG^-$ collects at the interface.

There are two advantages accruing from this stage of the back-extraction. The solution to be measured now has a blue rather than a yellow colour—which is preferable if a visual method is used; further the colour is developed in a smaller volume with a consequent increase in sensitivity.



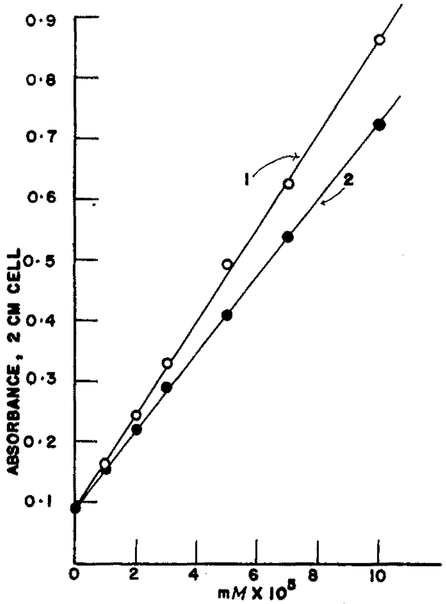


Fig. 1. Absorbance of bromocresol green at 615 nm in 0.1 *M* NaOH containing 10^{-3} *M* $NaClO_4$ following the extraction of varying amounts of tetra-*n*-hexylammonium iodide by a solution of bromocresol green in 1,2-dichloroethane from a buffer (1) of pH 4.70 (0.1 *M* HAc in 0.1 *M* NaAc; ●) or (2) of pH 5.40 (0.1 KHphthalate in 0.1 *M* phthalic acid; ○).

Fig. 2. Calibration curves showing the absorbance of bromocresol green at 615 nm in 0.1 *M* NaOH containing 10^{-3} *M* $NaClO_4$ in the final stage of the determination of (1) tri-*n*-octylamine (○) and (2) tetra-*n*-hexylammonium iodide (●) according to the recommended *Procedure*.

Figure 1 compares the effect of using a phthalate buffer of pH 5.4 with that of an acetate buffer of pH 4.7. The problem of the choice of buffer with respect to the volume of blanks has been discussed in detail by HARIOKA[5] in connection with the determination of organic amines (especially sympathomimetic amines) in pharmaceutical preparations with the aid of bromocresol green.

EXPERIMENTAL

Reagents

Hydrochloric acid, acetic acid and sodium acetate trihydrate were all of analytical-reagent grade. The 10^{-4} M bromocresol green solution was prepared by dilution of a 10^{-3} M solution prepared by dissolving 700 mg of bromocresol green in 20.0 ml of 0.100 M sodium hydroxide and diluting to 1000 ml with distilled water.

Procedure

The procedure may be modified for other conditions of concentration. The one given below is for 0 to 10^{-4} mmoles of tri-*n*-octylamine or tetra-*n*-hexylammonium iodide in 100 ml of aqueous solution, *i.e.*, solutions which are 0 to 10^{-6} M.

To the sample add hydrochloric acid if necessary to bring the solution to *ca.* pH 0. Place in a separatory funnel of at least 170-ml total volume (the nominal 100 ml pear-shaped funnel) and extract 3 times with 15-ml portions of 1,2-dichloroethane, collecting the extract in a second separating funnel. Avoid vigorous shaking, especially with the quaternary salt where the tendency towards emulsion formation is quite pronounced. To this second separating funnel add 100 ml of a 0.1 M acetic acid – 0.1 M sodium acetate buffer and 2.0 ml of 10^{-4} M bromocresol green solution. Shake gently and allow the phases to separate. If the colour of the aqueous phase is significantly diminished from that of a comparison solution which is $2 \cdot 10^{-6}$ M in bromocresol green in a similar acetate buffer, add 10^{-4} M bromocresol green dropwise to a visual match of the colour intensity. Shake gently and again allow the two phases to separate completely. Draw off the 1,2-dichloroethane layer into a third separating funnel. Add 5 ml of 1,2-dichloroethane to the aqueous phase remaining in the second separating funnel, invert the funnel 5 times, allow the phases to separate and combine the 1,2-dichloroethane layer with the 1,2-dichloroethane previously added to the third separating funnel. Add exactly 10.0 ml of a solution which is 0.1 M in sodium hydroxide and 0.001 M in sodium perchlorate to the third separating funnel, shake gently and allow the phases to separate completely. Draw off and reject the 1,2-dichloroethane layer, together with the interface. Wipe off any solvent adhering to the inside of the funnel stem with absorbent paper and then run off sufficient of the aqueous layer into a 2.00-cm spectrophotometer cell and measure the absorbance at 615 nm against a solution which is 0.1 M in sodium hydroxide and 0.001 M in sodium perchlorate. The absorbance, after correction for the blank, is proportional to concentration.

Figure 2 shows the results of carrying out such a procedure with tri-*n*-octylamine and with tetra-*n*-hexylammonium iodide. Although both lines are essentially straight, in neither case is the number of millimoles of BCG^{2-} in the final solution (measured after correction for blank) exactly equal to the number of millimoles of tri-*n*-octylamine or tetra-*n*-hexylammonium iodide present in the original aqueous solution, but amounts to 95% and 78% respectively. Nevertheless, if the procedure is carried out consistently, the calibration curve is reproducible.

The effect of iron

Solutions of amines containing in addition 0.1 *M* iron(III) chloride in 0.1 *M* hydrochloric acid were analysed by the above method with no apparent interference from the iron.

If solutions are free of iron and other heavy metals, the procedure may be shortened by adding the bromocresol green directly to a solution which has been buffered to pH 4.7 and extracting $(R_3NH)HBCG$ or $(R_4N)HBCG$ into 1,2-dichloroethane. This direct approach was found to be impossible if the solution contained iron since the hydrous oxide precipitated. By using citrates or tartrate in the buffer, it was possible to prevent the precipitation; but the magnitude of the blank was increased and the calibration curve was less steep and became non-linear. This is illustrated in Fig. 3 which shows the curve obtained for tri-*n*-octylamine in a solution of 0.1 *M* iron(III) chloride buffered with tartrate to pH 4.7.

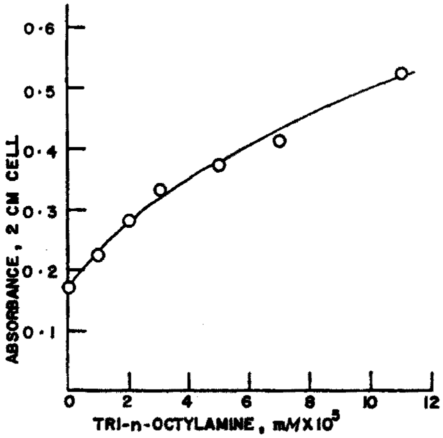


Fig. 3. Absorbance of the final bromocresol green extract at 615 nm in 0.1 *M* NaOH containing 10^{-3} *M* $NaClO_4$ in the determination of tri-*n*-octylamine in a solution containing 0.1 *M* $FeCl_3$ in 4.0 *M* HCl. Tartrate was present in the first stage to prevent the precipitation of iron oxide.

Analysis of very dilute solutions

Although the molar absorptivity of bromocresol green is only about 3 times that of erdmannate, $\varepsilon_{615} = 4.08 \cdot 10^4$ as against $\varepsilon_{353} = 1.4 \cdot 10^4$, the present method lends itself to the analysis of quite dilute solutions provided that a sufficient volume of sample is available. There is a concentration step not only in extracting the amine or quaternary salt from the original aqueous solution into 1,2-dichloroethane, but also in stripping the bromocresol green from the 1,2-dichloroethane into the 0.1 *M* hydroxide −0.001 *M* perchlorate solution. However, such a procedure is equally applicable to the erdmannate method[1] as the erdmannate in the 1,2-dichloroethane as R_3HNE or R_4NE can be displaced by perchlorate into a smaller volume of water for measurement, thus:

$$(R_3HN^+E^-)_{org.} + ClO_4^- \rightleftarrows (R_3HN^+ClO_4^-)_{org.} + E^- \qquad (12)$$

$$(R_4N^+E^-)_{org.} + ClO_4^- \rightleftarrows (R_4N^+ClO_4^-)_{org.} + E^- \qquad (13)$$

Apart from increasing the sensitivity of the erdmannate method, such a procedure obviates the step of drying and filtering.

One of us (J.J.M.) thanks the United States Department of Health, Education and Welfare for support received under Fellowship IF-WP-26, 091-1.

SUMMARY

Bromocresol green has been investigated as an alternative to ammonium erdmannate for the absorptiometric determination of small amounts of long-chain alkylamines and quaternary ammonium salts in aqueous solution in a solvent extraction procedure. The molecular absorption coefficient of the reagent at 615 nm is about 3 times that of the erdmannate ion at 353 nm; visual methods of comparison are simplified by the blue colour of the bromocresol green anion. The sensitivity of both the bromocresol green and the erdmannate method may be increased by stripping the coloured reagents into a small volume of aqueous solution. Both methods are free of interference from iron, but the present procedure has the disadvantage of a blank which depends both on the pH and on the concentration of excess reagent.

RÉSUMÉ

On propose l'emploi de vert de bromocrésol pour le dosage absorptiométrique de faibles teneurs d'alcoylamines à longue chaîne et de sels d'ammonium quaternaires, avec extraction dans un solvant. Cette méthode est comparée à celle utilisant l'erdmannate d'ammonium. Dans ces deux procédés, le fer ne gêne pas; cependant dans la méthode décrite, il faut tenir compte du pH et de la concentration du réactif en excès.

ZUSAMMENFASSUNG

Es wurde untersucht, inwieweit für die absorptiometrische Bestimmung kleiner Mengen langkettiger Alkylamine und quarternärer Ammoniumsalze in wässriger Lösung Bromkresolgrün besser geeignet ist als Ammoniumerdmannat. Der molekulare Absorptionskoeffizient des Reagenzes bei 615 nm ist etwa dreimal so gross wie der des Erdmannat-Ions bei 353 nm. Für visuelle Methoden eignet sich die blaue Farbe des Bromkresolgrün-Anions besser als die des gelben Erdmannat-Ions. Die Empfindlichkeit beider Methoden kann durch Anreicherung der gefärbten Reagenzien in einem kleinen Wasservolumen gesteigert werden. Beide Methoden werden durch Eisen nicht gestört, jedoch besitzt das beschriebene Verfahren den Nachteil, dass es einen Blindwert besitzt, welcher sowohl vom pH als auch von der Konzentration des überschüssigen Reagenzes abhängt.

REFERENCES

1 H. M. N. H. IRVING AND A. D. DAMODARAN, *Analyst*, 90 (1965) 180.
2 B. TRÉMILLON, *Bull. Soc. Chim. France*, (1964) 1057.
3 A. W. ASHBROOK, *Analyst*, 84 (1959) 177.
4 I. M. KOLTHOFF AND H. A. LAITINEN, *pH and Electro Titration*, John Wiley, New York, 1941.
5 M. HARIOKA, *Yakugaku Zasshi*, 77 (1957) 200.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

CATION ANALYSIS BY THIN-LAYER CHROMATOGRAPHY AND REFLECTANCE SPECTROSCOPY

PART I. THE RAPID IDENTIFICATION OF CATIONS RESOLVED ON THIN-LAYER PLATES

DAVID F. ZAYE, ROLAND W. FREI* AND MICHAEL M. FRODYMA
Department of Chemistry, University of Hawaii, Honolulu, Hawaii (U.S.A.)
(Received February 6th, 1967)

Recently, reliable methods have been devised for the analysis by means of spectral reflectance of the components of mixtures of dyes[1] and of amino acids[2-4] resolved on chromatoplates. By extending the technique to the ultraviolet portion of the spectrum, it has also become possible to analyze aspirin–salicylic acid mixtures[5] and mixtures of some vitamins of the B group[6] following their resolution on thin-plates. In many cases the resolved substances could be identified by means of their reflectance spectra and without recourse to R_F values; in all cases it was possible to carry out their determination without first eluting the species of interest from the adsorbent. In view of the obvious advantages afforded by such an approach, it was decided to investigate the feasibility of employing spectral reflectance in the analysis of some cations which had been resolved on thin-plates.

Although inorganic cations have been chromatographed on the usual inorganic layers, cellulose layers and on ion-exchange layers[7], the use of cellulose has the advantage that many of the techniques which have been developed for paper chromatography[8-12] can be employed with chromatoplates with little or no modification. Unfortunately, the problem of identifying cations separated on cellulose thin layers has not been satisfactorily resolved since the R_F values obtained with layers are not as reproducible as those obtained with paper. Although the use of chromogenic reagents, such as 8-hydroxyquinoline and hydrogen sulfide, is sometimes helpful, most reagents employed in this manner are not specific enough for the purpose at hand. To circumvent this difficulty, use is often made of several chromogenic reagents. This device, however, is time-consuming in that a separate thin-plate is usually required for each reagent, and some of the advantage accruing to the use of cellulose layers rather than paper is thus dissipated.

EXPERIMENTAL

All reagents employed were of analytical grade or comparable purity. The cations — Al^{3+}, Bi^{3+}, Cd^{2+}, Cr^{3+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Mn^{2+}, Hg^{2+}, Ni^{2+}, Ag^{+},

---

* Present address: Department of Chemistry, Dalhousie University, Halifax, Nova Scotia.

Sn^{2+} and Zn^{2+} — were employed in the form of aqueous stock solutions. A 1 mg/ml solution of each cation was prepared by dissolving appropriate amounts of the nitrate salt in distilled water. In the case of bismuth, mercury, and tin, the solutions were also made 3 *M* with respect to nitric acid. These stock solutions were applied as spots by means of a 10-μl Hamilton microsyringe.

A Desaga-Brinkmann Model S11 applicator was used to coat the 5 × 20 × 0.35 cm plates with a 17:3 water–MN-cellulose powder 300 (Macherey, Nagel and Co.; 516 Düren, Germany) mixture. The height of the applicator gate was set at 0.50 mm. After the plates had been dried at 75° for 30 min in a mechanical convection oven, they were stored in a desiccator.

After spotting, the plates were dried with compressed air and then developed in one dimension by the ascending technique with the use of 25% (v/v) hydrochloric acid (12 *N*) in 1-butanol similar to a procedure devised by REEVES AND CRUMPLER[10]. The developed plates were dried at 75° for 30 min and then sprayed with a mixture consisting of equal volumes of dithizone (0.05% w/v in carbon tetrachloride) and 8-hydroxyquinoline (1% w/v in carbon tetrachloride), which was applied by an atomizer used in conjunction with compressed air. After the plates had been air-dried for 10 min, the spots were excised from the plates, ground in an agate mortar for approximately 10 sec, and then packed into a windowless reflectance cell by means of a fitted tamp made of an aluminum planchet affixed to a cork stopper[6]. The reflectance spectra of these samples were recorded with a Beckman Model DK-2 Spectrophotometer fitted with a standard reflectance attachment. The reference standard in all cases consisted of approximately 90 mg of adsorbent from the plate under examination.

RESULTS AND DISCUSSION

When plates spotted with 10 μl (10 μg) of each of the stock solutions of cations were developed as described above, the order of separation of the ions was consistent with that observed with the use of paper[8–12]. Whenever comparative data were available[10], the R_F values (Table I) were found in most cases to be similar to those reported for paper chromatography. With the exception of aluminum and chromium, the cations reacted with the dithizone in the chromogenic spray to give highly colored spots which were easily visible to the naked eye. In the case of the aluminum and chromium, which reacted with the 8-hydroxyquinoline in the spray, the spots became visible when the plates were viewed under ultraviolet light (maximum at 350 nm). When the spots were excised from the plates and prepared for the measurement of reflectance as described above, the analytical samples were found to weigh from 80–90 mg. In all cases except aluminum and chromium, the reflectance spectra had well-defined absorption maxima whose locations are listed in Table I. Representative of the reflectance spectra which were obtained for the different cations adsorbed on cellulose after the plates had been sprayed with the dithizone–oxine reagent are the 3 spectra depicted in Fig. 1. Although it was possible by means of such spectra to distinguish among many of the ions, there were several ion-pairs whose spectra were so similar as to rule out the possibility of making an unequivocal identification on the basis of spectral data alone.

This situation was resolved by taking advantage of the fact that the structure

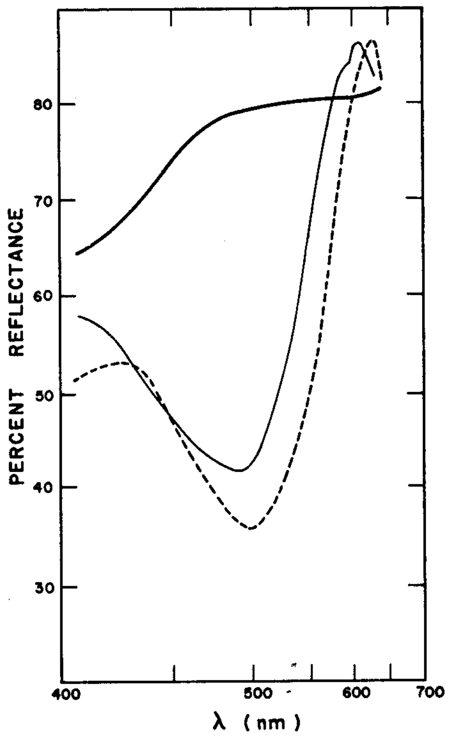
TABLE I

R_F VALUES AND SPECTRAL DATA FOR CATIONS ADSORBED ON MN-CELLULOSE

Cation	*R_F value*		*After spraying with dithizone–oxine reagent*		*After spraying with dithizone–oxine reagent followed by ammonia treatment*	
	MN-300	*Paper*[10]	*Absorption maximum (nm)*	*Sensitivity (μg)*	*Absorption maximum (nm)*	*Sensitivity (μg)*
Aluminum	0.04	0.04	—	—	380	2.3
Bismuth	0.56	0.60	505	2.2	515	2.2
Cadmium	0.90	0.83	498	1.6	519	1.6
Chromium	0.07	—	—	—	414	6.5
Cobalt	0.41	0.39	512	0.5	564	0.5
Copper	0.51	0.51	502	0.6	398	0.6
Iron	0.93	0.92	380	2.7	597	0.9
Lead	0.30	—	498	0.5	556	2.2
Manganese	0.16	—	510	2.2	507	2.6
Mercury	0.88	0.86	492	0.5	—	—
Nickel	0.09	0.04	503	1.2	514	0.6
Silver	0.00	0.00	492	2.0	574	0.6
Tin	0.80	—	510	0.9	—	—
Zinc	0.87	0.79	513	0.7	526	0.7

of the spectra was pH-dependent. After the first set of spectra had been obtained, the reference and sample cells were exposed to ammonia fumes for at least 2 min in a chamber containing 15 *M* ammonia and a second set of reflectance spectra were recorded. Except for the ones obtained for mercury and tin, these spectra, which were always recorded directly after the reflectance cells had been removed from the ammonia chamber, also exhibited well-defined absorption maxima. The 3 spectra shown in Fig. 2 are characteristic of the reflectance spectra which constituted the second set. Since these are spectra obtained for the same 3 cations whose spectra are also presented in Fig. 1, a comparison of the 2 Figures will give some indication of the spectral changes that were induced by the ammonia treatment. The wavelengths at which absorption maxima occurred in the spectra that were obtained for the various cations following this treatment are listed in Table I. By making use of the data provided by both sets of reflectance spectra, it should be possible to identify all 14 of the cations following their resolution on chromatoplates without too much difficulty. Even in the case of the bismuth–nickel cation-pair, which provides the least satisfactory set of spectral data for this purpose, the relative rates of migration of the 2 spots are so disparate that there is little likelihood of mistaking one cation for the other.

The sensitivities provided by this approach, which are also listed in Table I, were found to vary from 6.5 to 0.5 μg. A 2- to 4-fold increase in sensitivity was usually achieved if the analytical samples were prepared by centering the excised spot on top of a uniformly thick layer of 90 mg of adsorbent from the plate undergoing examination which had been packed in the reflectance cell beforehand with the use of the tamp. In a few cases where the color of the complex was especially intense, as with mercury, the increase was as much as 10-fold.



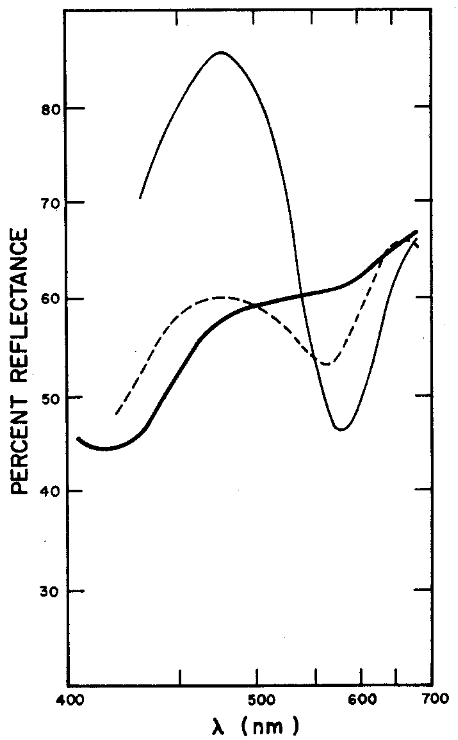


Fig. 1. Reflectance spectra obtained for 10 μg of chromium (———), lead (-----) and silver (———) cations adsorbed on cellulose after chromatoplates had been sprayed with dithizone–oxine reagent.

Fig. 2. Reflectance spectra obtained for 10 μg of chromium (———), lead (-----), and silver (———) cations adsorbed on cellulose after chromatoplates had been sprayed with dithizone–oxine reagent and subsequently exposed to ammonia fumes.

It was possible to identify the cations in some mixtures even more readily by recording the reflectance spectra without removing the spots from the chromatoplates. This involved positioning the plates at the sample exit port of the reflectance attachment so that each spot was centered, in turn, in the impinging beam of light. The reference beam was directed at the adsorbent on a second plate which had been treated in the same manner as the one under examination. In practice this is usually a plate on which another mixture of cations is being resolved. White paperboard was inserted behind both plates to serve as a reflecting background during the recording process. Although more rapid, this approach is effective only with thin-plates on which the spots are relatively well dispersed. Furthermore, spectra obtained in this manner, although still useful, tend to be less satisfactory for purposes of identification than those obtained with the use of reflectance cells. This is shown in Fig. 3, which contrasts spectra obtained by direct measurement with spectra obtained for the same cations by means of the procedure outlined in the experimental section. Finally, if it is also intended to make quantitative use of the spectra, the precision of reflectance measurements carried out on spots removed from the plates and packed in a cell is significantly greater than that provided by direct measurements[1].

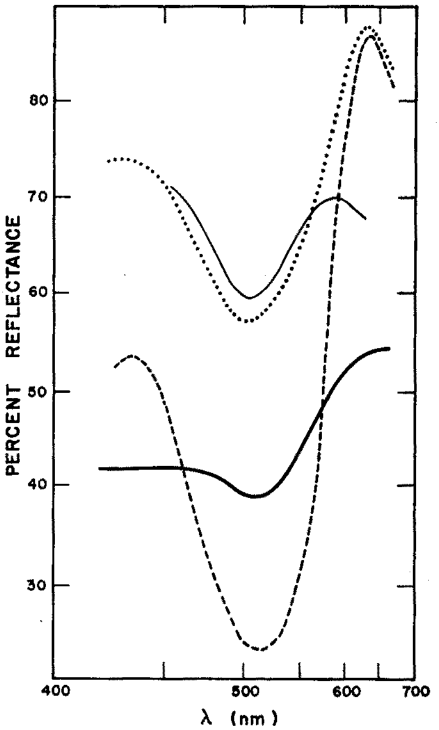


Fig. 3. Reflectance spectra of 5 μg of cobalt and zinc cations adsorbed on cellulose after thin-plates had been sprayed with dithizone–oxine reagent. Cobalt (———) and zinc (———) spectra obtained by direct measurement contrasted with cobalt (.....) and zinc (-----) spectra obtained with the use of reflectance cells.

SUMMARY

A rapid method has been devised whereby 14 cations — Al^{3+}, Bi^{3+}, Cd^{2+}, Cr^{3+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Mn^{2+}, Hg^{2+}, Ni^{2+}, Ag^{+}, Sn^{2+} and Zn^{2+} — can be separated on one-dimensional, cellulose thin-layer plates and then identified by means of their reflectance spectra. The procedure requires micro-amounts of sample and only one spray reagent.

RÉSUMÉ

Une méthode rapide est proposée pour la séparation de 14 cations (Al^{3+}, Bi^{3+}, Cd^{2+}, Cr^{3+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Mn^{2+}, Hg^{2+}, Ni^{2+}, Ag^{+}, Sn^{2+} et Zn^{2+}) par chromatographie sur cellulose en couches minces, et pour leur identification à l'aide de leurs spectres de réflectance. Ce procédé utilise de microquantités d'échantillon et seulement un réactif à vaporiser.

ZUSAMMENFASSUNG

Es wird eine Methode entwickelt, bei der 14 Kationen mit der Dünnschichtchromatographie getrennt und durch ihre Reflektionsspektren nachgewiesen werden. Das Verfahren benötigt Mikromengen und nur ein Sprühmittel.

REFERENCES

1 M. M. Frodyma, R. W. Frei and D. J. Williams, *J. Chromatog.*, 13 (1964) 61.
2 M. M. Frodyma and R. W. Frei, *J. Chromatog.*, 15 (1964) 501.
3 M. M. Frodyma and R. W. Frei, *J. Chromatog.*, 17 (1965) 131.
4 R. W. Frei, I. T. Fukui, V. T. Lieu and M. M. Frodyma, *Chimia (Aarau)*, 20 (1966) 23.
5 M. M. Frodyma, V. T. Lieu and R. W. Frei, *J. Chromatog.*, 18 (1965) 520.
6 M. M. Frodyma and V. T. Lieu, unpublished data.
7 K. Randerath, *Thin-Layer Chromatography*, 2nd Edn., Academic Press, New York, 1966, pp. 266–269.
8 M. Lederer, *Anal. Chim. Acta*, 3 (1949) 476.
9 I. I. M. Elbeih, J. F. W. McOmie and F. H. Pollard, *Discussions Faraday Soc.*, 7 (1949) 183.
10 W. A. Reeves and T. B. Crumpler, *Anal. Chem.*, 23 (1951) 1576.
11 F. H. Pollard, J. F. W. McOmie and I. I. M. Elbeih, *J. Chem. Soc.*, (1951) 466.
12 R. Guedes De Carvalho, *J. Chromatog.*, 4 (1960) 353.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

A BASIC STUDY OF COLUMN ADSORPTION CHROMATOGRAPHY

PART I. STANDARDIZATION OF ADSORBENT

TOSHIO NOMURA AND KAZUNORI TAKAOKA
Department of Chemistry, Faculty of Education, Fukui University, Makinoshima, Fukui (Japan)

(Received November 21st, 1966)

In order to use column adsorption chromatography in a quantitative way, the adsorption capacity of adsorbents must be standardized. Several methods for this purpose have been devised: the use of dye mixtures[1], a calorimetric method[2], the use of "Threshold Volume"[3], the azobenzene index[4] and a comparison of adsorption coefficients[5-7]. Most of these methods are insufficiently quantitative or practicable whereas other gas adsorption methods are time-consuming. The azobenzene method[4] is the most quantitative but is unsuitable as a standard method for various reasons: ordinary solutions of azobenzene contain the *cis* and *trans* forms, the former being adsorbed more strongly on alumina, and the *trans*→*cis* conversion is very sensitive to daylight; the molecular extinction coefficient of the *cis* form at the maximum adsorption band at 450 nm is greater than that of the *trans* form. Thus, the spectrophotometric determination of the amount of solute adsorbed is rendered difficult.

The theoretical and experimental development of the column adsorption chromatography has been discussed by DEVAULT[8], WEISS[9] and FUNAKUBO AND NAGAI[10]. In the present paper an improved method of standardizing adsorbents is described. First, an absolute method is introduced mathematically and then experimental confirmation that the value obtained on this basis pertains to the adsorbent itself, is given. A subsequent paper will deal with a comparison between this new chromatographic method and the old batch adsorption method.

THEORY

The nomenclature used is defined in Table I.

If, for a simple adsorption system consisting of one adsorbent, one adsorbate and one solvent, the relations $f=f(c)$, $f'>0$ and $f''<0$ are valid, then the leading boundary of the adsorbed zone will tend to be sharp (f' and f'' denote the first and second derivatives of the function $f(c)$). This has been discussed theoretically by DEVAULT[8] and applied to gas chromatography by KRIGE AND PRETORIUS[11]; it has also been verified experimentally by FUNAKUBO AND NAGAI[10]. The expression means that both the amount of solute adsorbed on an adsorbent and the concentration of the adjacent solution are constant throughout the zone during the chromatographic process *i.e.* $f=f(c)$ and $C=C$.

For the chromatographic system, the law of conservation of matter can be

TABLE I

NOMENCLATURE

A:	cross-sectional area of chromatographic tube (cm^2).
r_0:	radius of the tube (cm).
W:	amount of adsorbent (g).
d:	soaked density of adsorbent in solvent (g/ml).
L:	length of the packed column (cm).
C:	concentration of solution (mg/ml).
l_0:	displacement of the solution in the column, in units of length in empty tube (cm).
l:	displacement of the solvent in the column (cm).
x:	displacement of adsorbed zone on the column (cm).
$R = x/l = x/Sl_0$:	average progression rate of the zone; this is the same as R_g specified by FUNAKUBO AND MATSUMOTO[7], and depends on the concentration of the solution but is independent of the zone position when packing is uniform throughout the column.
$S = l/l_0$:	average degree of packing of the column, which equals $1/(1\text{-}W/dAL)$ (see eqn. (9)).
$\alpha = A/S$:	pore volume per unit length of the column (ml/cm).
$M = W/L$:	amount of adsorbent per unit length of the column (g/cm).
v:	average flow velocity of the solution entering the column (cm/min).
B:	amount of solvent, in units of length in empty tube (cm).
T:	temperature (°).
t:	time in min.
$\mathrm{f} = \mathrm{f}(c)$:	adsorption isotherm, amount of solute adsorbed per gram of adsorbent when the concentration of the adjacent solution is equal to C (mg adsorbate/g adsorbent).
$\mathrm{f}(1)$:	the quantity adsorbed per g of adsorbent when $C = 1$ (mg/g).

expressed as follows:

$$xM\mathrm{f}(c) = (l-x)\alpha C \tag{1}$$

where the left side represents the amount of solute adsorbed in the zone, and $(l-x)$ is the displacement of solvent passed down the sharp front of the zone. Substitution of the relation: $\mathrm{R} = x/l$ into eqn. (1) and rearrangement gives

$$R = \frac{1}{1 + \dfrac{M}{\alpha}\dfrac{\mathrm{f}(c)}{C}} \tag{2}$$

which can be rewritten as

$$\mathrm{f}(c) = \frac{1-R}{R}\frac{AL}{SW}C = \frac{1-R}{R}\frac{1}{d(S-1)}C \tag{3}$$

If R is replaced by R_1 when the progression rate of the zone is measured for the solution of $C = 1$, then

$$\mathrm{f}(1) = \frac{1-R_1}{R_1}\frac{AL}{SW} = \frac{1-R_1}{R_1}\frac{1}{d(S-1)} \tag{4}$$

Equation (4) is a theoretical equation based on a sharp zone front, on the assumption that instantaneous equilibrium exists at all points and that there is no diffusion. The equation shows the relation between the movement of the adsorbed zone R_1, the degree of packing of the column S and the adsorption capacity of adsorbent, f(1) for a unit concentration of solution. The adsorption capacity is a characteristic of the adsorbent for a definite system, both R_1 and S being mutually variable, independently of the f(1). Since R_1 and S can be measured, f(1) can be calculated from eqn. (4). If the f(1) value thus obtained is reproducible, it could be used as an absolute method of standardizing adsorbents. Experimental studies of this equation were therefore carried out.

EXPERIMENTAL

Apparatus

Ordinary 25-ml burettes were used as chromatographic tubes. The characteristics of the tubes are listed in Table II. Each tube was fixed into a water jacket by means of rubber stoppers and water was circulated from a thermostat to keep the column temperature constant within ±0.1°. Suction was provided through a Witt bottle. A calcium chloride guard tube was placed on the top of the tube.

TABLE II

CHARACTERISTICS OF THE CHROMATOGRAPHIC TUBES

Tube no.	$2r_0$[a]	A[a]	$\Delta A/A$(%)[b]
7	1.016	0.812	0.52
9	0.966	0.733	0.84
19	0.975	0.747	0.72
24	1.018	0.814	0.52
26	1.021	0.817	0.28
27	0.972	0.742	0.80
37	1.010	0.800	0.64
52	0.998	0.783	0.24
58	0.975	0.747	0.80
62	0.966	0.732	0.80
65	1.002	0.788	0.60
66	0.979	0.752	0.92
67	0.998	0.783	0.40
75	0.972	0.742	0.32

[a] Average value throughout the tube.
[b] Maximum deviation for each part at 5-ml mark intervals.

Chemicals

Adsorbents. Al-30: Active aluminium oxide for chromatography (Kanto Chemicals Co.).

Al-33: Al-30, heated at 300° for 8 h.

Al-43: Regenerated alumina; the method will be described later.

The particle size was 170–270 mesh. When 1 g of adsorbent was shaken with 20 ml of water[12], the pH was *ca.* 10.4 for Al-33 and 4.3 for Al-43. Adsorbents were stored in glass-stoppered bottles in a desiccator over calcium chloride.

Solvent. The solvent for the preparation of the column and test solutions was benzene (Wako Chemicals Co.), which had been dried over sodium metal and purified by fractional distillation the day before use, and stored in a tightly sealed bottle in a desiccator.

Adsorbate. As a standard adsorbate, *trans-p*-methoxyazobenzene (*t*MA) was chosen. It was moderately adsorbed on alumina and could be followed visually on the column; its adsorption system in benzene with alumina satisfied various necessary assumptions.

The *t*MA was separated chromatographically from *p*-methoxyazobenzene as follows. A solution of 4 g of the latter, recrystallized from methanol, in 80 ml of benzene was poured into a 15 × 4 cm column of Al-30 and then developed with about 200 ml of benzene. The eluate was evaporated under reduced pressure until free from benzene. Bright orange crystals (m.p. 55°) of *t*MA were obtained (yield 3.8 g). All the work was done in darkness.

Standard solution. A solution containing 1 g of *t*MA per liter of benzene was prepared and stored in a tightly sealed bottle in a desiccator. The stability of the solution was examined photometrically, since the absorbances of *cis* and *trans* azo compounds are generally different[13]. When aliquots of test solution were diluted ten-fold with benzene, the absorbance of the solution at 432 nm increased from 0.453 to 0.492 during the first 19 h, then decreased to 0.485 after 3 days and thereafter remained constant for at least 216 days after the preparation of the original test solution. The standard solution always contains a little *cis* form in a state of equilibrium; the *cis* form is adsorbed on alumina much more firmly than the *trans* form[14], and the *trans*→*cis* conversion is accelerated by irradiation[15]. Consequently, the component of the solution in the column may be in the *trans* form only for a moment. Once the *cis* form has been produced in the solution on exposure to light, it would probably be rapidly eliminated. In the chromatographic processes where such production and removal of the *cis* form occur continuously, the concentration of the *trans* form in the solution will gradually decrease. This causes the value of R to decrease*, so that f(1) increases**. Accordingly, the change in f(1) on irradiation of the column during the measurement of the progression rate of zone, was studied; experiments were carried out with uncovered columns, columns covered with black paper and water-jacketed columns. The results are shown in Table III, from which it can be seen that the f(1) obtained on the jacketed column is independent of the exposure to daylight, whereas reactions in an unprotected column are greatly affected by light.

PROCEDURES

Measurement of R_1

The zone movement is greatly affected by the method of packing the column, *e.g.* the dry, the wet and the slurry methods. The methods used are outlined below.

---

* Differentiation of eqn. (3) by C yields the expression

$$\frac{\mathrm{d}R}{\mathrm{d}C} = \frac{R(1-R)}{\mathrm{f}(c)}\left\{\frac{\mathrm{f}(c)}{C} - \mathrm{f}'(C)\right\} \qquad (5)$$

in which $\{\mathrm{f}(c)/C - \mathrm{f}'(c)\} > 0$ because of the isotherm concave C-axis, hence the R decreases as C decreases.

** Differentiation of eqn. (4) by R_1 results in

$$\frac{\mathrm{d}\mathrm{f}(1)}{\mathrm{d}R_1} = -\frac{\mathrm{f}(1)}{R_1(1-R_1)} \qquad (6)$$

From eqn. (6), it is evident that a decrease in R_1 causes the f(1) to increase.

TABLE III

VARIATION OF f(1) ON EXPOSURE OF THE COLUMN TO LIGHT

(Al-33-*t*MA system; dry method; $B/L = 2$)

Exp.[a] *no.*	*Irradiation*[b] *time (min)*	T	W	S	R_1	$f(1)$	$\Delta f(1)$[c] (%)
1a	170	20 ± 1	10	1.400	0.409	1.06	
1b	170	20 ± 1	10	1.408	0.383	1.16	+ 9.4
2a	70	20 ± 1	10	1.400	0.394	1.13	
2b	70	20 ± 1	10	1.391	0.390	1.18	+4.4
3a	50	25 ± 0.1	8	1.380	0.464	0.896	
3b	50	25 ± 0.1	8	1.375	0.462	0.912	+1.8
4a	40	25 ± 0.1	8	1.397	0.460	0.874	
4b	40	25 ± 0.1	8	1.383	0.464	0.888	+1.6

[a] Exp. (1, 2) irradiation of the column with mercury lamp; (3, 4) exposure of the water-jacketed column to daylight on a fine summer day. In experiments (a), columns were covered by black paper; (b) indicates the same conditions without black covers.

[b] This time also equals the displacement time of zone from the upper to the lower ends of the column.

[c] Percentage deviation of (b) from (a).

Dry method. The chromatographic tube was packed with a piece of glass tubing, a 2-cm layer of cotton wool and a disk of filter paper placed successively in the bottom of the tube. A roughly weighed quantity of adsorbent (8–10 g) was added gradually, the tube being kept at constant temperature. The column was then tapped with a stick for 5–10 min, rotating it so that the adsorbent settled uniformly. A disk of filter paper was then pressed on to the top of the column. The adsorbent was washed with solvent, in a volume 1.5–2 times the volume of the adsorbent.

Immediately after the solvent had sunk into the adsorbent, the test solution was added, an adsorption band being formed. After the adsorbed zone had increased to about 10 scale divisions from the top of the adsorbent column, both the sharp front of the zone and the meniscus of the solution were recorded as x_1 and l_{01}, respectively. The zone was allowed to move down the column, and the upper level of the solution was maintained above the top of the adsorbent column by addition of definite known amounts of the solution, l_0, when necessary. When the zone front had travelled to about 10 divisions from the bottom of the column, the readings of the two positions were noted as before, x_2 and l_{02}. Then, the progression rate, R, was calculated from:

$$R = (x_2 - x_1)/S(l_{02} - l_{01} + l_0) \tag{7}$$

where S is the degree of packing of the column.

Wet method. The tube was prepared initially as in the dry method and filled with solvent, to which a known weight of adsorbent was slowly added. The air-free suspension of the adsorbent was allowed to settle with gentle tapping of the tube as the stop-cock was opened. The top of the adsorbent column was covered with a disk of filter paper. Addition of test solutions was done as described for the dry method.

Slurry method. A mixture of the adsorbent and about 10 ml of solvent was stirred to remove air and the slurry was poured into the tube, prepared as before. The further procedures were the same as for the wet method.

Determination of d

The tube was kept at 25±0.1°, about 15 ml of solvent was added and 8 g of adsorbent was added. From the increase in volume, ΔV, the soaked density was calculated from $d=8/\Delta V$. The soaked density of the alumina Al-33 was found to be 3.4±0.1; the values found decreased from 3.49 for particles above 170 mesh to 3.33 for particles below mesh 400.

Measurement of S

If the adsorbent column length is L cm when W g of adsorbent is packed in the tube, then the volume of the column is AL and the volume of adsorbent in the column is W/d; thus, the interstitial space in the column, α, is $AL-W/d$. Since the average degree of packing in the column is defined as $S=l/l_0=A/\alpha$, then

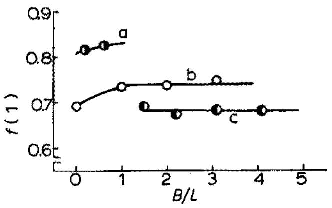
$$S = \frac{1}{1-W/dAL} \tag{8}$$

RESULTS AND DISCUSSION

The factors affecting f(1) were studied experimentally.

Influence of the pretreatment of column

The column is generally prewashed with solvent before a test solution is added. The influence of the amount of the solvent on f(l) is shown in Fig. 1. The amount of solvent is represented as the ratio of the length (or volume) of solvent in an empty tube to the length (or volume) of the adsorbent column: B/L (or AB/AL), the amount of adsorbent being fixed. For the wet and slurry methods, AB includes the amounts used in preparing and prewashing the column. Since the decrease of f(1) with decreasing B/L might be due to air in the column, the amount of solvent for pretreatment was kept above 1.5 times the volume of the column.



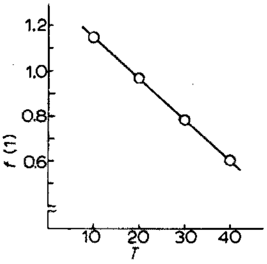


Fig. 1. Influence of the pretreating amount of benzene on f(1). Al-30–*t*MA system. T = 20 ± 1. W = 10. Packing method: (a, b) dry; (c) wet.

Fig. 2. Influence of temperature on f(1). Al-30–*t*MA system. W = 6. B/L = 2. Dry packing method.

Influence of temperature

The temperature variation of R has been found[16] negligible for the range 20–35°. However, in this quantitative f(1) method, R depended markedly on temperature.

The variation of R is related to that of f(1), as in eqn. (6), hence the temperature dependence of f(1) is shown in Fig. 2.

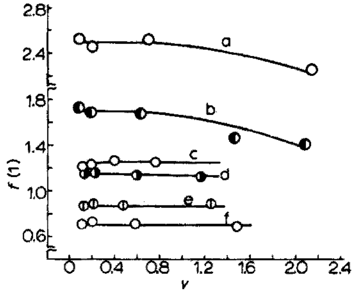
Influence of the flow rate

For the proposed method, the solute adsorbed must be in equilibrium with the adjacent solution and diffusion must be negligible. Thus, the flow rate of the solution entering the column is important. The average flow rate, v, is given by

$$v = l_0/t \tag{9}$$

where t is time in minutes for the front of zone to progress from the top to the bottom of the column with l_0 cm of solution.

Figure 3 shows the effect of v on f(1) at different temperatures. The value of v was regulated by means of the stop-cock of the tube and by suction. It can be seen that for the slurry method, f(1) is independent of v in the region 0.1–1.5, while for the dry method the decrease in f(1) becomes pronounced for $v > 0.8$. At both very slow and fast flow rates, f(1) decreases. The former is ascribed to diffusion and the latter is probably due to lack of equilibrium[17]. With slurry method, the zone front was sometimes obscured, as if the zone center moved faster than the outer parts. This may be due to residual air pockets in the column, because the phenomenon appeared more often at higher temperatures and especially in the wet method. With the dry method, the faster the flow rate, the larger the irregularity of the moving front across the column. "Percent distortion"*, which is a measure of unevenness defined by DRAKE[17], was greatly affected by the flow rate, *e.g.*, the percent distortions were 0, 0.6 and 4.9 when the values of v were 0.082, 0.697 and 2.15, respectively, at the bottom of the column in the dry method at 20°.



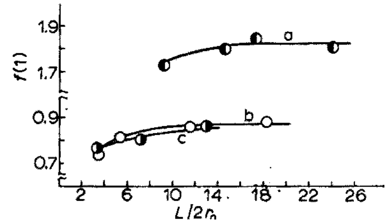


Fig. 3. Influence of the flow rate on f(1). Alumina–*t*MA system. $B/L = 2$. Packing method: (a, b) dry; (c, d, e, f) slurry. T: (c) 10 ± 0.1; (a, b, d) 20 ± 0.1; (e) 30 ± 0.1; (f) 40 ± 0.1. W: (a, b) 8; (c, d, e, f) 6. Adsorbent: (a) Al-33; (b, c, d, e, f) Al-30.

Fig. 4. Effect of the amount of adsorbent on f(1). Al-30–*t*MA system. $t = 20 \pm 0.1$. $v = 0.2$–0.5. $B/L = 1.5$–2.5. Packing method: (a, c) slurry; (b) dry. W: (a) 6, 9, 12, 15; (b) 2, 4, 8, 12; (c) 2, 4, 8 in order from the left to the right points, respectively.

In general, the flow rate of solution should lie between 0.2 and 0.6; 0.2 is the spontaneous flow rate for the dry method and 0.6 that for the slurry method.

---

* The length of the front along the column, times 100, divided by the average distance that the front has moved, $(\pm\ \Delta x/x)\cdot 100$.

Influence of the amount of adsorbent

The size of tube chosen depends of course on the amount of adsorbent to be used. The optimal length of the column for the measurement of f(l) was investigated. The results are shown in Fig. 4; the amount of adsorbent is represented by the ratio of the column length to the tube diameter, $L/2r_0$. Clearly, f(l) is greatly affected by $L/2r_0$. This effect might be related to the amount of adsorbent alone; the smaller the value of W, the larger the deactivation of adsorbent by adsorption of moisture during weighing, packing and pretreatment. Hence, the amount of adsorbent taken should correspond to a $L/2r_0$ value considerably larger than 13, which corresponds to more than 8 g in the tubes used.

Influence of the degree of packing

The degree of packing of the column varies with each particular preparation of the column. The value of f(1), however, must be independent of the degree of packing and of the particular packing method for the same adsorbent. In order to study the relation between f(1) and S, adsorbent particles with three different mesh ranges were used; the results are shown in Fig. 5. The degree of packing was adjusted by tapping the tube as described in the procedures; the minimum and maximum values of S (see Fig. 5) were obtained by simply pouring in the adsorbent and by packing it firmly by tapping, respectively. The results show that for the slurry method, f(1) is independent of S, while for the dry method f(1) depends strongly on S but approaches a constant value as S increases. For the dry method, f(1) decreases as S decreases, probably because air pockets remained in the column after the prewashing process; the existence of air pockets was confirmed by irregular fronts.

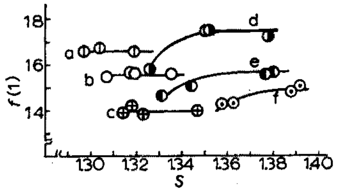


Fig. 5. Influence of the degree of packing on f(1). Al-33-tMA system. $T = 25 \pm 1$. $v = 0.14$–0.4. $W = 8$. $B/L = 2$–2.5. Packing method: (a, b, c) slurry; (d, e, f) dry. The particle size of adsorbent (mesh): (a, d) 250–200; (b, e) 200–170; (c, f) 170–150.

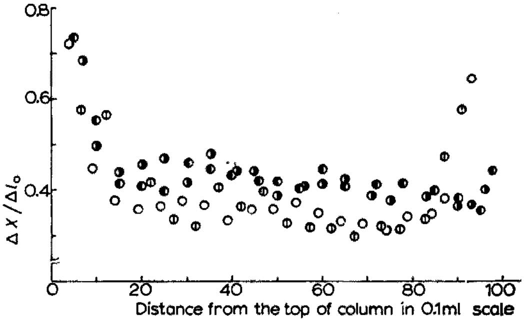


Fig. 6. Partial rate of the zone movement at different parts of the column. Al-43-tMA system. $T = 20 \pm 0.1$. $W = 8$. $B/L = 1.5$. $v = 0.14$. Packing method: (⦶, ○) dry; (◐, ◑) slurry. In order of marks ⦶, ○, ◐, ◑, AL: 9.36, 9.60, 10.70, 10.24; S: 1.335, 1.325, 1.282, 1.298; R_1: 0.263, 0.266, 0.324, 0.319, respectively.

It is impossible to obtain a completely uniform degree of packing throughout the column. Figure 6 shows a plot of a partial rate of zone movement, $\Delta x/\Delta l_0$, against the column position. The $\Delta x/\Delta l_0$ value is not suitable as a measure of the degree of packing of the part of the column involved, but some conclusions can be drawn; clearly, the lower end of the column is loosely packed, whereas the deviations at the top of the column are probably due to decreased activity of the adsorbent, by adsorption of traces of water from the atmosphere or from the solutions used. Accordingly, for the measurement of R, the upper and lower ends of the column (about 10 scale divisions for each) were omitted.

Optimum condition for the f(1) method

The above studies allowed the following optimum conditions to be chosen for the measurement of f(1). A chromatographic tube is covered with a water jacket to keep the temperature constant within ±0.1° and to protect the standard solution from daylight. The benzene for pretreatment is purified and dried the day before use; moisture is particularly important for the slurry method, where twice the column volume is used. The flow rate of solution entering the column must be in the range 0.2–0.6 cm/min. The amount of adsorbent used is 8–10 g. For the dry method, the adsorbent should be packed until there is no further drop at the top of the column on tapping.

Results for the f(1) value under such optimum conditions with alumina as adsorbent and *t*MA in benzene as test solution, are given in Table IV, from which it can be seen that the percentage deviation from the mean is less than ±2% irrespective of the packing method used.

TABLE IV

CONSTANCY OF f(1) UNDER THE OPTIMUM CONDITION

(Al-33-*t*MA system. $T = 25 \pm 0.1$. $W = 8$. $B/L = 1.5–2.5$. $d = 3.4$)

Method	*Tube no.*	AL	v	S	x/l_0	R_1	$f(1)$	$\Delta f(1)$[a](%)
Dry	37	8.34	0.19	1.393	0.443	0.318	1.605	− 1.05
Dry	67	8.38	0.24	1.390	0.444	0.319	1.611	− 0.63
Dry	19	8.43	0.25	1.388	0.437	0.315	1.648	+ 1.60
Slurry	24	9.63	0.22	1.324	0.475	0.359	1.622	0
Slurry	75	9.37	0.23	1.335	0.465	0.348	1.646	+ 1.48
Slurry	9	9.42	0.25	1.334	0.470	0.352	1.621	− 0.06
Slurry	58	9.45	0.23	1.332	0.474	0.356	1.602	− 1.23

[a] Percentage deviation against mean value, 1.622.

Errors of measurement

The errors in the f(1) value caused by parallax errors in the measurement of the terms W, AL, d and x/l_0, are best considered for an actual example. If the experiment with tube no. 24 in Table IV is chosen, the observations were as follows: $W=8$; $B/L=2.5$; $d=3.4$; $AL=24.77–15.14=9.63$; the displacement of the front was from 16.1 to 23.4 on the milliliter scale while the displacement of the solution meniscus was from 0.41 to 10.75 on the same scale. During the passage, a further 5 ml of solution was supplied and the total time was 86 min. Then, the calculations are as follows:

$$\frac{x}{l_0}=\frac{Ax}{Al_0}=\frac{23.4-16.1}{10.75-0.41+5}=0.475;\ S=1/(1-W/dAL)=1.324;\ R_1=x/Sl_0=0.359;$$

$$f(1)=(1-R_1)/R_1d(S-1)=1.622;\ v=\frac{Al_{02}-Al_{01}}{A(t_2-t_1)}=\frac{10.75-0.41+5}{0.814\times 86}=0.22.$$

To see how these errors affect f(1), eqn. (4) is first differentiated by these terms:

$$\frac{\mathrm{df}(1)}{\mathrm{d}W} = -\frac{\mathrm{f}(1)}{W}\,\frac{1-SR_1}{1-R_1} \tag{10}$$

$$\frac{\mathrm{df}(1)}{\mathrm{d}AL} = \frac{\mathrm{f}(1)}{AL}\,\frac{1-SR_1}{1-R_1} \tag{11}$$

$$\frac{\mathrm{df}(1)}{\mathrm{d}\,d} = -\frac{1}{d^2} \tag{12}$$

$$\frac{\mathrm{df}(1)}{\mathrm{d}\,x} = -\frac{\mathrm{f}(1)}{x}\,\frac{1}{1-R_1} \tag{13}$$

When small variation is replaced by δ and the values given in the example are substituted into eqns. (10)–(13), the deviation in f(1) arising from the errors can be seen:

$$\frac{\delta\mathrm{f}(1)}{\mathrm{f}(1)} = -0.818\,\frac{\delta W}{W} \tag{14}$$

$$\frac{\delta\mathrm{f}(1)}{\mathrm{f}(1)} = -0.818\,\frac{\delta AL}{AL} \tag{15}$$

$$\frac{\delta\mathrm{f}(1)}{\mathrm{f}(1)} = -0.182\,\frac{\delta d}{d} \tag{16}$$

$$\frac{\delta\mathrm{f}(1)}{\mathrm{f}(1)} = -1.561\,\frac{\delta x}{x} \tag{17}$$

From eqns. (14)–(17), it can be seen that x causes a much greater error than the others. The divisions on the tube graduations are 0.1 ml apart, and there is a parallax error of *ca.* 0.05 ml in reading the position of the sharp front of zone, so that the maximum error in reading two positions, is 0.1 ml or 1 scale division. The maximum percentage error in measuring R in this example is thus $\pm 100(234-161) = \pm 1.4\%$, so that the error in the final result is increased to $-1.561 \cdot (\pm)\ 1.4 = \pm 2.1\%$.

The error in the reading of x arises from the frontal irregularity and blurring; irregularity can be decreased by lowering the flow velocity, and frontal blurring can be reduced by making the column free from air. The wet method seemed to be most prone to diffusion of the zone front because of air pockets.

The authors wish to express their thanks to Professor TAITIRO FUJINAGA of Kyoto University for his invaluable encouragement.

SUMMARY

The method of measuring f(1) values is proposed as a measure of the adsorption capacity of adsorbents. The f(1) value, a characteristic figure for a particular system, can be obtained chromatographically by measuring the progression rate of zone and the degree of packing of the column. For a system involving a unit concentration of *trans-p*-methoxyazobenzene in benzene as standard solution and alumina as adsorbent, optimum conditions for the measurement of f(1) were established. The effects of daylight, pretreatment of column, temperature, flow rate of solution, amount of adsorbent and degree and mode of packing were studied. Under optimum conditions, the value of f(1) was reproducible within ±2%.

RÉSUMÉ

On a effectué une étude de base sur la chromatographie par adsorption sur colonne. La méthode mesurant les valeurs f(1) est proposée comme mesure de la capacité d'adsorption des adsorbants. On a établi les conditions optima pour la mesure de f(1) avec unité de concentration de *trans-p*-méthoxyazobenzène dans le benzène, comme solution étalon et avec alumine comme adsorbant. Divers facteurs ont été examinés: influence de la lumière, prétraitement de la colonne, température, débit de la solution, quantité d'adsorbant. Reproductibilité de la valeur de f(1): ±2%.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen zur Messung von f(1)-Werten als Mass für die Adsorptionskapazität von Adsorbentien. Die f(1)-Werte eines bestimmten Systems können chromatographisch erhalten werden, indem die Vorwärtsbewegung der Zone und der Packungsgrad der Säule gemessen werden. Für ein System mit *trans-p*-Methoxyazobenzol in Benzol als Standardlösung und Aluminiumoxid als Adsorbens wurden optimale Bedingungen für die Messung von f(1) festgesetzt. Die Einflüsse des Tageslichtes, die Vorbehandlung der Säule, die Temperatur, die Flisesgeschwindigkeit der Lösung, die Menge des Adsorbens' und die Packungsart wurden untersucht. Unter optimalen Bedingungen war der f(1)-Wert innerhalb von ±2% reproduzierbar.

REFERENCES

1 H. BROCKMANN AND H. SCHODDER, *Ber.*, 74 (1941) 73.
2 P. B. MÜLLER, *Helv. Chim. Acta*, 27 (1944) 404, 443.
3 H. WEIL-MALHERBE, *J. Chem. Soc.*, (1943) 303.
4 G. HESSE, *Angew. Chem.*, 64 (1952) 103.
5 A. L. LEROSEN, *J. Am. Chem. Soc.*, 67 (1945) 1683.
6 A. L. LEROSEN, P. H. MONAGHAN, C. A. RIVET AND E. D. SMITH, *Anal. Chem.*, 23 (1951) 730.
7 E. FUNAKUBO AND Y. MATSUMOTO, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, 72 (1951) 403, 484.
8 D. DEVAULT, *J. Am. Chem. Soc.*, 65 (1943) 532.
9 J. WEISS, *J. Chem. Soc.*, (1943) 297.
10 E. FUNAKUBO AND T. NAGAI, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 64 (1961) 167, 317.
11 G. J. KRIGE AND V. PRETORIUS, *Anal. Chem.*, 37 (1965) 1195, 1202.
12 T. CUMMINGS, H. C. GRAVEN, C. H. GILES, S. M. K. RAHMAN, J. G. SNEDDON AND C. E. SEWART, *J. Chem. Soc.*, (1959) 537.
13 A. H. COOK, D. G. JONES AND J. B. POLYA, *J. Chem. Soc.*, (1939) 1315.
14 H. FREUNDLICH AND W. HELLER, *J. Am. Chem. Soc.*, 61 (1939) 2228.
15 G. S. HARTELY, *Nature*, 140 (1937) 281.
16 A. L. LEROSEN AND C. A. RIVET, *Anal. Chem.*, 20 (1948) 1093.
17 B. DRAKE, *Anal. Chim. Acta*, 3 (1949) 452.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

A BASIC STUDY OF COLUMN ADSORPTION CHROMATOGRAPHY

PART II. RELATION BETWEEN CHROMATOGRAPHIC AND BATCH-WISE ADSORPTION

TOSHIO NOMURA, KAZUNORI TAKAOKA AND GEN-EMON KURATA
Department of Chemistry, Faculty of Education, Fukui University, Makinoshima, Fukui (Japan)

(Received November 21st, 1966)

In the previous paper[1], a method involving measurement of f(1) values for standardizing adsorbents was proposed. The f(1) value is the amount of solute adsorbed per gram of adsorbent, with a unit concentration of standard adsorbate in benzene. In the present paper, the relation between the f(1) value thus obtained and the value obtained from the old batch-wise method is discussed. Furthermore, it is confirmed that the adsorption isotherm of the system of alumina–*trans-p*-methoxyazobenzene is concave toward the concentration axis.

A subsequent paper will deal with the regeneration of old alumina portions, based on the f(1) method.

EXPERIMENTAL

Chemicals

The adsorbents used were the same aluminas as those described previously[1], and benzene for the solvent was purified similarly.

Adsorbate and test solution. 3-Nitro-*o*-toluidine (3-NOT) was chosen as the standard adsorbate, because benzene solutions of *trans-p*-methoxyazobenzene (*t*MA) always contain in equilibrium a little *cis* form, which is adsorbed on alumina more strongly than the *trans* form; moreover, the *trans*→*cis* conversion is very sensitive to daylight[1], so that the method could not be used quantitatively by the batch-wise method.

The 3-NOT was synthesized from *o*-toluidine[2] (orange prisms after chromatographic purification; m.p. 95.5°). Benzene solutions of the compound obeyed Beer's law at 405 nm over the range 0.0–0.04 mg 3-NOT/ml.

Test solutions of 3-NOT in benzene, stored in tightly sealed bottles in a desiccator over calcium chloride, were stable for a long time.

Batch method

Into a dry, glass-stoppered, 50-ml centrifuge tube an amount of adsorbent was weighed (W g), and 25 ml of the test solution (concentration: C_0 mg/ml) was added. The tube was placed in a thermostat bath and the contents were stirred for 5 min with a glass stirrer placed through a water-cooled condenser.

The suspension was centrifuged and the supernatant liquid was transferred to a volumetric flask and diluted with benzene so that the 3-NOT concentration lay in the range 0.005–0.02 mg/ml. The final equilibrium concentration (C mg/ml) was determined spectrophotometrically at 405 nm. The quantity adsorbed, when the concentration of the adjacent solution is C, is given by the formula

$$f(c)=25\cdot(C_0-C)/W \qquad (1)$$

Photometric measurements were carried out with an Ito spectrophotometer DU-3.

Chromatographic method

The fundamental equation for the adsorption isotherm in the chromatographic method[1] is:

$$f(c) = \frac{1-R}{R}\,\frac{1}{d(S-1)}\,C \qquad (2)$$

where R, S and d denote the progression rate of the zone, the degree of packing of the column and the soaked density of the adsorbent, respectively. Hence, $f(c)$ represents the amount of solute adsorbed per gram of adsorbent when the concentration of test solution is C. The value of d was 3.4 throughout this study[1]; R and S were measured as described previously, and $f(c)$ was calculated.

RESULTS AND DISCUSSION

Effect of the stirring time for the batch method

HESSE[3] showed that adsorption equilibrium is attained within 1 min for systems consisting of alumina, azobenzene and cyclohexane. Similar results were obtained for the Al-30–3-NOT–benzene solution (Table I) and a stirring time of 5 min was chosen.

TABLE I

EFFECT OF STIRRING TIME ON $f(c)$

(Batch method. Al-30–3-NOT system. C_0 = 0.613 mg/ml. T = 20 ± 0.1°)

Stirring time (min)	*W (g)*	*C (mg/ml)*	$25\cdot(C_0-C)$	$f(c)$
1	1.991	0.305	7.70	3.86
3	2.003	0.315	7.45	3.73
5	1.984	0.310	7.58	3.82
10	1.983	0.310	7.58	3.82

Isotherm by the batch method

Adsorption isotherms of the Al-30–3-NOT system are shown in curves a_1, a_2, a_3, a_5 and a_{10} of Fig. 1; the subscripts correspond to the amount of adsorbent used with 25 ml of the test solution.

It can be seen that the isotherm depends markedly on the amount of adsorbent used. Addition of more than 10 g of adsorbent to 25 ml of solution was impossible, because the adsorption system could not be made uniform.

Isotherm by the chromatographic method

As the adsorbability of 3-NOT on alumina was about 10 times greater than that of *trans-p*-methoxyazobenzene, 5 g of adsorbent was used to save time. The measurement of the progression rate of zone was carried out at room temperature without a water jacket. The result is shown in curve b of Fig. 1.

Comparison between the chromatographic and the batch adsorptions

The adsorption isotherms obtained by the two methods are both of the Freundlich type. The amount adsorbed at a fixed concentration of the solution differs greatly for the two methods. In Fig. 2 the amounts of solute adsorbed for $C=1$ are plotted against the ratio of the weight of adsorbent to the volume of solution (W/V). The values of f(1) in the batch method are taken from the intersections of the isotherms with a straight line of $C=1$, in Fig. 1. The value of W/V in the chromatographic method was calculated on the assumption that W/V is equal to M/α, where M and α denote the amount of adsorbent and pore volume per unit length of the column respectively[1]:

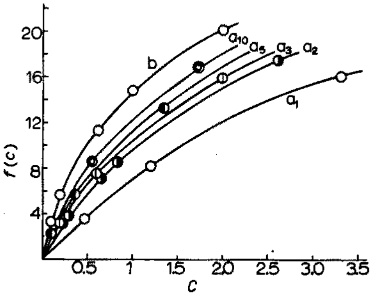


Fig. 1. Adsorption isotherms of Al-30–3-NOT system. (a_1, a_2, a_3, a_5, a_{10}): batch method; $V = 25$ ml; W, respectively 1, 2, 3, 5, 10 g; $T = 20 \pm 0.1°$. (b): chromatographic method with the dry-packing method; $W = 5$ g; $B/L = 1.5$; $d = 3.4$; $v = 0.28$–0.4 cm/min; $T = 20 \pm 1°$.

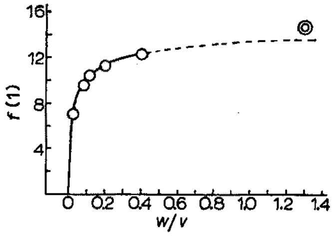


Fig. 2. Effect of the amount of adsorbent on f(1). (○): batch method. (◎): chromatographic method.

$$W/V = M/\alpha = d(S-1) = 3.4\cdot(1.373-1) \doteqdot 1.3$$

The f(1) value for the batch method increases as W/V increases but never reaches the chromatographic value.

CUMMING *et al.*[4] have shown that isotherms vary considerably with the liquid: solid ratio used, owing to etching by the solution; the oxide film is very slightly soluble in water with alumina–aqueous dye solution systems. In the present alumina–3-NOT–benzene system, the fact that the f(1) values decrease with decreasing W/V values may be ascribed to contamination of the adsorbent by moisture in the benzene solution. In the chromatographic adsorption method, the f(1) value with the slurry-packing method is affected by the contaminated solvent, while with the dry-packing method, the f(1) value is substantially independent of contamination because any moisture from solvent or solution is completely adsorbed on the upper end of the column (Table II). In the batch adsorption method, there is no means of avoiding such contamination, so that the smaller the W/V value, the lower the f(1) value. Thus, the

TABLE II

EFFECT OF STANDING TIME OF BENZENE ON f(1)

(Chromatographic method. Al-33-*t*MA system. $T = 25 \pm 0.1°$. $W = 8$ g. $v = 0.14$–0.4 cm/min. $B/L = 2$–2.5)

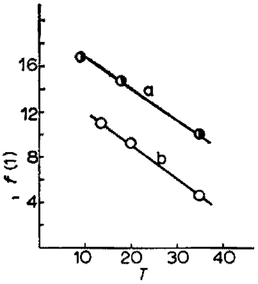
Packing method	*Adsorbent*	*Standing time*[a] *(day)*	*S*	R_1	*f(1)*	*Δf(1)*[b]
Slurry	Al-33	0	1.345	0.348	1.603	
		11	1.343	0.362	1.513	− 5.6
Dry	Al-30	0	1.407	0.486	0.768	
		58	1.412	0.478	0.779	+1.4

[a] The purified benzene was allowed to stand in a sealed bottle in a desiccator over calcium chloride.
[b] Percentage deviation from the result for zero standing time.

chromatographic method gives much truer values pertaining to the adsorbent itself than the batch method.

Influence of temperature

The influence of temperature on the f(1) value is shown in Fig. 3. In the Figure, curve (a) for the chromatographic method was obtained with a $C = 1$ solution, and curve (b) for the batch method was obtained from the intersections of the isotherms with a straight line of $C = 1$. The percentage variation of f(1) per degree of temperature was about 2% in both cases, the value being similar to that obtained for the Al-30-*t*MA system[1].



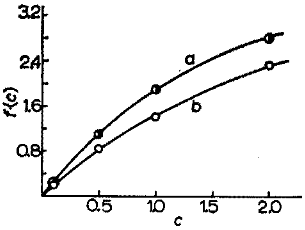


Fig. 3. Influence of temperature on f(1). Al-30-3-NOT system. (a): chromatographic method with the dry-packing method; $W = 5$ g; $B/L = 1.5$; $v = 0.3$ cm/min. (b): batch method; $W = 2$ g; $V = 25$ ml.

Fig. 4. Isotherm of alumina-*t*MA system. Chromatographic method with the wet-packing method. $W = 9$ g; $d = 3.4$; $T = 25 \pm 0.1°$; $v = 0.24$–0.47 cm/min. Adsorbent: (a) Al-43; (b) Al-30.

*Isotherm of alumina-*tMA *system*

From the above experiments, it was clear that the chromatographic adsorption method gives a much more probable value for the activity of the adsorbent than the batch method. The isotherm of the alumina-*t*MA system which could not be obtained by the batch method could be determined chromatographically. The result is shown in Fig. 4; the experiments were done with a jacketed chromatographic tube[1]. From Fig. 4 it is clear that the system is concave toward the concentration axis, and so the choice of *t*MA as a standard adsorbate for the f(1) method is quite justified.

The authors wish to express their thanks to Professor TAITIRO FUJINAGA of Kyoto University for his invaluable encouragement.

SUMMARY

The adsorption isotherm for the alumina–3-nitro-*o*-toluidine–benzene system was measured by the chromatographic and the batch methods. The chromatographic method gave a much higher value for the amount of solute adsorbed than the batch method. The isotherm of the alumina–*trans*-*p*-methoxyazobenzene–benzene system was also measured chromatographically; it was confirmed that this isotherm is concave to the *C*-axis. The proposed f(1) method for standardizing adsorbents was thus confirmed.

RÉSUMÉ

On a mesuré l'isotherme d'adsorption du système alumine–3-nitro-*o*-toluidine–benzène par chromatographie et par "batch" adsorption. La méthode chromatographique a donné une valeur beaucoup plus élevée pour la quantité de solute adsorbé. On a également mesuré chromatographiquement l'isotherme du système alumine–*trans*-*p*-méthoxyazobenzène–benzène; ce qui a confirmé que cet isotherme est concave par rapport à l'axe *C*. La méthode f(1) proposée pour les adsorbants d'étalonnage est ainsi confirmée.

ZUSAMMENFASSUNG

Die Adsorptionsisotherme des Aluminiumoxid–3-Nitro-*o*-toluidin–Benzol-Systems wurde mittels chromatographischer und schubweiser Methoden gemessen. Die chromatographische Methode ergab einen sehr viel höheren Wert für den Anteil des adsorbierten Gelösten als die schubweise Methode. Die Isotherme des Aluminiumoxid–*trans*-*p*-methoxyazobenzol–Benzol-Systems wurde ebenfalls chromatographisch gemessen. Diese Isotherme verläuft konkav zur *C*-Achse. Die vorgeschlagene f(1)-Methode zur Standardisierung von Adsorbentien wurde damit bestätigt.

REFERENCES

1 T. NOMURA AND K. TAKAOKA, *Anal. Chim. Acta*, 39 (1967) 19.
2 D. F. DETAR AND J. C. HOWARD, *J. Am. Chem. Soc.*, 77 (1955) 4393.
3 G. HESSE, *Z. Elektrochem.*, 55 (1951) 60.
4 T. CUMMING, H. C. GARVEN, C. H. GILES, S. M. K. RAHMAN, J. G. SNEDDON AND C. E. STEWART, *J. Chem. Soc.*, (1959) 535.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THIAZOLYLAZO DYESTUFFS AS COORDINATING LIGANDS

PART I. THE STABILITY CONSTANTS FOR 4-(2-THIAZOLYLAZO)-RESORCINOL AND RELATED COMPOUNDS

G. NICKLESS, (the late) F. H. POLLARD AND T. J. SAMUELSON*
Department of Inorganic Chemistry, School of Chemistry, The University, Bristol, 8 (Great Britain)
(Received December 29th, 1966)

As a sequel to the work of GEARY *et al.* on the stability constants of pyridylazo and azo-methine compounds[1], the complex-forming properties of the thiazole analogues have been studied. Potentiometric titrations were employed for the determinations, following the method outlined by IRVING AND ROSSOTTI[2]. After various methods had been attempted for the determination of the stability constants K_1 and K_2 from the formation curves, it was decided to solve the Bjerrum equations: for 1:2 metal:ligand complex formation,

$$\bar{n}+(\bar{n}-1)\,K_1\,[L]+(\bar{n}-2)\,K_1K_2\,[L]^2=0 \qquad (1)$$

and for 1:1 metal:ligand complex formation,

$$\bar{n}+(\bar{n}-1)\,K_1\,[L]=0 \qquad (2)$$

by means of an IBM 1620 computer. $\bar{n}$ refers to the degree of formation of the metal: ligand complex, while [L] represents the concentration of deprotonated ligand, the form present in the complex ML; charges are omitted for convenience. From the titration curves, several sets of values of $\bar{n}$ and [L] were obtained, and the simultaneous equations were solved[3] for K_1 and K_2. The values of K_1 and K_2, were then improved by a weighted least-squares technique. The weight of each value of $\bar{n}$ was calculated as follows:
from eqn. (1)

$$\bar{n} = \frac{K_1\,[L]+2K_1K_2\,[L]^2}{1+K_1\,[L]+K_1K_2\,[L]^2}$$

For each value of L, a value of $\bar{n}$ was calculated, knowing K_1 and K_2. The difference between this calculated value of $\bar{n}$ ($\bar{n}$ calc), and the actual value of $\bar{n}$ ($\bar{n}$ pract), was denoted by:

$$\sigma\bar{n} = \bar{n}\text{ calc.} - \bar{n}\text{ pract.}$$

The weight of each value of $\bar{n}$ is[4]

$$w = \frac{1}{\delta u^2}$$

---

* Present address: Technische Hochschule, Zurich, Switzerland.

where

$$\delta u = \frac{\partial u}{\partial n}\,\sigma n$$

The error ν in each set of values is given by:

$$\nu = \bar{n}_{\text{pract}} + (\bar{n}_{\text{pract}} - 1)\,K_1\,[\text{L}] + (\bar{n}_{\text{pract}} - 2)\,K_1 \cdot K_2\,[\text{L}]^2$$

thus

$$\delta\nu = (\bar{n}_{\text{calc}} - \bar{n}_{\text{pract}})(1 + K_1\,[\text{L}] + K_1K_2\,[\text{L}]^2)$$

The simultaneous forms of eqn. (1) were again solved for K_1 and K_2 giving these weights to each value of $\bar{n}_{\text{pract}}$. The new values of K_1 and K_2 were fed back to give a new set of weights, and the procedure was iterated until a reasonable agreement was obtained in successive values of K_1 and K_2.

A similar procedure was developed for the more simple eqn. (2) for the 1:1 metal:ligand complexes. Similarly the Bjerrum equations for the ligand:proton stability constants

$\sum_{j=0}^{j=J} (\bar{n}_{\text{A}} - j)\beta_j^{\text{H}}\,[\text{H}]^j = 0$ were solved for K_j^{H}.

EXPERIMENTAL

Many of the ligands studied were insoluble in water and hence the titrations were carried out in 50% aqueous methanol. In aqueous dioxan, some oxidation of the ligands always occurred because of the traces of peroxy compounds present in the solvent. In purely aqueous solution the practical stability constants were assumed[2] to be equal to the stoichiometric constants. In aqueous methanol the pH values were slightly lowered in strong alkali, and raised in strong acid. This is because the electrolytes become weaker in the organic solvent. A calibration graph for converting the pH to its equivalent value in aqueous solution was constructed from titrations of dilute perchloric acid with 0.1 *M* sodium hydroxide in purely aqueous solution, and in 50% aqueous methanol.

For water-insoluble dyes the titration mixture consisted of 75 ml of methanol, 25 ml of approximately 0.01 *M* ligand in methanol, 79 ml of water, 1 ml of 0.1 *M* metal solution, 10 ml of 0.04 *M* perchloric acid and 10 ml of 2 *M* sodium perchlorate solution. The latter was added to keep the ionic strength constant at 0.1.

A small correction had to be made to account for the small decrease in volume encountered on mixing equal amounts of methanol and water. For the purely aqueous titrations, the same quantities were used simply replacing the methanol by water. The mixtures were titrated against May & Baker "Volucon" 0.1 *M* sodium hydroxide which was taken as the primary standard, and used to standardise the perchloric acid. Generally, the metal solutions were standardised against ethylenediaminetetraacetic acid and a metal indicator, or by some similar accepted method.

Titrations were done in 250-ml 5-necked reaction vessels and end-points detected by means of reference calomel and glass electrodes with a "Pye Dynacap" pH meter. The solutions were stirred with saturated nitrogen, which also provided an atmosphere free from oxygen and carbon dioxide. The reaction vessel was placed in a thermostat tank maintained at 25 ± 0.5°, a thermometer in the titration mixture serving as a check for constant temperature.

THE STABILITY CONSTANTS FOR 4-(2-THIAZOLYLAZO)-RESORCINOL

Titrations of thiazolylazo-resorcinol (TAR)

In dilute acidic and neutral solutions TAR was yellow, in dilute alkali, orange-red, and in concentrated alkali, red. From the potentiometric titrations the following values were obtained:

$$\log K_2{}^{\mathrm{H}} = 6.53 \qquad \text{and} \qquad \log K_1{}^{\mathrm{H}} = 10.76$$

These values agreed well with values obtained spectrophotometrically by means of SCHWARZENBACH-type plots[5].

$$\log K_2{}^{\mathrm{H}} = 6.7 \qquad \text{and} \qquad \log K_1{}^{\mathrm{H}} = 10.8$$

For the calculations, the potentiometric values were used. TAR had a surprisingly low log $K_1{}^{\mathrm{H}}$ value compared with those of 4-(2-pyridylazo)-resorcinol (PAR) (12.31 in water)[1] and 4-(benzeneazo)-resorcinol (13.2 in 50% aqueous methanol). Similarly 4-(2-benzothiazolylazo)-resorcinol (BTAR) had a comparatively low log $K_1{}^{\mathrm{H}}$ value (10.6 in 50% aqueous methanol) determined spectrophotometrically. Log $K_1{}^{\mathrm{H}}$ for all the monohydroxythiazolylazo dyes was approximately 9, lower than those of the pyridine and benzene dyes. These comparatively low values of log $K_1{}^{\mathrm{H}}$ for TAR and BTAR together with their redness in dilute alkali, caused them to be inferior to 4-(2-pyridylazo)-resorcinol (PAR) as analytical reagents. PAR could be used for colorimetric work at a higher pH than TAR or BTAR. In strong acid, TAR protonated to give an orange solution. Log $K_3{}^{\mathrm{H}}$ was found spectrophotometrically to be equal to 0.9, lower than the corresponding value for PAR, since the thiazole nitrogen atom was less basic than that of pyridine. TAR did not protonate during the potentiometric titrations, since these were only operative over a pH range from 2.5 to 11.5.

$\bar{n}$ for the formation curvations was found from the amount of hydrogen ions released due to chelation. [L], the concentration of deprotonated ligand, was obtained from the equation[2]:

$$[\mathrm{L}] = \frac{T_{\mathrm{L}} - \bar{n}T_{\mathrm{M}}}{1 + K_1{}^{\mathrm{H}}[\mathrm{H}] + K_1{}^{\mathrm{H}} \cdot K_2{}^{\mathrm{H}}[\mathrm{H}]^2 + K_1{}^{\mathrm{H}} \cdot K_2{}^{\mathrm{H}} \cdot K_3{}^{\mathrm{H}}[\mathrm{H}]^3 \ldots} \tag{3}$$

T_{L} refers to the total amount of ligand present, and T_{M} the total amount of the metal with which the ligand is chelating.

Except for the strongest chelates (those of palladium, copper, bismuth etc.) the $K_3{}^{\mathrm{H}}$ term referring to the protonation of the dye, could be neglected. Also since $K_2{}^{\mathrm{H}}$ was the stability constant for the ionisation of the hydroxyl group of TAR *para* to the azo-link, and since this was not involved in the chelation, this term was omitted, giving:

$$[\mathrm{L}] = \frac{T_{\mathrm{L}} - \bar{n}T_{\mathrm{M}}}{1 + K_1{}^{\mathrm{H}}[\mathrm{H}]} \tag{3a}$$

K_1^H was the stability constant for the ionisation of the *o*-hydroxyl group of TAR. However, since the chelation of TAR generally took place in dilute acid solution, when the *p*-hydroxyl group was not ionised, the stability constant used for the calculation of L for the metal : ligand stability constants really referred to ionisation of the *o*-hydroxyl group. This unstable mono-ionised form was unobtainable and the stability constant could not be calculated. The value of $\log K_1^H = 10.76$ was employed for the calculations but a value of about 9 may have been nearer, since the mono-hydroxythiazolylazo dyes, such as those from *p*-cresol and *β*-naphthol-6-sulphonic acid ionised at this pH. This difficulty has been discussed by FREISER *et al.*[6] who determined the stability constants of the metal complexes of pyridylazo-resorcinol (PAR). They also found that chelation affected the pH values at which the *p*-hydroxyl group of PAR (which was not involved in the bonding) ionised[7]. Only when the solid complex precipitated out, did erroneous values occur.

In some cases chelation was already considerable in the acidic conditions at the beginning of the titration. When partial chelation had occurred, the titrations were performed with the concentration of ligand and metal reduced to a tenth. This was equivalent to reducing the pH by a factor of 1, as it reduced [L] by a tenth (see eqn. (3)). These titrations were not accurate owing to the small amount of protons released on chelation, and could only be used to supplement information obtained from more concentrated solutions. In other cases, when chelation occurred in strongly acidic solution, a spectrophotometric method was devised where $\bar{n}$ was determined from the concentration of complex present. For the 1:1 complexes, as in the case of copper, $\bar{n}$ could be readily determined from the absorption at the peak wavelength of the complex, but when K_1 and K_2 were close together, the presence of 1:2 complex caused the computation of $\log K_1$ to be only approximate.

TABLE I

STABILITY CONSTANTS FOR COMPLEXES OF 4-(2-THIAZOLYLAZO)-RESORCINOL

Metal	*Log K_1*	*Log K_2*	*Log β_2*	*Method used*[a]
ZrO^{2+}, TiO^{2+}	13 ± 1			S
VO_3^-	12.5 ± 0.5	—	—	S
Cu^{2+}	12.3 ± 0.2	9.9 ± 0.1	22.2 ± 0.3	P &S
Au^{3+}, Pt^{2+}, Rh^{3+}	12 ± 1	—	—	S
Ga^{3+}, Tl^{3+}	12 ± 0.5	—	—	S
VO^{2+}	11.2 ± 0.1	9.8 ± 0.2	21.0 ± 0.3	p
In^{3+}	10.8 ± 0.2	—	—	P &S
Fe^{2+}	(10.9)	(10.6)	21.6 ± 0.3	p
UO_2^{2+}	10.7 ± 0.2	9.7 ± 0.1	20.4 ± 0.3	p
Sc^{3+}	10.4 ± 0.1	9.9 ± 0.1	20.3 ± 0.3	P
Cr^{3+}	10	—	—	S
Pb^{2+}	9.7 ± 0.2	—	—	P
NbO_3^-	9.5 ± 1	—	—	S
Zn^{2+}	—	—	17.2 ± 0.2	P
Cd^{2+}	—	—	16.0 ± 0.2	P
Mn^{2+}	—	—	13.1 ± 0.2	P
Ca^{2+}	3.5 ± 0.3	—	—	P
Sr^{2+}	$\leqslant 3$	—	—	P
Tl^+, Mg^{2+}, Ba^{2+}	< 3	—	—	P

[a] P refers to potentiometric determinations and p refers to supplementary titrations performed at a tenth concentration. S refers to spectrophotometric determinations.

When $K_2 > K_1$ or $\simeq K_1$, errors of computation become excessive and only the cumulative constant $\beta_2 = K_1K_2$ is shown (with approximate values of K_1 and K_2 in brackets) in Table I. The major error in the determination of the stability constants was the measurement of pH, the pH meter being standardised with a freshly prepared 0.05 M potassium hydrogen phthalate solution. A further large error lay in the value of log K_1^H for TAR, but since this quantity remained the same for all metals, it was neglected. Precipitates were formed in titrations with Pd, Th, Hg, Ag, Bi, Fe(III) and all rare earths and therefore, the constants are not given.

The sensitivity of TAR for the different metals was generally parallel to that of pyridylazo-resorcinol (PAR). Usually the least electropositive elements formed the strongest complexes, because of the covalent character of the bonding. For the first transition series, the IRVING–WILLIAMS[8] order Cu(II) > Zn(II) was obeyed for the values of log K_1. Log K_2 for Cu(II) was low since this metal prefers to form square planar complexes. TAR donates from 3 points in the molecule, and so the formation of a 1:1 complex satisfies the coordination number of the copper atom. The formation of a 1:2 complex does not improve on this, and as copper is reluctant to form 6-coordinate complexes, the value of log K_2 is relatively low. Calcium formed a stronger complex than magnesium which was unexpected from electrostatic considerations, since magnesium has a smaller ionic radius. The calcium complex of ethylenediaminetetraacetic acid is also more stable than the magnesium complex[9], and this reversal of the order may be related to the ease of packing the ligand around the central metal atom.

Chelate formation was very slow with chromium(III), rhodium(III) and platinum(II) and -(IV); the complex was only formed on heating or on standing for several days. TAUBE has explained this slow substitution of the aquo-complexes of these metals from considerations of their electronic structures[10]. The stability constants of these metals could only be determined very roughly therefore. Osmium(IV) and ruthenium(IV) also complexed rather slowly, and iridium(IV), palladium(II) and gold(III) reacted more slowly than the first transition series metals.

Many solid complexes of thiazolylazo-resorcinol and other dyes were prepared from ethanolic solutions of the dye and metal salt. Generally, the solid complex crystallised out, but occasionally the chelate was more soluble than the dye, and the solution had to be evaporated. A few drops of 0.880 M ammonia assisted formation especially for the weaker complexes, but excess metal could not be present or else the hydroxide was formed simultaneously.

The properties of the complexes are summarised in Table II. All the complexes were submitted to elemental analysis in order to prove the structures.

Complexes of several dyes were made, and the most successful are included in the Table, although the complexes of iron(III), lanthanum and thorium were not pure. Impure complexes of vanadium(V), indium and titanium were also prepared. With an excess of copper salt, the 1:1 complex was prepared with TAR. WILLEY[11] experienced this reluctance of TAR to form a 1:2 metal:ligand complex with copper, and only by taking the correct proportions of dye and metal salt was the 1:2 chelate produced. Even with excess of metal salt present, nickel and cobalt gave 1:2 complexes. The cobalt complex of TAR was a black-solid which gave a red solution in ethanol; however, on leaving this for some time, it became less soluble in ethanol, and gave a green solution. Also the freshly prepared chelate was paramagnetic

TABLE II

PROPERTIES OF METAL–TAR COMPLEXES

Metal	*Ligand*	*Structure of complex*	*Appearance*	*Visible absorption peaks*[a] *(nm)*	*Decomposition temperature*[b] *(°)*	*Magnetic susceptibility in unpaired electrons*[c]
Zn^{2+}	TAR	$Zn \cdot TAR \cdot CH_3CO_2$	Golden-brown powder	527	305	0
Zn^{2+}	TANβ	$Zn(TAN)_2$	Golden-brown crystals	540, 570	310	0
Cu^{2+}	TAR	$Cu(TAR) \cdot NO_3$	Black powder	555	200	1
Cu^{2+}	TAR	$Cu(TAR)_2$	Black powder	510	—	1
Ni^{2+}	TAR	$Ni(TAR)_2$	Black powder	525	300	2
Co^{3+}	TAR	$Co(TAR)_2$	Black powder	500	290	0
Co^{3+}	TANβ	$Co(TAN)_2(NO_3)$	Black powder	460, 610	270	0
Co^{2+}	BTANβ	$Co(BTAN)_2$	Golden powder	555	395	3
Fe^{2+}	TAR	$Fe(TAR)_2$	Black powder	505	220	0.6
Fe^{3+}	TAR	$Fe(TAR)(NO_3)_2$	Black powder	475	110	3
Mn^{2+}	TAR	$Mn(TAR)Cl$	Green-black powder	527	180	5
Ag^{+}	TANβ	Ag–TAN	Green-brown powder	535	230	0
V^{4+}	TAR	$Vo(TAR)(SO_4)$	Black-solid	455	250	1
U^{6+}	TAR	$UO_2(TAR)Cl$	Green black-solid	540	250	0
Pb^{2+}	TAR	$PbTAR(CH_3CO_2)$	Golden powder	547	265	0
Tl^{+}	TAR	Tl TAR	Silver-pink powder	480	205	0
La^{3+}	TAR	$La(TAR)_2NO_3$	Dark green-brown powder	535	170	0
Th^{4+}	TANβ	$Th(TAN)_2(OH)_2$	Maroon powder	540	200	0
Zr^{4+}	TAR	$ZrO(TAR)Cl$	Golden black-solid	515	270	0
Bi^{3+}	TAR	$Bi(TAR)(NO_3)_2$	Black powder	550	270	0
Hg^{2+}	TAR	$Hg(TAR)(NO_3)$	Red-solid	525	180	0
Cr^{3+}	TAR	$Cr(TAR)(OH)_2 \cdot 3H_2O$	Red black-solid	495	180	3
Cd^{2+}	TAR	$Cd(TAR)_2$	Green-black powder	530	240	0

[a] Measured on a Unicam SP500 spectrophotometer.

[b] Obtained by heating samples (*ca.* 0.5 g) on a Stanton Thermobalance; this also showed the amount of solvent present.

[c] Measured on a Gouy balance.

(corresponding to a little more than 1 unpaired electron), but an old sample was diamagnetic. This shows that the cobalt in the complex was being oxidised to the trivalent state. The analytical figures of the complex corresponded to the formula $Co(TAR)_2$; calc. Co, 11.8%; C, 43.3%; H, 2.4%; N, 16.8% and found Co, 11.6%; C, 42.5%; H, 3.9%; N, 17.2%. This gave a blue solution in alcohol, and the green colour could only be produced by dissolving the complex in concentrated nitric acid, the cobalt(III) complexes being inert to acid attack. This oxidation of the cobalt complexes has already been noted for the pyridylazo dyes[12,13]. The cobalt complex of pyridylazo-β-naphthol (PAN β) is more readily oxidised to its green cobalt(III) form than that of pyridylazo-resorcinol (PAR)[13]. This phenomenon did not affect the potentiometric titrations of the cobalt complexes, since these were carried out under nitrogen, and there was no oxidation during the titrations.

THE STABILITY CONSTANTS OF OTHER THIAZOLYLAZO DYES AND RELATED COMPOUNDS

For each ligand, the following metal complexes were studied: Mn^{2+}, Fe^{2+},

Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^{+}, UO_2^{2+} and Pd^{2+}. Approximately the same sequence of stabilities was followed for each ligand, palladium and copper forming the strongest, and manganese and zinc the weakest complexes. Most of the stability constants were determined potentiometrically, but log K_1 for copper and palladium often had to be estimated spectrophotometrically.

2-(2-Thiazolylazo)-p-cresol (TAβC)

This was a yellow dye which gave blue complexes with metals, but this good colour change tended to occur at the expense of the sensitivity. The stability constants are given in Table III. Log K_1^H for TA*p*C was 8.95 ± 0.1. The errors on the log K_1^H were usually ± 0.1 units, while the error on the overall stability constants of the metal complexes, log β_2, was ± 0.3 units.

Iron(II), uranyl(II), lead(II), silver(I) and palladium(II) all formed precipitates, and hence values cannot be quoted.

TABLE III

STABILITY CONSTANTS FOR COMPLEXES OF 2-(2'-THIAZOLYLAZO)-*p*-CRESOL

Metal	*Log K_1*	*Log K_2*	*Log β_2*
Cu^{2+}	10.5	5.8	16.3
Ni^{2+}	8.3	7.9	16.2
Co^{2+}	—	—	14.5
Mn^{2+}	—	—	7.6
Zn^{2+}	6.1	5.4	11.5

1-(2-Thiazolylazo)-β-naphthol-6-sulphonic acid (TANβ6S)

This dye was water-soluble, but its stability constants were first determined in 50% aqueous methanol. In this solvent, log K_1^H for TANβ6S was 8.44, and the stability constants are given in Table IV.

The stability constants of the complexes in purely aqueous solution were also determined, using the same concentrations of reagents. Log K_1^H was scarcely altered for TANβ6S in aqueous solution and was 8.38. The stability constants are again given in Table IV.

The stability constants of TANβ6S are noticeably lower in the aqueous medium, and copper and lead do not form 1:2 metal–ligand complexes. GEARY *et al.*[1] found

TABLE IV

STABILITY CONSTANTS OF TANβ6S

Metal	*In 50% aqueous methanol*			*In water*		
	Log K_1	*Log K_2*	*Log β_2*	*Log K_1*	*Log K_2*	*Log β_2*
Pd^{2+}	13	6.4	19.4	13	5.7	18.7
Cu^{2+}	11.3	6.3	17.6	11.1	—	—
Ni^{2+}			17.1	8.5	8.3	16.7
Fe^{2+}			17.3			16.7
UO_2^{2+}	8.7	7.2	15.9	8.2	5.5	13.7
Co^{2+}			15.4	7.7	6.6	14.3
Zn^{2+}	7.0	6.3	13.4	6.3	5.7	12.0
Mn^{2+}	4.9	4.0	8.9	4.3	3.3	7.6

that the complexes of pyridylazo-resorcinol (PAR) were more stable in aqueous dioxan than in water, and MELLOR AND MALEY[14] found that with complexes in aqueous dioxan, the stabilities increased with increasing organic content of the solvent. TANβ6S formed stronger complexes than TA*p*C, and it was noted that the sensitivity of TA*p*C as an analytical reagent is inferior to that of the best of the thiazolylazo dyes.

1-(2-Benzothiazolylazo)-β-naphthol-6-sulphonic acid (BTANβ6S)

The log K_1^H value for BTANβ6S was 8.41, and the titrations were carried out in aqueous solution. The extra benzene ring on the thiazole ring caused the complexes to be considerably less soluble than those of TANβ6S. The solutions were deeply coloured, and precipitate formation or turbidity with all metals prevented the calculation of reliable stability constants by the present method.

1-(2-Thiazolylazo)-β-naphthol-6,8-disulphonic acid (TANβ6,8S)

Many other thiazolylazo dyes from sulphonated naphthols behaved similarly to TANβ6S. The stability constants of the metal complexes of the dyes from 1-naphthol-7-sulphonic acid and 2-naphthol-3,6-disulphonic acid were not calculated for the reasons given for BTANβ6S. However, TANβ6,8S and the dye from 2-naphthol-8-sulphonic acid containing a sulphonic acid group in the 8-position were considerably less sensitive towards metals.

Benzeneazo dyes

The benzeneazo dyes formed considerably less stable complexes than those of thiazole; cobalt, iron, lead, uranium and zinc salts hydrolyzed before the complexes were formed. Thus, it was obvious that the removal of the heterocyclic ring considerably lowers the complex-forming power of the ligands.

Attempts were made to prepare the dyestuffs, 2-(2-pyrrolylazo)-phenol and 2-(2-thienylideneazo)-phenol following the method of FISCHER AND HEPP[15]. However, in all cases either no reaction occurred or tarry black solids were formed which proved impossible to purify. Anils were prepared from thiazole-2-aldehyde and *o*-aminophenol (BT*o*AP) and 2-aminothiazole and salicylaldehyde (SAmT), respectively. These reagents were rapidly hydrolysed in aqueous solutions so that no reliable stability constants could be obtained. The sensitivities of these reagents for metals were only slightly less than those of the thiazolylazo dyes and insoluble red and yellow complexes were formed with BT*o*AP and SAmT respectively.

o-Hydroxystyrylbenzothiazole (HySBT)

The complete removal of the azo linkage was found to have a serious effect on the coordinating properties; HySBT formed complexes to an appreciable extent only with silver and palladium. Only weak complexes were formed with other metals, presumably because of the steric configuration of the reagent.

Benzothiazolyl-2-hydrazone of salicylaldehyde (BTHySa)

Similarly to HySBT, BTHySa was not hydrolysed in aqueous solution. Orange to yellow complexes were formed with Cu(II), Fe(III), Mn(II), Pb(II), UO_2^{2+} and Zn(II). Stability constant values are not given because of the limited solubility of the reagent. Some approximate stability constants obtained for BT*o*AP complexes indicated that BT*o*AP and BTHySa behave in a similar manner with regard to complex formation.

Attempts were also made to synthesize 2-pyrrolylidene-*o*-aminophenol (Pr*o*AP) and 2-thienylidene-*o*-aminophenol (TH*o*AP) but both these reagents were very easily hydrolysed in aqueous solution. In methanolic solution, the reagents were stable and Pr*o*AP was found to form much more stable complexes than TH*o*AP. The latter reagent had about the same tendency to form complexes as benzylidine-*o*-aminophenol, which indicates that the thiophene sulphur does not participate in the chelation.

4-(2-Thiazolylazo)-phenol (p-TAP)

p-TAP only formed appreciably strong complexes with certain heavier metals; the similar compound 4-(2-thiazolylazo)-1-naphthol has been used as a reagent for silver and palladium[16]. The removal of the *o*-hydroxyl group seriously affects the complexing properties, and *p*-TAP scarcely formed complexes with metals of the first transition series.

These stability constant determinations show that the order of importance of the donor atoms present in thiazolylazo-resorcinol is:

the *o*-hydroxyl group (most important),
the azo-nitrogen atom nearest to the phenol,
the heterocyclic nitrogen atom,
the azo-nitrogen atom nearest to the heterocyclic ring,
the *p*-hydroxyl group,
the heterocyclic sulphur atom.

SUMMARY

The complex forming properties of the thiazole azo dyestuffs and related compounds have been studied in order to try to ascertain the role of importance of the donor atoms present in thiazolylazo-resorcinol. Potentiometric titrations were employed for these determinations, although in many cases meaningful stability constants could not be obtained because of reagent instability or insolubility of the complexes formed on chelation.

RÉSUMÉ

On a étudié les propriétés de formation de complexes de colorants thiazole-azo et de leurs dérivés. Ceci pour essayer de préciser le rôle des atomes donneurs présents dans le thiazolylazorésorcinol. On procède par titrage potentiométrique, bien que dans de nombreux cas des constantes de stabilité valables ne peuvent être obtenues en raison de l'instabilité du réactif ou de l'insolubilité des complexes formés par chélation.

ZUSAMMENFASSUNG

Die komplexbildenden Eigenschaften der Thiazolazo-Farbstoffe und ver-

wandter Verbindungen wurden untersucht, um die Bedeutung der Donoratome im Thiazolylazoresorcinol zu ermitteln. Für diese Bestimmungen wurden potentiometrische Titrationen verwendet, obwohl in vielen Fällen Stabilitätskonstanten mit besonderem Aussagewert nicht erhalten werden konnten, da das Reagenz instabil oder die gebildeten Komplexe unlöslich waren.

REFERENCES

1 W. J. Geary, G. Nickless and F. H. Pollard, *Anal. Chim. Acta*, 27 (1962) 71.
2 H. Irving and H. S. Rossotti, *J. Chem. Soc.*, (1954) 2904.
3 J. Topping, *Errors of Observation and their Treatment*, Institute of Physics, 1955, p. 96.
4 J. C. Sullivan, J. Rydberg and W. F. Miller, *Acta Chem. Scand.*, 13 (1959) 2023.
5 G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, 31 (1948) 678.
6 A. Corsini, I. Mai-Ling Yih, Q. Fernando and H. Freiser, *Anal. Chem.*, 34 (1962) 1090.
7 A. Corsini, Q. Fernando and H. Freiser, *Inorg. Chem.*, 2 (1963) 224.
8 H. Irving and R. J. P. Williams, *J. Chem. Soc.*, (1953) 3192.
9 A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, 3rd ed., Longmans-Green, London, 1964, p. 418.
10 H. Taube, *Chem. Rev.*, 50 (1952) 69.
11 G. Willey, *B.Sc. Thesis*, University of Bristol, 1960.
12 K. L. Cheng and R. H. Bray, *Anal. Chem.*, 27 (1955) 782.
13 T. Iwamoto and M. Fujimoto, *Anal. Chim. Acta*, 29 (1963) 282.
14 D. P. Mellor and L. Maley, *Australian J. Sci. Res*, 2 (1949) 92; *Chem. Abstr.*, 44 (1950) 10567c.
15 O. Fischer and E. Hepp, *Ber.*, 19 (1886) 2251.
16 A. Kawase, *Japan-Analyst*, 12 (1963) 709; *Anal. Abstr.*, 11 (1964) 549; 12 (1965) 695.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SÉPARATION INDIUM-ÉTAIN EN PRÉSENCE D'EDTA

GIOVANNI LANFRANCO ET FRANCO CERRATO
Centro Ricerche Metallurgiche, Torino (Italia)

(Reçu le 23 décembre, 1966)

La séparation indium–étain est un problème très intéressant qui trouve application dans le contrôle de concentrés d'indium, contenant de l'étain ainsi qu'aux alliages indium–étain, comme certains alliages antifriction ou ceux à bas point de fusion.

Pour séparer ces 2 éléments on a proposé plusieurs méthodes comme la précipitation de l'indium par la soude 2 N, ou bien la précipitation de l'étain avec de la gélatine en solution sulfurique, ou la séparation à froid des sulfures d'indium et d'étain par le sulfure d'ammonium 1 M, ou la précipitation de l'étain d'une solution saturée de carbonate de sodium par adjonction de bromate et de bromure de potassium, ou enfin la séparation par le méthylviolet[1].

Dans l'étude d'une méthode pour la détermination de traces d'indium dans le plomb[2] par analyse par radioactivation par des neutrons, on a observé que la précipitation de l'étain(IV) par l'ammoniaque en présence d'EDTA permet de séparer, d'une façon rapide et avec de bons résultats, cet élément de l'indium.

On a contrôlé la séparation de macro et de microquantités d'indium de 10 mg d'étain au moyen d'étain et d'indium radioactifs.

PARTIE EXPÉRIMENTALE

Procédé

A la solution (10 ml à peu près), faiblement acidulée par l'acide chlorhydrique et contenant de l'étain(IV) (10 mg) et de l'indium (de 0.01 à 10 mg), on ajoute 1 ml pour chaque milligramme d'indium présent, d'une solution à 3.25 g/l de dihydrate du sel disodique de l'acide éthyléndiamintétracétique (EDTA), plus 7 ml en excès.

Il faut que le volume final de la solution soit compris entre 20 et 25 ml. On ajoute 1 g de nitrate d'ammonium et de l'ammoniaque concentré jusqu'à pH 7; on fait bouillir la solution dans une fiole conique de 50 ml pendant 20 min. On centrifuge et on lave le précipité avec une solution à 5% de nitrate d'ammonium.

L'indium reste dans la solution, l'étain est précipité.

Contrôle de la méthode

L'indium et l'étain radioactifs ont été produits par irradiation dans un flux de neutrons thermiques du réacteur nucléaire RA 1 (SORIN—Saluggia). Après irradiation on dissout l'échantillon d'indium dans l'acide nitrique et par dilutions successives on amène à une concentration de 0.001 mg/ml; l'échantillon d'étain est dissout dans l'acide chlorhydrique et purifié des impuretés radioactives (surtout de l'antimoine), enfin il est dilué à une concentration de 0.160 mg/ml.

Parmi les radioisotopes d'indium qui sont produits par radioactivation par les neutrons seulement ^{114m}In a une période suffisamment longue. Les plus importants des radioisotopes produits dans l'activation de l'étain sont: ^{121}Sn, ^{113}Sn, ^{117m}Sn. Les données caractéristiques de décroissance de ces radioisotopes sont rapportées dans le Tableau I.

TABLEAU I

DONNÉES DE DÉCROISSANCE CARACTÉRISTIQUES DES PRINCIPAUX RADIOISOTOPES OBTENUS PAR IRRADIATION DE L'INDIUM ET DE L'ÉTAIN PAR DES NEUTRONS THERMIQUES

Radioisotope	*Réaction de formation*	*Période*	*Type de désintégration (MeV)*	*Rayons-γ (MeV)*
^{114m}In	^{113}In(n,γ)^{114m}In	50 j	E.C. (3.5%)[a] I.T. (96.5%)[b]	0.56 (3.5%) 0.72 (3.5%) 0.19 (18.5%)
^{114}In	^{114m}In(I.T.)	72 s	β^-0.67 (0.2%) 1.98 (99%) E.C. (0.7%)	1.3 (0.2%)
^{113}Sn	^{112}Sn(n,γ)^{113}Sn	119 j	E.C.	0.26 (2%) Rayons X de In 0.024
^{113m}In	^{113}Sn(E.C.)^{113m}In	104 m	I.T.[b]	0.39 (64%)
^{117m}Sn	^{116}Sn(n,γ)^{117m}Sn	14 j	I.T.	0.160
^{121}Sn	^{120}Sn(n,γ)^{121}Sn	28 h	β^-0.38 (100%)	D'autres moins intenses

[a] E.C. Capture d'électrons.
[b] I.T. Transition isomérique.

Les mesures ont été effectuées avec un détecteur constitué par un scintillateur de INa(Tl) de 2″ × 2″ couplé à un photomultiplicateur RCA 6342 A. Le détecteur est placé dans une chambre blindée en plomb. Les impulsions, en provenance du détecteur sont envoyées par le moyen d'un préamplificateur TMC type DS 13 à un analyseur à 400 canaux type TMC 401*. On a mesuré la radioactivité des solutions placées dans des récipients en pyrex se trouvant sur un support de plexiglas placé sur le détecteur. On mesure la radioactivité des précipités après leur dissolution en acide chlorhydrique et dilution à un volume convenable.

La radioactivité de ces échantillons a été comparée à celle d'étalons d'indium ou d'étain radioactifs, mesurés dans les mêmes conditions. On a mesuré la radioactivité-γ de ^{114m}In sous le pic photoélectrique qui correspond à l'énergie de 0.19 MeV et celle de 117^{m}Sn sous le pic qui correspond à l'énergie de 0.16 MeV.

Dans l'exécution des mesures avec l'étain radioactif, il faut se rappeler que celui-ci contient toujours de l'indium radioactif produit par la décroissance de ^{113}Sn.

Après la séparation indium–étain, il faut donc attendre, avant d'effectuer les mesures, le temps nécessaire pour que ^{113m}In se remette en équilibre avec ^{113}Sn (à peu près 18.5 h). De cette façon on évite de corriger les résultats pour la contribution du

---

* Dans des expériences antérieures on a mesuré la radioactivité-β avec un compteur de Geiger pour liquides ou la radioactivité-γ avec un détecteur à scintillation de INa(Tl) et un analyseur d'impulsion à un canal. Les résultats obtenus dans ces expériences concordent avec ceux rapportés ici.

spectre de ^{113m}In dans le champ d'énergie où on mesure la radioactivité de l'étain.

Expériences avec l'étain radioactif. Les essais furent réalisés sur des solutions contenant 10 mg d'étain et des quantités d'indium variables de 0.01 à 10 mg, auxquelles on avait ajouté de l'étain radioactif. On a mesuré la radioactivité du précipité dissout en un peu d'acide chlorhydrique et dilué à 10 ml et celle de la solution séparée à laquelle on a ajouté les eaux de lavage. Les résultats des essais sont rapportés dans le Tableau II.

Expériences avec l'indium radioactif. On a conduit les essais avec des solutions contenant 10 mg d'étain et des quantités d'indium variables de 0.01 à 10 mg auxquelles on avait ajouté de l'indium radioactif. Les résultats des essais sont rapportés dans le Tableau II.

TABLEAU II

RÉSULTATS D'ESSAIS DE SÉPARATION ÉTAIN–INDIUM

Quantité d'étain et d'indium en solution (mg)	*Essais avec ^{117m}Sn (Etain resté en solution après l'essai) (%)*	*Essais avec ^{114m}In (Indium entraîné par l'étain) (%)*
Etain 10 Indium 10	1.4	1.2
	0.7	1.1
	1.3	0.4
Etain 10 Indium 0.1	1.5	1.2
	1.5	1.8
	0.7	2
Etain 10 Indium 0.010	1.3	2
	0.9	2.5
	1.4	1.8

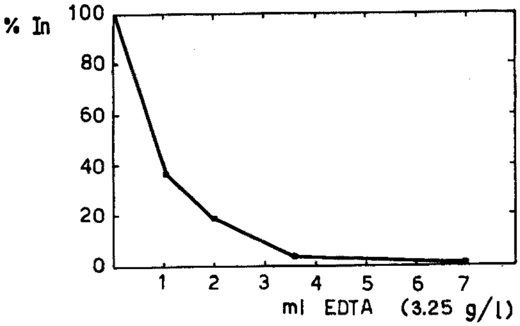


Fig. 1. % d'indium entraîné par l'étain en présence de quantités diverses d'EDTA.

CONCLUSION

Des résultats des essais on remarque que 98.5% de l'étain présent peuvent être séparé d'une solution indium–étain; à son tour la séparation de l'indium de l'étain est supérieure à 98%. Il faut tenir la concentration de l'EDTA dans les limites indiquées. Une concentration plus elevée d'EDTA empêche partiellement la précipitation de l'étain, tandis qu'une concentration plus basse rend incomplète la séparation de l'indium. La Fig. 1 représente le pour cent d'indium qui est entraîné par l'étain dans des essais de séparation de 0.1 mg d'indium de 10 mg d'étain, en présence de quantités diverses d'EDTA. Il est évident qu'en augmentant la concentration d'EDTA, le pour cent d'indium entraîné par l'étain diminue. Si on sépare l'étain de milligrammes d'indium on peut précipiter ensuite celui-ci en ajoutant une solution de soude jusqu'à pH 12.5. Dans ces conditions la précipitation de l'indium est pratiquement quantitative ($>99.9\%$). Des essais conduits avec de l'étain radioactif ont démontré que le précipité d'indium contient moins de 0.5% d'étain. On peut doser l'indium après une successive précipitation par l'ammoniaque. Le précipité est dissout en un peu d'acide chlorhydrique, on dilue et on précipite l'indium par la N-benzoyle-N-phénylhydroxylamine selon le procédé de DAS ET SHOME[3]. On pèse l'oxyde d'indium après calcination.

Dans des essais de dosage de l'indium en solutions contenant 10 mg d'indium et 10 mg d'étain on a trouvé des quantités variables de 97.5 à 100.5% de l'indium présent.

RÉSUMÉ

L'étain peut être précipité de solutions faiblement ammoniacales en présence d'EDTA. L'indium, présent en quantités de l'ordre de milligrammes ou de microgrammes, reste presque complètement en solution, avec 1–2% d'étain. La séparation a été contrôlée au moyen d'indium et d'étain radioactifs.

SUMMARY

Tin can be precipitated from weakly ammoniacal solutions in the presence of EDTA. Indium, in mg- or μg-amounts, remains almost completely in solution, together with 1–2% of the tin. The separation was checked with radioactive indium and tin.

ZUSAMMENFASSUNG

Zinn kann von schwach ammoniakalischer Lösungen in Anwesenheit von EDTA gefällt werden. Indium, in mg- oder μg-Mengen, verbleibt dabei vollständig in der Lösung zusammen mit 1–2% Zinn. Die Trennung wurde mittels radioaktiver Indium und Zinn geprüft.

BIBLIOGRAPHIE

1 A. I. BUSEV, *The Analytical Chemistry of Indium*, Pergamon Press, Oxford, 1962, p. 7, 37, 57, 63, 93.
2 A. BIANCHINI ET G. LANFRANCO, *Chim. Ind. (Milan)*, 48 (1966) 823.
3 H. R. DAS ET S. C. SHOME, *Anal. Chim. Acta*, 27 (1962) 545.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE SPECTROPHOTOMETRIC DETERMINATION OF ANIONS BY SOLVENT EXTRACTION WITH METAL CHELATE CATIONS. PART XX. TRICHLOROACETIC ACID WITH TRIS(1,10-PHENANTHROLINE)IRON(II) CHELATE*

Y. YAMAMOTO, T. KUMAMARU AND Y. UEMURA
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda, Hiroshima (Japan)

(Received January 9th, 1967)

Several methods for the colorimetric determination of trichloroacetic acid[1-4] have been published. Most of the methods are based on the well known FUJIWARA reaction[5], which gives a deep red coloration when trichloroacetic acid is boiled with concentrated sodium hydroxide solution and pyridine. In these methods, however, close attention has to be paid to the reaction conditions such as temperature, time of boiling, time of standing after heating, or diluent used.

The present determination of trichloroacetic acid is based on a different reaction mechanism from the known colorimetric methods and involves solvent extraction with metal chelate cations.

It has been observed that, if a considerable excess of tris(1,10-phenanthroline)-iron(II) chelate is added to an aqueous solution containing a small amount of trichloroacetate, tris(1,10-phenanthroline)iron(II) trichloroacetate can be extracted into nitrobenzene, the amount of extraction being proportional to the amount of trichloroacetic acid present. It is then possible to determine a small amount of trichloroacetic acid by measuring the absorbance of the red organic phase spectrophotometrically.

In this series of studies on the solvent extraction of anions with metal chelate cations, the determination of iodide[6], perchlorate[7], and pentachlorophenolate[8,9], has recently been reported.

EXPERIMENTAL

Apparatus

The spectrophotometric measurements were made with a Hitachi Model 139 Spectrophotometer using 10-mm glass cells. The shaking was done with a Iwaki Model KM shaker with a time switch. The pH measurements were made with a Hitachi-Horiba Model H-5 pH meter.

Reagents

Tris(1,10-phenanthroline)iron(II) sulfate solution. A $1.0 \cdot 10^{-2}$ *M* solution was prepared by using analytical reagent grade iron(II) ammonium sulfate hexahydrate and 1,10-phenanthroline monohydrate.

---

* Part XIX of this series: Y. YAMAMOTO, T. KUMAMARU AND Y. HAYASHI, *Talanta*, to be published.

Trichloroacetic acid solution. A standard solution of $1.0 \cdot 10^{-1}$ *M* trichloroacetic acid was prepared from analytical reagent grade material. This was accurately standardized against sodium hydroxide solution. More dilute trichloroacetic acid solutions were prepared by suitable dilution.

Buffer solution. The phosphate buffer was 0.1 *M* in potassium dihydrogen phosphate and was adjusted to pH 4.0 with 0.05 *M* sulphuric acid.

All other reagents (analytical grade) were used without further purification.

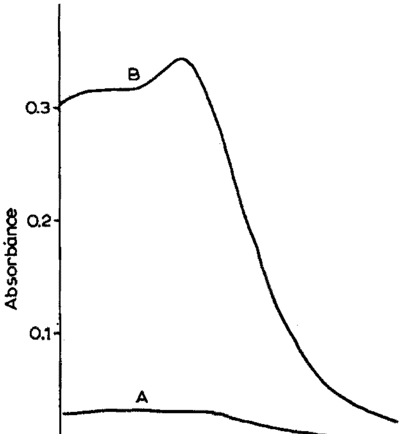
Procedure

Mix the tris(1,10-phenanthroline)iron(II) sulfate solution, buffer solution and standard trichloroacetic acid solution ($2.5 \cdot 10^{-4}$ *M*) in the appropriate concentrations. Adjust the pH of the solution to the required value with dilute sulphuric acid or sodium hydroxide solution. Dilute the solution with water to 25 ml, and shake it for 5 min with 10.0 ml of nitrobenzene. After 30 min, transfer the organic layer to a flask containing 1 g of anhydrous sodium sulfate and shake it vigorously in order to make the solution transparent. Measure the absorbance of the extracted solution using a reagent blank solution as reference.

RESULTS AND DISCUSSION

Absorption spectrum

The spectral absorbance curves with nitrobenzene as reference are shown in Fig. 1. It can be observed that the tris(1,10-phenanthroline)iron(II) cation is readily



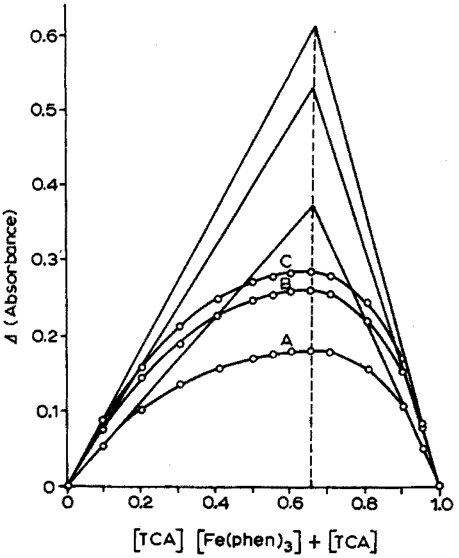


Fig. 1. Absorption spectra against nitrobenzene as reference. Spectra of organic extracts from aqueous solutions containing $2 \cdot 10^{-3}$ *M* Fe(phen)$_3$ and 0.1 *M* phosphate buffer. (A) In absence of trichloroacetic acid; (B) in presence of $1.0 \cdot 10^{-4}$ *M* trichloroacetic acid. pH of the aqueous phase: 4.0.

Fig. 2. Continuous variation plots for phenanthroline–iron(II) trichloroacetate at pH 4.0. Total concentration: $1.0 \cdot 10^{-3}$ *M*. (A) 540 nm, (B) 490 nm, (C) 516 nm.

extracted into nitrobenzene when a small amount of trichloroacetate is present in the aqueous phase. The maximum absorbance of the extracted species in nitrobenzene occurs at a wavelength of 516 nm, although the maximum of the tris(1,10-phenanthroline)iron(II) species is at 510 nm in the aqueous phase. The reason of the slight red shift of the spectrum in the organic phase may be attributed to an association between the cations and anions. The absorbance was measured at 516 nm in this work.

Effect of pH

The absorbances of the extracts were constant in the pH range 3–9. In more acidic or more alkaline solutions, the absorbance tended to decrease, presumably because of the decomposition of the phenanthroline–iron(II) trichloroacetate. In this work, the aqueous solution was adjusted at pH 4 in order to avoid the interference of lower chlorinated acetic acid derivatives as much as possible.

Several buffers were tested to maintain the aqueous solution at pH 4. Extraction of $1.0 \cdot 10^{-4}$ *M* trichloroacetic acid in the presence of varying amounts of acetate buffer showed an increase in absorbance with increase in acetate buffer concentration (0.01–0.12 *M*). Extraction from citrate-buffered solutions gave higher absorbance in the blank. Both the acetate and the citrate buffers affected the quantitative results adversely and there was some scatter of experimental points caused by relatively small changes in the concentration of the buffers. However, solutions buffered at pH 4 with phosphate buffer gave consistent results over the concentration range 0.04–0.16 *M*. Thus the phosphate buffer was preferred in this work, and its concentration was kept at 0.1 *M*.

Effect of tris(1,10-phenanthroline)iron(II) concentration

The absorbance of the nitrobenzene phase was constant when the chelate concentration was more than $1.5 \cdot 10^{-3}$ *M* in the aqueous solution when the concentration of trichloroacetic acid was kept at $1.0 \cdot 10^{-4}$ *M*. An excess of at least 15-fold (molar) of the phenanthroline chelate to trichloroacetic acid was necessary to obtain quantitative recoveries. The chelate concentration was usually kept at $2.0 \cdot 10^{-3}$ *M* in this work.

Effect of shaking time

The shaking time for the extraction was varied from 0.5 to 20 min, while the other variables were kept constant. The absorbance after extraction reached a maximum after shaking for about 4 min, hence a time of 5 min was chosen.

Color stability

The color intensity of the extracted species remained constant at room temperature for at least 45 min after the separation of organic layer.

Choice of organic solvent

Various water-immiscible organic solvents were tested for the extraction: isoamyl alcohol, benzene, *n*-butyl acetate, carbon tetrachloride, chloroform, cyclohexanone, 1,2-dichloroethane, methyl isobutyl ketone, nitrobenzene and isopropyl ether. Only nitrobenzene extracted phenanthroline–iron(II) trichloroacetate from aqueous solution.

The concentration of trichloroacetate anions was kept at $1.0 \cdot 10^{-4}$ M, and the other variables were the same as those of the standard procedure. The extraction was then carried out with successive portions of nitrobenzene. The extraction yield with one 10.0-ml portion of nitrobenzene was calculated to be *ca.* 50%. For convenience, the method developed here is based on the use of only a single extraction.

Calibration curve

The recommended procedure for the calibration curve is as follows.

Mix 5 ml of the tris(1,10-phenanthroline)iron(II) sulfate solution, 2.5 ml of phosphate buffer solution, and varying amounts (1–10 ml) of the standard trichloroacetic acid solution ($2.5 \cdot 10^{-4}$ M). Dilute the resulting solutions to 25 ml with distilled water. Then add 10.0 ml of nitrobenzene, and treat the mixture as on p. 52. Under these conditions, a linear relationship is obtained over the tested range of $1.0 \cdot 10^{-5}$ to $1.0 \cdot 10^{-4}$ M of trichloroacetic acid in an aqueous solution, and the sensitivity is 0.310 in absorbance for $1.0 \cdot 10^{-4}$ M trichloroacetic acid in aqueous solution.

Interferences

The effect on the extraction of the phenanthroline–iron(II) trichloroacetate into nitrobenzene by dichloroacetic acid, monochloroacetic acid, acetic acid, and chloride was studied. The results are given in Table I. For the extraction of $1.0 \cdot 10^{-4}$ M trichloroacetic acid, both acetic acid and chloride ions had no effect on the absorbance even when present in a molar quantity 10 times that of trichloroacetic acid.

TABLE I

DETERMINATION OF TRICHLOROACETIC ACID (TCA) IN THE PRESENCE OF VARIOUS SUBSTANCES (TCA taken: $1.0 \cdot 10^{-4}$ M)

Addition	*Concentration* $\cdot 10^{-4}$ *(M)*	*Recovery of TCA(%)*
Dichloroacetic acid	0.5	100
Dichloroacetic acid	1.0	103
Dichloroacetic acid	3.2	120
Monochloroacetic acid	1.0	100
Monochloroacetic acid	5.0	110
Monochloroacetic acid	10	128
Acetic acid	10	100
Acetic acid	100	116
Sodium chloride	10	100
Sodium chloride	100	114

Monochloroacetic acid in amounts approximately equal to the trichloroacetic acid concentration had no effect on the extraction, while the same amounts of dichloroacetic acid produced an error of +3%. Large amounts of phosphate and sulfate, which were, of course, contained in the reagent solution used, did not interfere.

Effect of temperature

Both the test solution containing $1.0 \cdot 10^{-4}$ M trichloroacetic acid and the nitrobenzene were kept at the desired temperature; the extraction was then carried out by the standard procedure. The temperature coefficient was −0.003 absorbance unit per degree over the range 5–20°. The relative error was 1.0% per degree with respect to the 15° value, and throughout this work, the temperature at the extraction was kept nearly at 15°.

Precision

The reproducibility of the proposed method was estimated from the results of 10 sample solutions, each $1.0 \cdot 10^{-4}$ *M* in trichloroacetic acid. The standard deviation was calculated to be 0.003 absorbance unit from a mean value of 0.310, *i.e.* a relative error of 1.0%.

Composition of extracted species

In order to study the composition of the extracted species, continuous variation plots were made at wavelengths of 490, 516 and 540 nm. Figure 2 shows the results obtained. The maximum absorbance obtained by extrapolating the straight-line portion of the plots occurred at a ratio of 0.67. This suggests that a 1:2 associated ion pair is formed in the nitrobenzene phase between tris(1,10-phenanthroline)iron(II) cation and trichloroacetate anion, and thus the chemical formula of the extracted species can probably be represented as $[Fe(phen)_3] \cdot (CCl_3COO)_2$.

SUMMARY

Trichloroacetic acid can be extracted from an aqueous solution by nitrobenzene with tris(1,10-phenanthroline)iron(II) chelate, and can be determined spectrophotometrically by measuring the extract at 516 nm. The extracted species is probably $[Fe(phen)_3] \cdot (CCl_3COO)_2$. Beer's law is obeyed over the concentration range $1.0 \cdot 10^{-5}$–$1.0 \cdot 10^{-4}$ *M* trichloroacetic acid in aqueous solution. Large amounts of phosphate and sulfate and moderate amounts of chloride, acetic acid, and monochloroacetic acid do not interfere; equal amounts of dichloroacetic acid give a slight positive error.

RÉSUMÉ

L'acide trichloracétique peut être extrait d'une solution aqueuse par le nitrobenzene renfermant le chélate fer(II)–1,10-phénanthroline. On procède ensuite au dosage spectrophotométrique à 516 nm. On admet que le composé extrait est $[Fe(phen)_3] \cdot (CCl_3COO)_2$. La loi de Beer s'applique de 1.0×10^{-5} à 1.0×10^{-4} *M* d'acide trichloracétique. De grandes quantités de phosphate et de sulfate, des teneurs moyennes en chlorure, acide acétique et acide monochloracétique ne gênent pas. L'acide dichloracétique en quantités égales donne une légère erreur positive.

ZUSAMMENFASSUNG

Trichloressigsäure kann mit tris(1,10-Phenantrolin)–eisen(II) in Nitrobenzol aus wässriger Lösung extrahiert werden und anschliessend spektralphotometrisch bei 516 nm bestimmt werden. Wahrscheinlich wird $[Fe(phen)_3] \cdot (CCl_3COO)_2$ extra-

hiert. Grosse Mengen Phosphat und Sulfat und kleinere Mengen Chlorid, Essigsäure und Monochloressigsäure stören nicht. Gleiche Anteile von Dichloressigsäure ergeben einen geringen positiven Fehler.

REFERENCES

1 R. FRANT AND J. WESTENDORP, *Analyst*, 75 (1950) 462.
2 G. L. MILLS, *Anal. Chim. Acta*, 7 (1952) 70.
3 P. J. FRIEDMAN AND J. R. COOPER, *Anal. Chem.*, 30 (1958) 1674.
4 K. C. LEIBMAN AND J. D. HINDMAN, *Anal. Chem.*, 36 (1964) 348.
5 K. FUJIWARA, *Sits. Nat. Ges. Rostock*, 6 (1916) 33.
6 Y. YAMAMOTO AND S. KINUWAKI, *Bull. Chem. Soc. Japan*, 37 (1964) 434.
7 Y. YAMAMOTO, K. KOTSUJI, S. KINUWAKI AND H. SAWAMURA, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 85 (1964) 869.
8 Y. YAMAMOTO, K. KOTSUJI AND S. TANAKA, *Bull. Chem. Soc. Japan*, 38 (1965) 499.
9 Y. YAMAMOTO, T. KUMAMARU AND Y. HAYASHI, *Talanta*, to be published.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

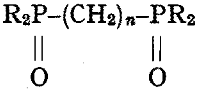
L'EXTRACTION DES LANTHANIDES ET DES ACTINIDES PAR LES OXYDES D'ALKYLPHOSPHINE

TOME III. L'EXTRACTION DE L'ACIDE NITRIQUE PAR QUELQUES DIOXYDES DE DIPHOSPHINE*

J. GOFFART** ET G. DUYCKAERTS
Laboratoire de Chimie Analytique et Nucléaire, 2, rue A. Stévart, Liège (Belgique)

(Reçu le 20 janvier, 1967)

Les composés organo-phosphorés neutres ont fait l'objet de nombreuses études concernant l'extraction liquide–liquide des métaux; nous avons effectué une étude assez complète de l'extraction des lanthanides et des actinides trivalents par une série d'oxydes d'alkylphosphine ainsi que par quelques dioxydes de diphosphine de formule générale $R_2P–(CH_2)_n–PR_2$ avec $n = 1$, 4 et 5.



$$R_2\underset{\underset{\displaystyle O}{\|}}{P}–(CH_2)_n–\underset{\underset{\displaystyle O}{\|}}{P}R_2$$

En vue d'interpréter les résultats d'extraction des métaux par ces réactifs et, en particulier, d'établir la stoechiométrie des complexes en phase organique, il est nécessaire de connaître non seulement la distribution de l'acide nitrique[1,2], mais également la concentration en réactif libre dans la phase organique. Ceci signifie la détermination des 2 constantes d'équilibre relatives à la neutralisation des 2 PO par l'acide nitrique.

L'étude de la distribution de HNO_3 en présence de dioxyde de diphosphine, discutée dans cette publication, a été réalisée avec une phase aqueuse dont la force ionique a été maintenue pratiquement constante en nitrate, pour 2 raisons:

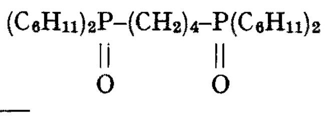
(*1*) l'addition de nitrate à la phase aqueuse favorise l'extraction des transplutoniens sans apport d'une quantité trop importante d'acide nitrique;

(*2*) la détermination des constantes d'équilibre en système biphasé est toujours facilitée par des expériences menées à force ionique constante.

Néanmoins, étant donné qu'il existe actuellement des valeurs précises sur l'activité de l'acide nitrique dans l'eau[3], nous avons également effectué une expérience de distribution d'acide sans addition de nitrate.

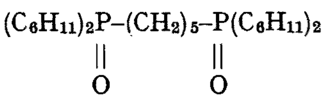
PARTIE EXPÉRIMENTALE

Réactifs



$$(C_6H_{11})_2\underset{\underset{\displaystyle O}{\|}}{P}–(CH_2)_4–\underset{\underset{\displaystyle O}{\|}}{P}(C_6H_{11})_2$$

(1,4-DiPO) et



$$(C_6H_{11})_2\underset{\underset{\displaystyle O}{\|}}{P}–(CH_2)_5–\underset{\underset{\displaystyle O}{\|}}{P}(C_6H_{11})_2$$

---

* Ce travail a été effectué dans le cadre du contrat Euratom 011-64-6 TPUB.

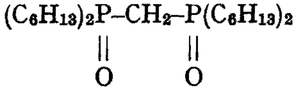
** Chercheur Agréé à l'Institut Interuniversitaire des Sciences Nucléaires.

(1,5-DiPO) ont été synthétisés par action du chlorure de l'acide cyclohexylphosphinique en excès[4] respectivement sur le MgBr–$(CH_2)_4$–MgBr et le MgBr–$(CH_2)_5$–MgBr[5,6]. La purification a été faite par recristallisations alternatives dans le *n*-octane et le cyclohexane: 5 recristallisations sont nécessaires pour obtenir un produit pur et incolore.

1,5-DiPO P.F.: 183–184°; $\% \, P_{\text{théor.}} = 12.47$, $\% \, P_{\text{exp.}} = 12.5$

1,4-DiPO P.F.: 220–221°; $\% \, P_{\text{théor.}} = 12.83$, $\% \, P_{\text{exp.}} = 12.8$

La pureté établie par titrage à l'acide perchlorique[1] est supérieure dans les 2 cas à 99%.



$(C_6H_{13})_2\underset{O}{\underset{\|}{P}}{-}CH_2{-}\underset{O}{\underset{\|}{P}}(C_6H_{13})_2$ (1,1-DiPO) a été préparé et purifié par la méthode de RICHARD *et al.*[7] modifiée par WALMSLEY ET TYREE[8]. La pureté est supérieure à 97%. $\% \, P_{\text{theor.}}$: 13.82, $\% \, P_{\text{exp.}}$: 13.7.

Dosage de l'acide nitrique

Nous avons utilisé 2 méthodes pour mesurer la distribution de l'acide nitrique entre la phase aqueuse et la solution benzénique de réactif.

(*1*) *Le titrage de l'acide nitrique dans les 2 phases par la soude.* Cette méthode, déjà décrite[1], a été utilisée pour 2 séries d'expériences menées en variant soit la concentration initiale en réactif basique, soit la concentration initiale en acide nitrique. Cette méthode est assez longue et nécessite une quantité assez importante de réactif. Par ailleurs, elle manque de précision dans le domaine des faibles concentrations en acide nitrique.

(*2*) *Le titrage potentiométrique à 2 phases.* Cette méthode, introduite par HÖGFELDT ET FREDLUND[9], consiste à titrer le système contenant les 2 phases de concentrations et de volumes connus par une solution d'acide nitrique 2 M en NO_3^-. Après chaque addition d'acide et équilibration, la concentration en acide nitrique restant dans la phase aqueuse est déterminée par une mesure de pH très précise, au moyen de la relation

$$E = E_0 + jC_a(HNO_3) + 59.155 \log C_a(HNO_3) \qquad (1)$$

où $C_a(HNO_3)$ est exprimé en mM. Cette méthode a l'avantage d'être plus rapide, d'exiger moins de réactif et de fournir des valeurs plus précises dans le domaine des faibles concentrations en acide nitrique. Elle exige cependant un étalonnage préalable en vue de déterminer E_0 et j, 2 constantes de l'éqn. (1).

Appareillage

L'appareil utilisé est identique à celui décrit dans la littérature[9]. Le pont de Wilhelm renferme du $NaNO_3$ 2 M. L'électrode de référence plonge dans du $NaNO_3$ 2 $M + AgNO_3$ 10^{-2} M. Une centaine de mg de AgCl solide se trouve au fond de la cellule de référence. La mesure de la force électromotrice est faite au moyen d'un potentiomètre Cambridge gradué au 0.2 mV et d'un électromètre Vibron permettant la mesure de 10^{-12} A sous 10 mV. Toutes les manipulations sont faites dans un local thermostatisé à 25 ±1° tandis que les électrodes indicatrice (électrode de verre Metrohm) et de référence (Ag/AgCl) plongent dans des cellules à double paroi thermostatique à 25±0.1° grâce à un Ultrathermostat Haake. La préparation de l'électrode de référence nécessite un soin attentif. La méthode suivante a été initialement utilisée: 2 fils de platine sont plongés dans une solution contenant 1 ml d'hydroxyde sodique 5 *M*, 8 mg de chlorure d'argent et 8 ml de cyanure de sodium 3 *M*. Les électrodes sont reliées à une batterie de 4 V pour électrodéposer l'argent pendant environ 5 min. Une autre méthode, utilisée plus tard, consiste à placer deux fils de platine dans une solution aqueuse de nitrate d'argent 10^{-1} $M+2\cdot10^{-1}$ M en cyanure de potassium. L'électrodéposition est faite avec une densité de courant inférieure à $5\cdot10^{-3}$ A/cm^2 pendant 3 heures[10].

Pour chlorurer l'électrode de référence, on plonge les 2 électrodes dans de l'acide chlorhydrique $5\cdot10^{-2}$ N après en avoir inversé les polarités et on électrolyse, en présence d'une trace d'hydroxylamine (1 goutte d'une solution à 10%), jusqu'au moment où l'électrode d'argent se colore uniformément (environ 5 min à 1.5 V). L'électrode est rincée rapidement à l'acide nitrique 6 *N*, puis à l'eau[11].

Quel que soit le soin apporté à la préparation des électrodes de référence Ag/AgCl, on observe souvent une différence de potentiel entre 2 électrodes préparées par la même méthode et plongées dans une même solution; cet écart peut être de l'ordre de 0.5 mV, ce qui est admissible d'après MACKAY *et al.*[12].

Etalonnage

Pour déterminer la concentration en acide nitrique de la phase aqueuse durant le titrage, il est indispensable de connaître E_0 et j de la relation (1). A cette fin, on place dans la cellule de mesures 35 ml de $NaNO_3$ 2 *M* et 10 ml de benzène. On ajoute alors, au moyen d'une burette, des volumes connus d'une solution contenant HNO_3 10^{-1} N et $NaNO_3$ 1.9 M. Après agitation mécanique de 15 min, on mesure la f.e.m. de

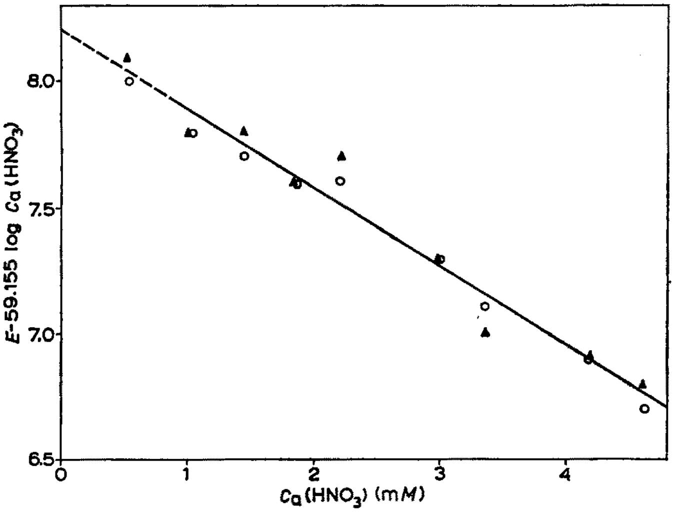


Fig. 1. Détermination des constantes E_0 et j. ○ en présence de 10 ml de benzène; ▲ en l'absence de benzène.

la pile à l'équilibre. Le liquide du pont de Wilhelm est renouvelé avant chaque mesure de potentiel afin de réduire au maximum les diffusions d'ions.

Si on porte en graphique $E-59.155 \log C_a(\mathrm{HNO_3})$ en fonction de $C_a(\mathrm{HNO_3})$, on obtient une droite de pente j (en mV/mM) dont l'extrapolation à $C_a(\mathrm{HNO_3})=0$ fournit E_0 (Fig. 1).

Les valeurs de E_0 et j varient quelque peu avec les différentes électrodes de référence, chacune étant utilisée durant une semaine. Les valeurs de E_0 se situent entre $+8.0$ et $+8.5$ mV et celles de j entre -0.025 et -0.031 mV/mM.

RÉSULTATS

(*a*) *Titrage de l'acide nitrique à la soude*

(1) Un certain volume d'une solution $5.0 \cdot 10^{-2}$ M en 1,5-DiPO dans le benzène est équilibré avec un volume égal d'une solution aqueuse de concentration connue en acide nitrique. La concentration en acide a été variée de 0.055 à 9.74 M. Des prélèvements dans les 2 phases à l'équilibre permettent la titration de $\mathrm{HNO_3}$ (Tableau I). Des mesures semblables ont été faites avec le 1,1-DiPO.

(2) Une solution aqueuse 10^{-2} N en $\mathrm{HNO_3}$ et 2 M en $\mathrm{NaNO_3}$ est équilibrée avec

TABLEAU I

DISTRIBUTION DE L'ACIDE NITRIQUE ENTRE LE 1,5-DiPO $5.00 \cdot 10^{-2}$ M DANS LE BENZÈNE ET UNE PHASE AQUEUSE

$C_a(\mathrm{HNO_3})$ (M)	$C_0(\mathrm{HNO_3})$ (M)	$C_0(\mathrm{HNO_3})_c$ (M)
0.055	0.0046	
0.072	0.0080	
0.086	0.0114	
0.0905	0.0120	
0.130	0.0205	
0.172	0.0283	
0.255	0.0447	
0.256	0.0437	
0.259	0.0410	
0.262	0.0410	
0.425	0.0649	
0.440	0.0600	
0.440	0.0638	
0.537	0.0690	
0.62	0.0774	
0.72	0.0800	
0.91	0.0876	
0.93	0.0885	
1.40	0.045	
1.40	0.097	
1.90	0.101	
3.84	0.110	0.109
5.86	0.138	0.130
7.82	0.182	0.162
9.74	0.259	0.213

TABLEAU II

DISTRIBUTION DE L'ACIDE NITRIQUE 10^{-2} *N* ENTRE LE 1,1-DiPO DANS LE BENZÈNE ET LE $NaNO_3$ 2 *M*

C_0^i(1,1-DiPO)·10^2 (M)	$C_0(HNO_3)\cdot 10^3$ (M)	$C_a(HNO_3)\cdot 10^3$ (M)
10.0	5.3	9.5
5.30	3.2	6.4
5.00	3.1	6.7
4.16	2.6	7.4
3.33	2.2	7.6
2.50	1.7	8.2
1.67	1.2	8.8
1.00	0.76	9.2
0.84	0.60	9.3

TABLEAU III

DISTRIBUTION DE L'ACIDE NITRIQUE 10^{-2} *N* ENTRE LE 1,4-DiPO DANS LE BENZÈNE ET LE $NaNO_3$ 2 *M*

C_0^i(1,4-DiPO)·10^3 (M)	$C_0(HNO_3)\cdot 10^3$ (M)	$C_a(HNO_3)\cdot 10^3$ (M)
23.7	4.8	5.1
19.8	4.2	5.7
15.8	3.3	6.6
11.9	2.9	7.0
7.95	1.95	8.1
5.0	1.4	8.6
4.0	1.1	8.9
2.5	0.7	9.3
1.95	0.5	9.2

TABLEAU IV

DISTRIBUTION DE L'ACIDE NITRIQUE 10^{-2} *N* ENTRE LE 1,5-DiPO DANS LE BENZÈNE ET LE $NaNO_3$ 2 *M*

C_0^i(1,5-DiPO)·10^3 (M)	$C_0(HNO_3)\cdot 10^3$ (M)	$C_a(HNO_3)\cdot 10^3$ (M)
3.0	0.9	9.0
3.3	0.95	9.1
4.0	1.20	8.8
5.0	1.30	8.5
5.5	1.57	8.2
9.1	2.55	7.5
10.0	2.70	7.6
14.9	3.30	6.5
16.5	3.84	6.2
18.2	4.14	5.9
20.0	4.20	5.9
27.5	4.96	4.7
30.0	6.2	3.8
40.0	6.9	3.3
50.0	8.1	1.9

TABLEAU V

DISTRIBUTION DE L'ACIDE NITRIQUE ENTRE UNE SOLUTION DE DIOXYDE DE DIPHOSPHINE DANS LE BENZÈNE ET UNE PHASE AQUEUSE DE FORCE IONIQUE CONSTANTE ($NO_3^- = 2$ *M*)

Phase aqueuse	C_0^i*(1,5-DiPO)*				C_0^i*(1,1-DiPO)*	
	0.0250 M		*0.0505 M*		*0.0966 M*	
	$C_a(HNO_3)$	$C_0(HNO_3)$	$C_a(HNO_3)$	$C_0(HNO_3)$	$C_a(HNO_3)$	$C_0(HNO_3)$
1. 10 ml HNO_3 10^{-1} *N* et $NaNO_3$ 1.9 *M* + 15 ml $NaNO_3$ 2 *M*	0.0365	0.021	0.032	0.039	0.0348 0.0346	0.026 0.026
2. 15 ml HNO_3 10^{-1} *N* et $NaNO_3$ 1.9 *M* + 15 ml $NaNO_3$ 2 *M*	0.047	0.0245	0.043	0.046	0.0447	0.030
3. 15 ml HNO_3 10^{-1} *N* et $NaNO_3$ 1.9 *M* + 10 ml $NaNO_3$ 2 *M*	0.055	0.026	0.050	0.048	0.0532	0.035
4. 10 ml HNO_3 $2 \cdot 10^{-1}$ *N* et $NaNO_3$ 1.8 *M* + 15 ml $NaNO_3$ 2 *M*	0.0755	0.0295	0.0685	0.0565	0.0722	0.042
5. 25 ml HNO_3 10^{-1} *N* et $NaNO_3$ 1.9 *M*	0.094	0.0312	0.088	0.060	0.0910	0.047
6. 50 ml HNO_3 10^{-1} *N* + $NaNO_3$ 1.9 *M*			0.091	0.061		
7. 15 ml HNO_3 $2 \cdot 10^{-1}$ *N* et $NaNO_3$ 1.8 *M* + 10 ml $NaNO_3$ 2 *M*	0.110	0.0320	0.106	0.064	0.1155	0.054
8. 25 ml HNO_3 $2 \cdot 10^{-1}$ *N* et $NaNO_3$ 1.8 *M* + 10 ml $NaNO_3$ 2 *M*	0.138	0.0342	0.184	0.072	0.132	0.057
9. 5 ml HNO_3 1 *N* et $NaNO_3$ 1 *M* + 20 ml $NaNO_3$ 2 *M*	0.193	0.0370	0.188	0.074	0.187	0.067
10. 10 ml HNO_3 1 *N* et $NaNO_3$ 1 *M* + 15 ml $NaNO_3$ 2 *M*			0.388	0.085	0.376	0.087
11. 15 ml HNO_3 1 *M* et $NaNO_3$ 1 *M*	0.595	0.0443	0.595	0.091	0.585	0.099

TABLEAU VI

TITRAGE POTENTIOMÉTRIQUE À 2 PHASES DE 10 ml DE 1,5-DiPO $5.05 \cdot 10^{-2}$ *M* DANS LE BENZÈNE PAR UNE SOLUTION DE HNO_3 0.100 *N* + $NaNO_3$ 1.9 *M* (1ÈRE EXPÉRIENCE)

(Volume initial de la phase aq.: 35 ml; E_0: 8.0 mV; j: − 0.026 mV/m*M*)

No.	*ml solution HNO_3 0.100 N + $NaNO_3$ 1.9 M ajoutés*	*Volume total de la phase aqueuse*	*$E-E_0$ (mV)*	*$j\,C_a(HNO_3)$ (mV)*	*$E-E_0-j\,C_a(HNO_3)$ (mV)*	*$C_a(HNO_3) \cdot 10^3$ (M)*	n_a[a] *(mM)*	n_0[a] *(mM)*	*$C_0(HNO_3) \cdot 10^3$ (M)*
1	1	36	− 165.2	—	− 165.2	1.61	0.058	0.042	4.2
2	1.5	36.5	− 154.5	− 0.1	− 154.4	2.45	0.089	0.061	6.1
3	2	37	− 146.9	− 0.1	− 146.8	3.30	0.122	0.078	7.8
4	2.5	37.5	− 141.1	− 0.1	− 141.0	4.14	0.155	0.095	9.5
5	3	38	− 136.4	− 0.1	− 136.3	4.96	0.188	0.112	11.2
6	3.5	38.5	− 132.7	− 0.1	− 132.6	5.73	0.221	0.129	12.9
7	4	39	− 129.1	− 0.2	− 128.9	6.62	0.258	0.142	14.2
8	5	40	− 123.5	− 0.2	− 123.3	8.24	0.330	0.170	17.0
9	6	41	− 118.7	− 0.3	− 118.4	9.94	0.408	0.192	19.2
10	7	42	− 114.9	− 0.3	− 114.6	11.4	0.479	0.221	22.1
11	8	43	− 111.6	− 0.3	− 111.3	13.1	0.563	0.237	23.7
12	9	44	− 108.7	− 0.4	− 108.3	14.8	0.651	0.249	24.9
13	10	45	− 106.2	− 0.4	− 105.8	16.3	0.734	0.266	26.6
14	11	46	− 104.1	− 0.5	− 103.6	17.7	0.814	0.286	28.6
15	12	47	− 101.9	− 0.5	− 101.4	19.3	0.907	0.293	29.3
16	13	48	− 100.3	− 0.5	− 99.8	20.6	0.989	0.311	31.1
17	14	49	− 98.5	− 0.6	− 97.9	22.1	1.083	0.317	31.7
18	15	50	− 97.1	− 0.6	− 96.5	23.4	1.170	0.330	33.0
19	16	51	− 95.6	− 0.6	− 95.0	24.8	1.265	0.335	33.5
20	17	52	− 94.4	− 0.7	− 93.7	26.1	1.357	0.343	34.3
21	18	53	− 93.3	− 0.7	− 92.6	27.2	1.442	0.358	35.8
22	19	54	− 92.2	− 0.7	− 91.5	28.3	1.528	0.372	37.2
23	20	55	− 91.3	− 0.8	− 90.5	29.5	1.623	0.377	37.7
24	22	57	− 89.5	− 0.8	− 88.7	31.7	1.807	0.393	39.3
25	24	59	− 87.7	− 0.9	− 86.8	34.1	2.012	0.388	39.8
26	26	61	− 86.3	− 0.9	− 85.4	36.0	2.196	0.404	40.4
27	28	63	− 85.1	− 1.0	− 84.1	37.9	2.388	0.412	41.2
28	30	65	− 84.1	− 1.0	− 83.1	39.4	2.561	0.439	43.9

[a] n_a, n_0: nombre de millimoles de HNO_3 respectivement dans les phases aqueuse et organique.

un volume égal de phase benzénique de concentration connue en 1,1-DiPO (Tableau II), en 1,4-DiPO (Tableau III) ou en 1,5-DiPO (Tableau IV).

(*3*) 5 ml d'une solution de 1,5-DiPO soit 0.0250 *M*, soit 0.0505 *M* sont équilibrés avec des volumes variables (de 25 à 50 ml) d'une solution aqueuse (xHNO$_3$+ yNaNO$_3$=2 *M*) permettant de neutraliser jusqu'à 90% des groupements PO du dioxyde de diphosphine (Tableau V). Des mesures identiques ont été effectuées avec le 1,1-DiPO (Tableau V).

(*b*) *Titrage potentiométrique à 2 phases*

Trois séries d'expériences ont été réalisées à partir de systèmes biphasés contenant initialement 35 ml de NaNO$_3$ 2 *M* et 10 ml d'une solution de 1,5-DiPO soit 0.0250 *M*, soit 0.0505 *M*, soit 0.0623 *M* dans le benzène (Tableaux VI, VII, VIII et IX).

TABLEAU VII

TITRAGE POTENTIOMÉTRIQUE À 2 PHASES DE 10 ml DE 1,5-DiPO $5.05 \cdot 10^{-2}$ *M* DANS LE BENZÈNE PAR UNE SOLUTION DE HNO$_3$ 0.100 *N* + NaNO$_3$ 1.9 *M* (2ÈME EXPÉRIENCE)

(Volume initial de la phase aq.: 35 ml; E_0: 8.1 mV; j: − 0.027 mV/m*M*)

No.	*ml solution HNO$_3$ 0.100 N + NaNO$_3$ 1.9 M ajoutés*	$E-E_0-j\,C_a(HNO_3)$ *(mV)*	$C_a(HNO_3)\cdot 10^3$ *(M)*	$C_0(HNO_3)\cdot 10^3$ *(M)*
1	1	− 164.7	1.64	4.1
2	1.5	− 153.9	2.50	5.9
3	2	− 146.6	3.33	7.7
4	2.5	− 140.9	4.15	9.4
5	3	− 136.2	4.98	11.1
6	3.5	− 132.2	5.82	12.6
7	4	− 128.9	6.62	14.2
8	5	− 123.1	8.30	16.8
9	6	− 118.3	10.0	19.0
10	7	− 114.6	11.6	21.3
11	8	− 111.2	13.2	23.2
12	9	− 108.6	14.7	25.3
13	10	− 106.0	16.2	27.1
14	11	− 103.5	17.8	28.1
15	12	− 101.5	19.2	29.8
16	13	− 99.7	20.6	31.1
17	14	− 98.0	22.1	31.7
18	15	− 96.6	23.3	33.5
19	16	− 95.1	24.7	34.0
20	17	− 93.8	26.0	34.8
21	18	− 92.5	27.3	35.3
22	19	− 91.5	28.4	36.6
23	20	− 90.5	29.5	37.7
24	22	− 88.6	31.8	38.7
25	24	− 86.9	34.0	39.4
26	26	− 85.5	35.9	41.0
27	28	− 84.0	38.0	40.6
28	30	− 83.1	39.4	39.4

TABLEAU VIII

TITRAGE POTENTIOMÉTRIQUE À 2 PHASES DE 10 ml DE 1,5-DiPO $2.50\cdot 10^{-2}$ *M* DANS LE BENZÈNE PAR UNE SOLUTION DE HNO_3 0.101 *N* + $NaNO_3$ 1.9 *M*

(Volume initial de la phase aq.: 35 ml; E_0 = 8.0 mV; j = − 0.027 mV/m*M*)

ml solution HNO_3 0.101 N + $NaNO_3$ 1.9 M ajoutés	*$E-E_0-j\,C_a(HNO_3)$ (mV)*	*$C_a(HNO_3)\cdot 10^3$ (M)*	*$C_0(HNO_3)\cdot 10^3$ (M)*
1	− 158.0	2.13	2.4
1.5	− 147.3	3.24	3.55
2	− 139.9	4.31	4.20
2.5	− 134.3	5.37	5.15
3	− 129.7	6.42	5.90
3.5	− 125.3	7.62	6.05
4	− 122.4	8.53	7.10
5	− 117.0	10.52	8.40
6	− 112.4	12.6	8.90
7	− 109.0	14.4	10.3
8	− 106.0	16.2	11.4
9	− 103.3	17.9	12.0
10	− 101.1	19.5	13.1
11	− 98.8	21.4	12.8

INTERPRÉTATION DES RÉSULTATS

Méthode de calcul des constantes d'équilibre

En négligeant, en première approximation, le rôle de l'eau d'hydratation du dioxyde de diphosphine, nous pouvons considérer les 2 réactions:

$$H^+_a + NO_3{}^-_a + DiPO_0 \rightleftharpoons DiPO\cdot HNO_{3_0} \qquad (2)$$

et

$$H^+_a + NO_3{}^-_a + DiPO\cdot HNO_{3_0} \rightleftharpoons DiPO\cdot 2\ HNO_{3_0} \qquad (3)$$

auxquelles nous pouvons appliquer la loi d'action des masses

$$K_I = \frac{[DiPO\cdot HNO_3]_0\gamma_2}{a_{HNO_3}[DiPO]_0\gamma_1} \qquad (4)$$

et

$$K_{II} = \frac{[DiPO\cdot 2\ HNO_3]\ \gamma_3}{a_{HNO_3}[DiPO\cdot HNO_3]_0\gamma_2} \qquad (5)$$

où a_{HNO_3} est l'activité stoechiométrique de l'acide nitrique[3], $[DiPO\cdot HNO_3]_0$ et $[DiPO\cdot 2\ HNO_3]_0$ représentent les concentrations molaires des 2 complexes en phase organique à l'équilibre tandis que γ_1, γ_2 et γ_3 sont les coefficients d'activité de $DiPO_0$, de $DiPO\cdot HNO_{3_0}$ et de $DiPO\cdot 2\ HNO_{3_0}$.

Dans les expériences menées à force ionique constante ($NO_3^- = 2$ *M*), et en supposant les coefficients d'activité des espèces présentes en phase organique constants, les équilibres (4) et (5) deviennent:

$$K_I'' = \frac{[DiPO\cdot HNO_3]_0}{C_a(HNO_3)\ [DiPO]_0} \qquad (6)$$

TABLEAU IX

TITRAGE POTENTIOMÉTRIQUE À 2 PHASES DE 10 ml DE 1,5-DiPO $6.23 \cdot 10^{-2}$ M DANS LE BENZÈNE PAR UNE SOLUTION DE HNO_3 0.101 N + $NaNO_3$ 1.9 M

(Volume initial de la phase aq.: 35 ml; E_0: 8.1 mV; j: − 0.028 mV/mM)

ml solution HNO_3 0.101 N + $NaNO_3$ 1.9 M ajoutés	*$E-E_0-j\,C_a(HNO_3)$ Moyenne 2 essais (mV)*	*$C_a(HNO_3)\cdot 10^3$ (M)*	*$C_0(HNO_3)\cdot 10^2$ (M)*
2	− 149.1	3.02	0.88
2.5	− 143.3	3.78	1.10
3	− 138.2	4.61	1.28
3.5	− 134.4	5.35	1.48
4	− 130.8	6.15	1.64
5	− 124.8	7.77	1.94
6	− 120.2	9.29	2.25
7	− 116.3	10.8	2.53
8	− 112.9	12.3	2.79
9	− 109.8	14.0	2.93
10	− 107.1	15.5	3.12
11	− 104.8	16.9	3.34
12	− 102.7	18.9	3.47
13	− 100.7	19.9	3.58
14	− 99.0	21.2	3.75
15	− 97.9	22.1	4.10
16	− 96.4	23.5	4.17
17	− 95.0	24.8	4.27
18	− 93.6	26.2	4.29
19	− 92.6	27.2	4.50
20	− 91.6	28.2	4.69
22	− 89.7	30.5	4.83
24	− 87.9	32.7	4.95
26	− 86.5	34.5	5.21
28	− 85.0	36.6	5.22
30	− 83.8	38.3	5.40
35	− 81.1	42.6	5.53
40	− 78.9	46.4	5.60

et

$$K_{II}'' = \frac{[\mathrm{DiPO}\cdot 2\ \mathrm{HNO_3}]_0}{C_a(\mathrm{HNO_3})\ [\mathrm{DiPO}\cdot\mathrm{HNO_3}]_0} \qquad (7)$$

Comme dans la méthode de titrage potentiométrique, nous travaillons avec des volumes de phases différents, le bilan d'acidité s'écrira:

$$C_a^i(\mathrm{HNO_3}) = C_a(\mathrm{HNO_3}) + \{[\mathrm{DiPO}\cdot\mathrm{HNO_3}]_0 + 2\ [\mathrm{DiPO}\cdot 2\ \mathrm{HNO_3}]_0\}\ \frac{V_0}{V_a} \qquad (8)$$

où V_0 et V_a sont les volumes des phases organique et aqueuse. De plus, le bilan de l'acide nitrique en phase organique vaut

$$C_0(\mathrm{HNO_3}) = [\mathrm{DiPO}\cdot\mathrm{HNO_3}]_0 + 2[\mathrm{DiPO}\cdot 2\ \mathrm{HNO_3}]_0 \qquad (9)$$

tandis que

$$C_0{}^1(\text{DiPO}) = [\text{DiPO}]_0 + [\text{DiPO}\cdot\text{HNO}_3]_0 + [\text{DiPO}\cdot 2\ \text{HNO}_3]_0 \tag{10}$$

En combinant (6), (7), (8) et (10), on obtient

$$K_{\text{I}}''K_{\text{II}}'' \frac{C_a{}^2(\text{HNO}_3)\ [C_a{}^1(\text{HNO}_3) - C_a(\text{HNO}_3) - 2C_0{}^1\ (\text{DiPO})\ V_0/V_a]}{C_a{}^1(\text{HNO}_3) - C_a(\text{HNO}_3)} +$$
$$K_{\text{I}}'' \frac{C_a(\text{HNO}_3)\ [C_a{}^1(\text{HNO}_3) - C_a(\text{HNO}_3) - C_0{}^1(\text{DiPO})\ V_0/V_a]}{C_a{}^1(\text{HNO}_3) - C_a(\text{HNO}_3)} + 1 = 0 \tag{11}$$

Cette dernière équation est celle d'une droite et nous permet le calcul de K_{I}'' et de K_{II}'': en effet,

$$K_{\text{I}}''K_{\text{II}}''x + K_{\text{I}}''y + 1 = 0 \tag{12}$$

La pente $dy/dx = -K_{\text{II}}''$ et la valeur de l'ordonnée pour $x = 0$ donne $-1/K_{\text{I}}''$.

Résultats à force ionique constante

Concentration constante en réactif basique. Le calcul des x et y a été effectué à l'aide d'un ordinateur IBM 7040 avec un programme Fortran établi par le Dr. F. CALIGARA de l'Euratom. Nous pouvons constater, dans la Fig. 2, qu'en portant x en fonction de y pour le 1,5-DiPO, par exemple, nous obtenons une droite dans tout le domaine de neutralisation des 2 groupements PO. Ceci démontre que nos hypothèses de départ concernant tant la stoechiométrie des complexes que la constance des coefficients d'activité sont correctes: nous pouvons alors calculer K_{I}'' et K_{II}''. Le Tableau X résume les résultats provenant soit des titrages classiques, soit du titrage potentiométrique à 2 phases pour le 1,5-DiPO. Il apparaît que les 2 PO ont une basicité

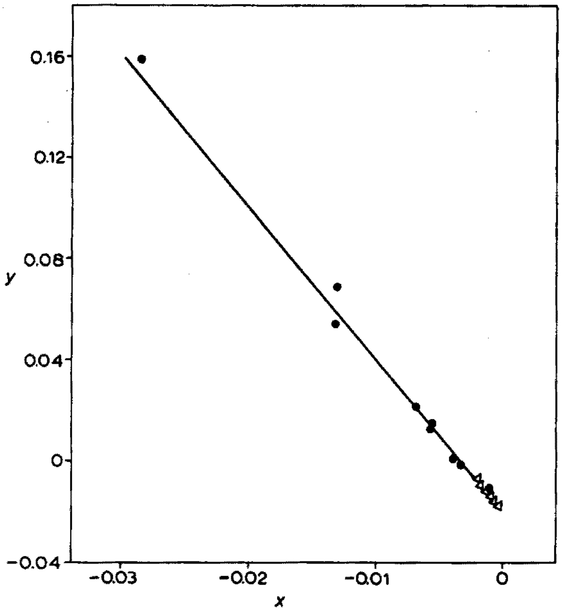


Fig. 2. Détermination graphique des constantes K_{I}'' et K_{II}''. $C_0{}^1$(1,5-DiPO) = $5.05\cdot10^{-2}$ M dans le benzène. ● Titrage classique à la soude; ▽ titrage potentiométrique à 2 phases.

TABLEAU X

DÉTERMINATION DES CONSTANTES K_I'' ET K_{II}'' POUR LES COMPLEXES FORMÉS ENTRE LE 1,5-DiPO ET L'AC NITRIQUE

Concn. (M)	*Résultats fournis par le titrage potentiométrique à 2 phases*		*Résultats fournis par la méthode de titrage classique*		*Résultats combinés*		*Résultat moyen*	
	K_I'' $(M)^{-1}$	K_{II}'' $(M)^{-1}$	K_I'' $(M)^{-1}$	K_{II}'' $(M)^{-1}$	K_I'' $(M)^{-1}$	K_{II}'' $(M)^{-1}$	K_I'' $(M)^{-1}$	K_{II}'' $(M)^-$
0.0250	47 ± 2	—	—	6.0 ± 0.05	46 ± 2	6.2 ± 0.1		
0.0505	54 ± 1	5.3 ± 0.2	54 ± 5	6.1 ± 0.2	52 ± 1	6.1 ± 0.05	51 ± 1	6.2 ± 0.0
0.0623	53 ± 1	6.1 ± 0.3	—	—	—			

suffisamment différente que pour être déterminée. Cette constatation est également vérifiée pour le 1,1-DiPO pour lequel on trouve

$$K_I'' = 9.8 \pm 0.1\ (M)^{-1} \text{ et } K_{II}'' = 0.35 \pm 0.01\ (M)^{-1}$$

Concentration variable en réactif basique. Il apparaît qu'aux faibles concentrations en acide (Fig. 3) ($<0.01\ N$), le groupement PO le plus basique est pratiquement le seul à réagir avec l'acide nitrique. Ce résultat a été prouvé pour les 1,1-DiPO, 1,4-DiPO et 1,5-DiPO en déterminant la distribution de l'acide nitrique $10^{-2}\ N$

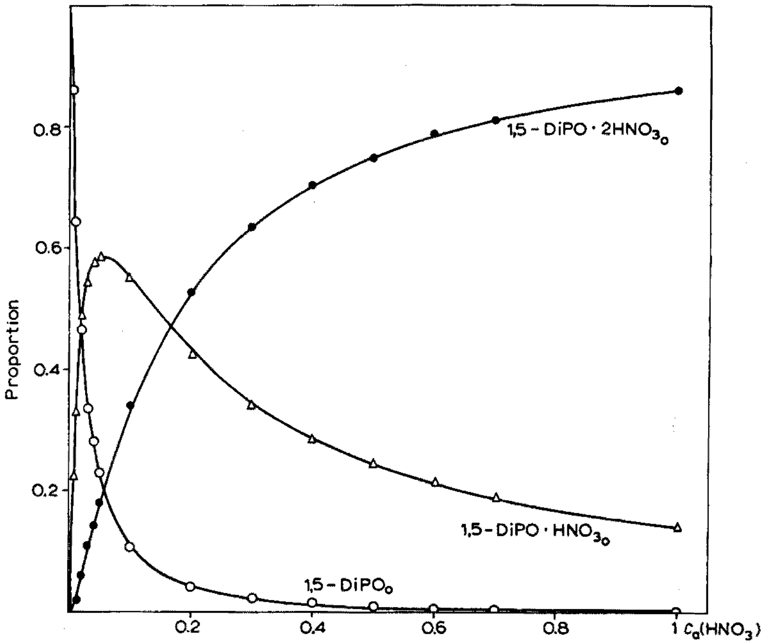


Fig. 3. Evolution des formes libre et associées de 1,5-DiPO en fonction de l'acidité.

entre $NaNO_3$ 2 M et une solution benzénique de dioxyde de diphosphine (Tableaux II à IV). Ces mesures permettent de calculer K_I'' respectivement pour le 1,1-DiPO·HNO_3 (9.2±0.4 $(M)^{-1}$), pour le 1,4-DiPO·HNO_3 (44±3 $(M)^{-1}$) et pour le 1,5-DiPO·HNO_3 (47±3$(M)^{-1}$).

Ces valeurs sont en accord satisfaisant avec les résultats fournis dans le paragraphe précédent et le Tableau X.

Résultats à force ionique variable

La mesure de la distribution de l'acide entre l'eau et le 1,5-DiPO 0.0500 M dans le benzène permet également de calculer la constante de stabilité du complexe 1,5-DiPO·HNO_3 et celle de 1,5-DiPO·2 HNO_3. En supposant les rapports γ_2/γ_1 et γ_3/γ_2 des équations générales (4) et (5) constants, on peut écrire

$$K_I' = \frac{[1{,}5\text{-DiPO}\cdot HNO_3]_0}{a_{HNO_3}[1{,}5\text{-DiPO}]_0} \qquad (13)$$

$$K_{II}' = \frac{[1{,}5\text{-DiPO}\cdot 2\ HNO_3]_0}{a_{HNO_3}[1{,}5\text{-DiPO}\cdot HNO_3]_0} \qquad (14)$$

Comme $C_0(HNO_3)$ est une donnée expérimentale et $V_0/V_a = 1$, (11) est modifié en conséquence

$$K_I'K_{II}' \frac{a^2_{HNO_3}\{C_0(HNO_3) - 2\,C_0^1(1{,}5\text{-DiPO})\}}{C_0(HNO_3)} + K_I' \frac{a_{HNO_3}\{C_0(HNO_3) - C_0^1(1{,}5\text{-DiPO})\}}{C_0(HNO_3)} + 1 = 0 \qquad (15)$$

On déduit de cette éqn. (15), par la même méthode que celle décrite plus haut:

$K_I' = 54 \pm 7\ (M)^{-2}$ et $K_{II}' = 6.5 \pm 0.4\ (M)^{-2}$ à 25°.

Pour le 1,1-DiPO, on trouve

$K_I' = 10.2 \pm 0.9\ (M)^{-2}$ et $K_{II}' = 0.35 \pm 0.02\ (M)^{-2}$

à la même température.

CONCLUSIONS

De l'examen des résultats obtenus, il ressort que les 1,4-DiPO et 1,5-DiPO ont une basicité sensiblement égale et supérieure à celle du 1,1-DiPO[13]. Le 1,4-DiPO présente le désavantage d'être peu soluble dans le benzène (sa solubilité dans le benzène anhydre est de 0.048 M à 25°). Aucune indication concernant la formation d'un complexe de chélation entre les dioxydes de diphosphine et l'acide nitrique n'a été relevée dans nos conditions expérimentales.

Nous tenons à remercier Euratom et spécialement le Dr. J. KOOI ainsi que l'Institut Interuniversitaire des Sciences Nucléaires pour les subsides accordés à notre laboratoire. Que Mr. F. GILNAY soit aussi remercié pour son aide technique.

RÉSUMÉ

La distribution de l'acide nitrique entre une phase aqueuse de force ionique soit constante, soit variable et une phase benzénique de dioxyde de diphosphine peut s'expliquer par les réactions suivantes:

$$H^+_a + NO_3{}^-_a + DiPO_0 \rightleftharpoons DiPO \cdot HNO_{3_0}$$

$$H^+_a + NO_3{}^-_a + DiPO \cdot HNO_{3_0} \rightleftharpoons DiPO \cdot 2\ HNO_{3_0}$$

A force ionique constante, les constantes de stabilité (K_I'') pour les complexes 1,1-DiPO·HNO$_3$ (9.8±0.1 $(M)^{-1}$), 1,4-DiPO·HNO$_3$ (44±3 $(M)^{-1}$) et 1,5-DiPO·HNO$_3$ (51±1 $(M)^{-1}$) ont été déterminées. Les constantes K_{II}'' pour les complexes 1,1-DiPO·2 HNO$_3$ et 1,5-DiPO·2 HNO$_3$ valent respectivement 0.35 ±0.01 $(M)^{-1}$ et 6.2±0.05 $(M)^{-1}$ à 25°. A force ionique variable, des valeurs de $K_I'=54\pm7$ $(M)^{-2}$ pour le 1,5-DiPO·HNO$_3$ et de $K_{II}'=6.5\pm0.4$ $(M)^{-2}$ pour le 1,5-DiPO·2 HNO$_3$ ont été obtenues.

SUMMARY

The distribution of nitric acid between an aqueous phase of constant or variable ionic strength and a benzene solution of diphosphine dioxide can be explained by the following reactions

$$H^+_a + NO_3{}^-_a + DiPO_0 \rightleftharpoons DiPO \cdot HNO_{3_0}$$

$$H^+_a + NO_3{}^-_a + DiPO \cdot HNO_{3_0} \rightleftharpoons DiPO \cdot 2\ HNO_{3_0}$$

At constant ionic strength, the stability constants K_I'' were determined for the complexes 1,1-DiPO·HNO$_3$ (9.8±0.1 $(M)^{-1}$), 1,4-DiPO·HNO$_3$ (44±3 $(M)^{-1}$) and 1,5-DiPO·HNO$_3$ (51±1 $(M)^{-1}$). The constants K_{II}'' for the complexes 1,1-DiPO·2 HNO$_3$ and 1,5-DiPO·2 HNO$_3$ are respectively 0.35±0.01 $(M)^{-1}$ and 6.2 ±0.05 $(M)^{-1}$ at 25°. With an aqueous phase of variable ionic strength, values of $K_I'=54\pm7$ $(M)^{-2}$ for 1,5-DiPO·HNO$_3$ and $K_{II}'=6.5 \pm 0.4$ $(M)^{-2}$ for 1,5-DiPO·2 HNO$_3$ were obtained.

ZUSAMMENFASSUNG

Die Verteilung der Salpetersäure zwischen einer wässrigen Phase konstanter oder veränderlicher Ionenstärke und einer benzolischen Lösung von Diphosphindioxiden kann durch folgende Reaktionen interpretiert werden:

$$H^+_a + NO_3{}^-_a + DiPO_0 \rightleftharpoons DiPO \cdot HNO_{3_0}$$

$$H^+_a + NO_3{}^-_a + DiPO \cdot HNO_{3_0} \rightleftharpoons DiPO \cdot 2\ HNO_{3_0}$$

Bei konstanter Ionenstärke wurden die Stabilitätskonstanten K_I'' der folgenden Komplexe bestimmt: 1,1-DiPO·HNO$_3$ (9.8±0.1 $(M)^{-1}$), 1,4-DiPO·HNO$_3$ (44±3 $(M)^{-1}$) und 1,5-DiPO·HNO$_3$ (51±1 $(M)^{-1}$). Die Werte der Konstanten K_{II}'' der

Komplexe 1,1-DiPO·2 HNO_3 und 1,5-DiPO·2 HNO_3 betragen: 0.35 ± 0.01 $(M)^{-1}$ und 6.2 ± 0.05 $(M)^{-1}$ bei 25°. Bei veränderlicher Ionenstärke wurden die Werte $K_I' = 54 \pm 7$ $(M)^{-2}$ für 1,5-DiPO·HNO_3 und $K_{II}' = 6.5 \pm 0.4$ $(M)^{-2}$ für 1,5-DiPO·2 HNO_3 erhalten.

BIBLIOGRAPHIE

1 J. Goffart et G. Duyckaerts, *Anal. Chim. Acta*, 36 (1966) 499.
2 J. Goffart et G. Duyckaerts, *Anal. Chim. Acta*, 38 (1967) 529.
3 W. Davis et H. J. de Bruin, *J. Inorg. & Nucl. Chem.*, 26 (1964) 1069.
4 K. Issleib et A. Brack, *Z. Anorg. Allgem. Chem.*, 227 (1954) 260.
5 J. V. Braun et W. Sobecki, *Ber.*, 44, 2 (1911) 1918.
6 J. Goffart, *Rapport Annuel Euratom*, 1964–1965.
7 J. J. Richard, K. E. Burke, J. M. O'Laughlin et C. V. Banks, *J. Am. Chem. Soc.*, 83 (1961) 1722.
8 J. A. Walmsley et S. Y. Tyree, *Inorg. Chem.*, 2 (1963) 312.
9 E. Högfeldt et F. Fredlund, *Trans. Roy. Inst. Technol., Stockholm*, 226, 1964.
10 L. Martinot et F. Caligara, Communication personnelle.
11 T. W. Olcott, *A.E.C. Report AECU. 3372*, 1956.
12 H. A. C. MacKay, J. H. Miles et M. J. Waterman, *J. Chem. Soc.*, 4209 (1965).
13 J. E. Mrochek et C. V. Banks, *J. Inorg. & Nucl. Chem.*, 27 (1965) 589.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DOSAGE DU PLUTONIUM DANS LES ALLIAGES PLUTONIUM–ALUMINIUM PAR FLUORESCENCE-X

M. GANIVET ET TH. ARNAL
Services des Eléments Combustibles au Plutonium et d'Etudes Radiométallurgiques, Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires de Cadarache (France)

(Reçu le 29 décembre, 1966)

Le dosage du plutonium dans les alliages plutonium–aluminium est réalisé d'une façon courante en France par potentiométrie à intensité constante[1]. Cette méthode est précise, ne subit pas d'interférence dûe à la présence du fer, mais est longue et délicate; elle est peu adaptée à un contrôle de série lié aux fabrications d'éléments combustibles.

Nous avons cherché une méthode rapide, de mise en oeuvre aisée et d'une précision suffisante, permettant de doser le plutonium. L'analyse par fluorescence-X nous a donné satisfaction sur ces différents points.

Principe de la méthode

Le dosage du plutonium se fait en solution pour éliminer les causes d'erreur dûes à l'état de surface de l'alliage. La raie $L\alpha$ du plutonium est excitée par le rayonnement-X émis par un tube à anticathode de molybdène. L'intensité de la raie $L\alpha$ est comparée à une raie $K\alpha$ Compton du molybdène qui lui est voisine.

Cette méthode utilisée déjà par ANDERMAN ET KEMP[2] permet d'éliminer les influences de la matrice et de l'instabilité de l'électronique.

Ce procédé a l'avantage de donner des courbes d'étalonnage indépendantes de la matrice dans une large mesure, linéaires dans un grand domaine de concentration en plutonium, ainsi que nous le verrons plus loin. De plus, il est possible de travailler à courbe fixe, ce qui évite un étalonnage fastidieux.

PARTIE EXPÉRIMENTALE

Appareillage

L'appareil utilisé est un spectromètre de fluorescence-X LAMBDA 100 de la Compagnie Générale de Radiologie. Sa puissance est de 2.5 kW et la tension maximum d'utilisation 100 kV. Le tube est à anticathode de molybdène.

Le passeur d'échantillon a été adapté en boîte à gants extrêmement facilement en raison de la disposition des différents organes de l'appareil. La géométrie est telle que l'angle Φ utilisé pour le calcul de la longueur d'onde de la diffusion Compton est très favorable (Fig. 1).

Le Tableau I donne la valeur de l'angle θ et la longueur d'onde de la raie $K\alpha$ Compton du molybdène.

Les opérations de mise en solution se font dans une boîte à gants particulière.

Le remplissage des porte-échantillons se fait dans une boîte à gants attenante à l'ensemble de spectrométrie.

Mode opératoire

La mise en solution des alliages plutonium–aluminium se fait en milieu acide nitrique 5.5 M–nitrate mercurique $5 \cdot 10^{-4}$ M. Pour être assuré d'avoir un échantillon représentatif, 15 à 20 g d'alliage plutonium–aluminium sont mis en solution. La solution à analyser est ajustée à 500 ml avec de l'acide nitrique normal de façon à être à une concentration convenable en plutonium.

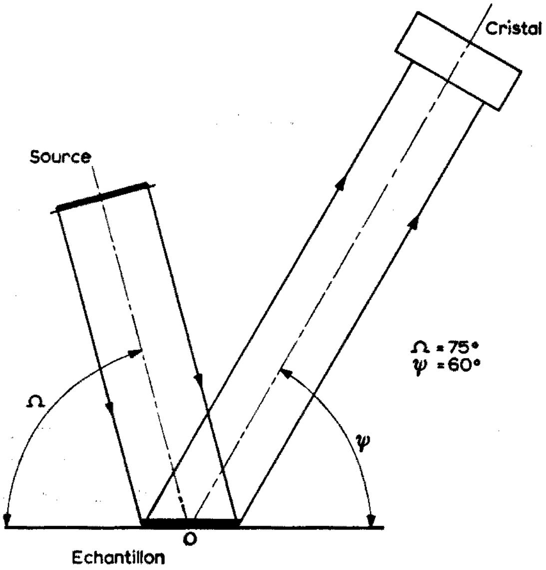


Fig. 1. Géométrie du spectromètre.

TABLE I

VALEUR DE L'ANGLE θ ET DE LA LONGUEUR D'ONDE DE LA RAIE Kα COMPTON DU MOLYBDÈNE

Φ 75° + 60° (°)	$\Delta\lambda$ 0.0247(1 − cos Φ) (Å)	*Kα Mo*		*Kα Mo Compton*	
		λ(Å)	θ(°)	λ(Å)	θ(°)
135	0.0413	0.7092	10.16	0.7505	10.75

L'analyse spectrométrique est réalisée sur 2 prises d'essai placées dans les porte-échantillons du spectromètre. Chaque porte-échantillon renferme 4 ml de solution.

Les conditions opératoires sont indiquées sur le Tableau II.

Pour obtenir une bonne précision, on doit compter environ $3 \cdot 10^5$ coups pour la raie Lα du plutonium; le comptage sur la raie Mo Kα est toujours supérieur du fait de la nature de la matrice.

On calcule ensuite le rapport:

$$k = \frac{N_{\mathrm{L\alpha\,Pu}}}{N'_{\mathrm{K_\alpha Compton\,Mo}}} \qquad (1)$$

TABLE II

CONDITIONS OPÉRATOIRES

Excitation	Tension Intensité	80 kV 31 mA	
Nature du cristal analyseur		LiF	
Fentes (en mm)		2 × 2 × 2	
Réglage de l'amplification	Seuil Canal	38 V 44 V	
Tension compteur		900 V	
Raies d'analyse	Pu Lα Mo Compton	$\lambda = 0.866$ $\lambda = 0.7505$	$\theta^\circ = 12.43$ $\theta^\circ = 10.75$

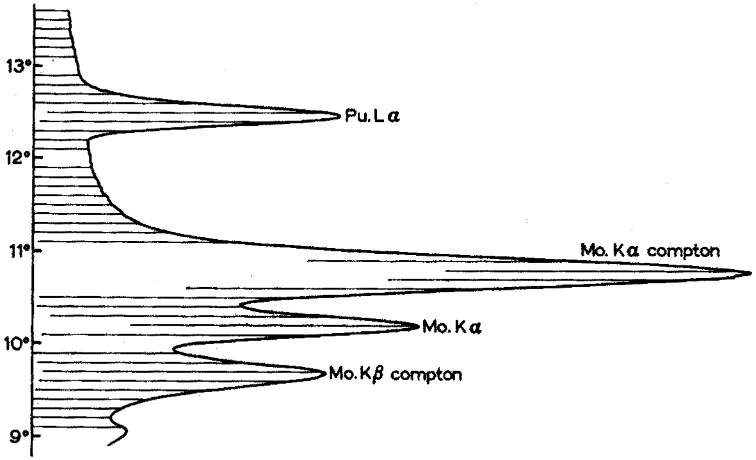


Fig. 2. Position relative des raies Pu Lα et Mo Kα Compton.

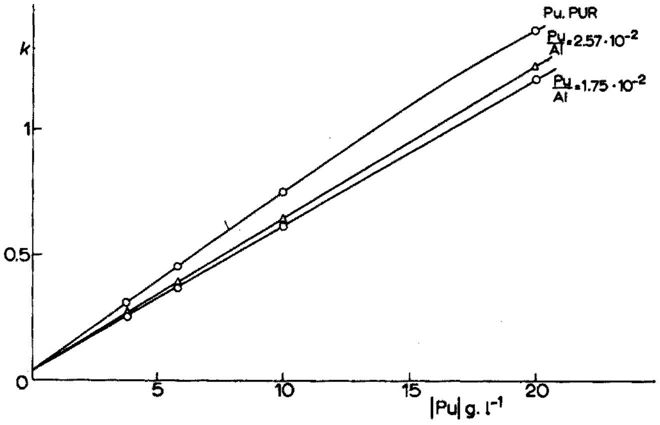


Fig. 3. Courbes d'étalonnage.

On lit la teneur en plutonium sur une courbe:

$$k = \mathrm{f}([\mathrm{Pu}])$$

établie par étalonnage préalable. Cet étalonnage est réalisé à partir d'une solution titrée de plutonium contenant des ions aluminium. La Fig. 2 montre l'enregistrement obtenu pour une solution à 3.5 g/l plutonium et 23 g/l aluminium. La Fig. 3 montre les courbes d'étalonnage pour différents rapports [Pu]/[Al].

DISCUSSION DU MODE OPÉRATOIRE

Les différents facteurs ayant une influence sur la qualité du dosage ont été examinés.

Nature de l'échantillon

L'analyse sur échantillon solide devrait avoir l'avantage d'une plus grande rapidité et d'une meilleure sensibilité. Toutefois, la précision est médiocre en raison de l'épaisseur critique de l'aluminium. Or, il est difficile d'obtenir un état de surface parfait. De plus, sur solide, on n'analyse qu'une très faible partie de l'échantillon.

Pour ces deux raisons, nous préférons opérer sur une solution.

Caractéristiques de la solution

Influence de l'acidité. On a vérifié que l'acidité du milieu est sans influence sur le rapport k (v. eq. (1)).

Toutefois, en raison de la faible solubilité du nitrate d'aluminium en milieu fortement acide, on évitera de travailler à une acidité supérieure à 3 N.

D'autre part, pour éviter l'hydrolyse des ions aluminium et plutonium, on se placera à une acidité supérieure à 1 N.

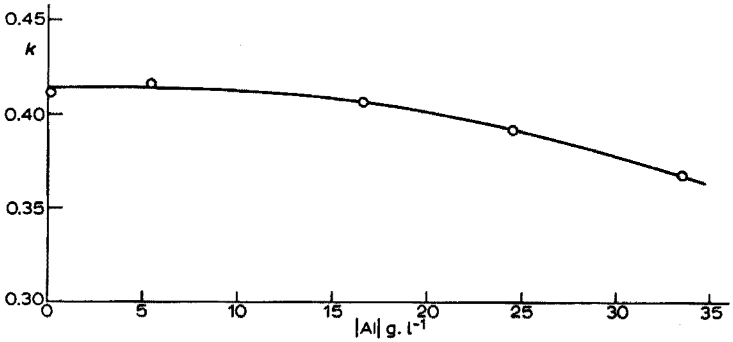


Fig. 4. Influence de la teneur en aluminium. Variation du facteur analytique en fonction de la concentration en aluminium.

Influence de la teneur en aluminium. Les analyses sur combustibles nucléaires sont pratiquées sur des échantillons dont les teneurs en plutonium et aluminium varient relativement peu. La Fig. 4 montre les variations d'absorption dûes à l'aluminium.

Influence de la teneur en plutonium. Indépendamment de la précision cherchée, la limite inférieure de dosage est fixée par le taux de comptage obtenu sur la raie $L\alpha$ du plutonium pour un temps raisonnable (100 sec). Cette limite est de 0.1 g/l.

La limite supérieure est fixée de 2 façons différentes: dans le cas des faibles teneurs en aluminium par la non linéarité de la courbe de dosage au-delà d'une concentration en plutonium de 20 g/l; et dans le cas de fortes teneurs en aluminium par la saturation de la solution en nitrate d'aluminium. Le Tableau III montre ces limites.

TABLE III

LIMITES DE DOSAGE DU PLUTONIUM

Teneur en plutonium de l'alliage (%)	*Limite inférieure (g/l)*		*Limite supérieure (g/l)*
	Ecart type relatif		
	$1\% < \sigma\% < 3\%$	$\sigma\% \leqslant 1\%$	
1	0.1		0.65[a]
10	0.1	3.6	7
50	0.1	3.6	20

[a] Limites dûes à la saturation de la solution en nitrate d'aluminium.

AVANTAGES DE LA MÉTHODE

Par rapport à la méthode utilisant uniquement le comptage de la raie $L\alpha$ du plutonium, l'usage de la raie Compton du molybdène permet:

(*a*) d'éliminer l'addition d'un étalon interne, d'où un gain de temps appréciable.

(*b*) d'effectuer des dosages dans un domaine de concentration plus large comme le montre la Fig. 5.

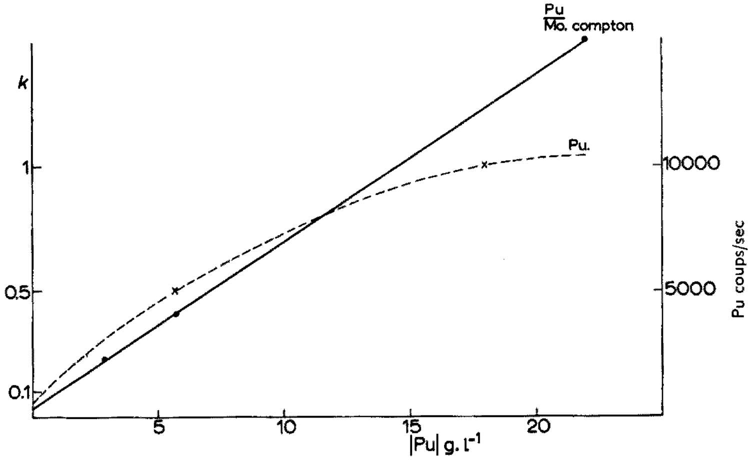


Fig. 5. Comparaison entre la méthode utilisant le rapport $k = \frac{L\alpha\ \text{Pu}}{K\alpha\ \text{Mo Compton}}$ et le comptage direct de Pu $L\alpha$.

(*c*) de travailler à courbe fixe en raison de l'élimination des paramètres mal contrôlables intervenant de la même façon sur les 2 termes du rapport k (géométrie du porte-échantillon, jeux mécaniques, etc.).

PRÉCISION DE LA MÉTHODE

Le calcul montre qu'il est nécessaire de compter $3 \cdot 10^5$ coups pour avoir un écart type relatif de 1%.

Compte tenu de ce qu'on limite le temps de comptage à 100 sec pour des questions de rapidité d'analyse, cette précision de 1% ne peut être atteinte que pour des teneurs en plutonium dans la solution supérieure à 3.6 g/l.

La Fig. 6 indique la précision théorique du dosage en fonction de la teneur en plutonium.

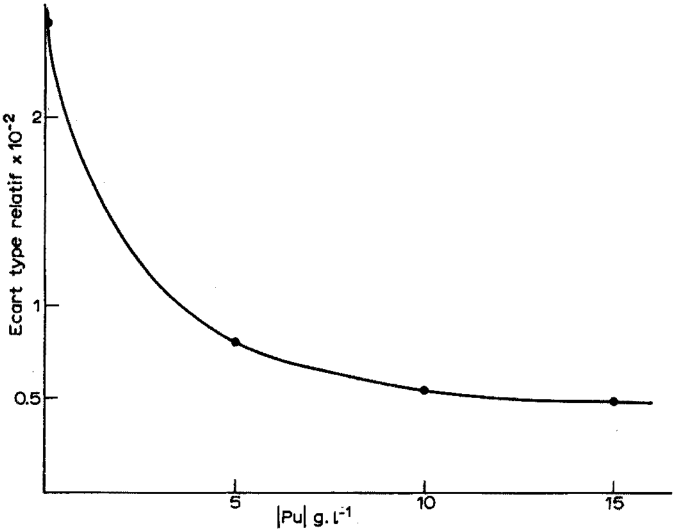


Fig. 6. Valeur de l'écart type relatif en fonction de la teneur en plutonium.

TABLE IV

COMPARAISON ENTRE LES MÉTHODES CHIMIQUES ET SPECTROMÉTRIQUES

No. de l'échantillon	*Méthode de dosage*		*Ecart relatif (%)*
	Chimique (g/l ± 0.5%)	*Fluorescence-X (g/l ± 1%)*	
1	3.23	3.24	+0.30
2	5.08	5.07	−0.20
3	4.66	4.65	−0.21
4	3.59	3.62	+0.83
5	3.42	3.42	0.00
6	2.94	2.95	+0.34
7	5.00	4.96	−0.80
8	4.48	4.50	+0.44
9	4.94	4.92	−0.44

La reproductibilité expérimentale des mesures confirme l'écart type calculé. La comparaison des résultats avec ceux obtenus par analyse chimique permet de vérifier un bon accord entre les deux méthodes (Tableau IV).

DOMAINE D'APPLICATION

Cette méthode est appliquée avec succès dans notre laboratoire au contrôle de la fabrication des éléments combustibles à base d'alliages plutonium–aluminium ainsi qu'au dosage du plutonium au cours du retraitement chimique des déchets de ces alliages.

Nous envisageons de l'appliquer à chaque fois qu'il est nécessaire de doser avec une précision de l'ordre du % du plutonium dans un milieu contenant des ions gênant une détermination chimique directe.

RÉSUMÉ

Une méthode de fluorescence-X a été développée pour la détermination quantitative du plutonium dans les alliages plutonium–aluminium. Pour obtenir une bonne reproductibilité, l'analyse est réalisée après mise en solution de l'alliage dans l'acide nitrique additionné d'ions mercuriques. Le dosage est fait en mesurant la raie $L\alpha$ du plutonium. Pour éliminer les effets dûs à la matrice, on a utilisé un étalon interne (Compton du molybdène) dont la longueur d'onde est voisine de celle de la raie $L\alpha$ du plutonium. L'équipement et la technique de préparation des échantillons sont décrits. Une extension de la méthode à d'autres déterminations du plutonium est envisagée.

SUMMARY

An X-ray fluorescence method is described for the determination of plutonium in Pu–Al alloys. In order to obtain satisfactory reproducibility, the alloy is first dissolved in a nitric acid–mercury(II) nitrate mixture. The $L\alpha$ emission of plutonium is measured; to eliminate matrix effects, an internal standard with a wavelength near that of the Pu emission is used. Equipment and sample preparation are described. Extension of the method to other determinations is discussed.

ZUSAMMENFASSUNG

Es wird die Bestimmung von Plutonium in Pu–Al-Legierungen mittels der Röntgenfluoreszenzanalyse beschrieben. Um eine befriedigende Reproduzierbarkeite zu erhalten, wird die Legierung zuerst in einer Mischung aus Salpetersäure und Quecksilber(II)-nitrat gelöst. Die $L\alpha$-Linie des Plutoniums wird gemessen und zur Eliminierung von Matrixeffekten ein innerer Standard verwendet, dessen Wellenlänge nahe der des Plutoniums liegt. Die Apparatur und die Herstellung der Proben wird beschrieben. Die Ausdehnung der Methode auf andere Bestimmungen wird diskutiert.

BIBLIOGRAPHIE

1 J. Corpel et F. Regnaud, *Anal. Chim. Acta*, 35 (1966) 508.
2 G. Anderman et J. W. Kemp, *Anal. Chem.*, 30 (1958) 1306.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE DETERMINATION OF ALUMINUM AND BERYLLIUM BY ATOMIC ABSORPTION SPECTROSCOPY

T. V. RAMAKRISHNA, PHILIP W. WEST AND JAMES W. ROBINSON
Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La. 70803 (U.S.A.)

(Received January 11th, 1967)

Recently it was demonstrated that atomic absorption spectroscopy offers a rapid, convenient and reliable means for monitoring air and water for lead[1], calcium and magnesium[2], and cadmium, copper and zinc[3]. An investigation has now been made to extend atomic absorption techniques for the determination of aluminum and beryllium.

CHAKRABARTI, LYLES AND DOWLING[4] have reported absorption by aluminum as the cupferrate in 4-methyl-2-pentanone using a fuel-rich oxy–acetylene flame. SLAVIN AND MANNING[5] also reported absorption using an oxy–acetylene flame and ethanolic solutions of some metals, including aluminum and beryllium. These procedures gave poor sensitivity and were somewhat tedious for routine monitoring purposes.

Recently, AMOS AND THOMAS[6] demonstrated that aluminum can be determined in aqueous samples using pre-mixed flames of enriched air and acetylene. This was followed by the introduction of nitrous oxide–acetylene flames by WILLIS[7]. This flame enables the determination of a wide range of metals that previously resisted detection by atomic absorption spectroscopy. The advantages of nitrous oxide–acetylene flames over that of enriched air–acetylene flames are the lower burning velocity involved and the reduced danger of flash-back. An investigation was therefore undertaken to develop methods for the determination of aluminum and beryllium using nitrous oxide–acetylene flames. The results indicated that low concentrations of these metals can be determined accurately in the presence of various extraneous ions and compounds. In addition, an examination of the effect of various miscible organic solvents led to the development of another convenient and reliable method for the estimation of beryllium in oxy–acetylene flames. Details of these investigations and pertinent aspects of the procedures are discussed below.

EXPERIMENTAL

Equipment

A Perkin-Elmer (Model 303) atomic absorption spectrophotometer was used for absorption measurements. For oxy–acetylene flame studies a Beckman total consumption burner-atomizer (No. 4090) was used and for nitrous oxide–acetylene flame the standard burner head on the Perkin-Elmer burner mount was replaced by a nitrous oxide burner head with a slot length of 7.5 cm and a width of 0.015 cm. A

Hoke flow-meter was employed to record the flow rates of oxygen and acetylene. An additional regulator was provided to control the nitrous oxide input to the premix burner-atomizer. Hollow cathode lamps (Atomic Spectral Lamps, Australia) were used as radiation source.

Reagents

Aluminum and beryllium stock solutions containing 1.00 mg/ml of the metal in question were prepared from reagent-grade aluminum metal and beryllium carbonate, respectively. Standard solutions were made by appropriate dilution of the stock solutions. Reagent-grade chemicals were used in the interference studies and double-distilled water was used for dilution purposes.

Procedure

Investigations with oxy–acetylene flames were confined to the determination of beryllium. Sensitivities for aluminum in water–organic mixtures were insufficient to justify detailed studies.

Standard solutions were prepared containing 30 p.p.m. of beryllium in 10% solutions of commonly available water-soluble organic solvents. Absorption measurements were made under conditions listed in Table I, while adjusting the burner height and, if necessary, the fuel ratio to obtain maximum absorption. Under these conditions, the sample uptake for aqueous solutions was approximately 4 ml/min. A blank containing the solvent alone was used in each instance to set the zero of the instrument.

TABLE I

OPERATING CONDITIONS

Metal	*Wave-length (Å)*	*Lamp current (mA)*	*Slit (mm)*	*Oxygen (l/min)*	*Acetylene (l/min)*	*Nitrous oxide (p.s.i.)*		*Sensitivity (p.p.m. for 1% absorption)*
						Atomizer	*Auxiliary*	
Al	3092	14	1.0	—	6	35	15	1.0
Be	2349	20	0.3	3.5	4	—	—	0.9
					6	35	15	0.025

For investigations with nitrous oxide–acetylene flames, the Beckman total consumption burner assembly was replaced by a Perkin-Elmer premix type burner fitted with a nitrous oxide–acetylene burner head. With aqueous solutions containing 20 p.p.m. of aluminum and 1 p.p.m. of beryllium, the optimum operating conditions listed in Table I for each metal were established. Absorption measurements were made at the rose red inner cone of the flame, about 1 cm from the burner head. Under these conditions the sample uptake was about 4 ml/min; and the sensitivities for aluminum and beryllium were 1 p.p.m. and 0.025 p.p.m. respectively for 1% absorption.

In the interference studies, sodium or potassium salts were used for anionic interference and chlorides, nitrates or sulfates for cationic interference studies. Concentrated acids were used to study the effect of the addition of acids.

RESULTS AND DISCUSSION

Oxy–acetylene flame

Organic solvents are known to enhance the absorption signal of many metals and, as a result, have found a very wide application in atomic absorption spectroscopy. Since the sensitivity observed for pure aqueous beryllium solutions was low, it was thought worthwhile to examine the effect of organic solvents as a means of improving the sensitivity. An extraction procedure was not pursued because it would detract from the usual simplicity of the atomic absorption technique. The investigation was, therefore, confined to water-soluble organic solvents.

Table II lists the sensitivities obtained upon the use of commonly available organic solvents with beryllium. An enhancement in sensitivity was obtained in the presence of diethylene glycol; this observation suggested that a more detailed investigation should be conducted with glycols in order to obtain a better solvent system for beryllium determinations. Solutions were prepared containing 20 p.p.m. of beryllium in 10% solutions of the commonly available glycols. These solutions were then atomized under the conditions listed in Table I and the results obtained are shown in Table III. The increase in absorption was not due to an increase in the amount of solution reaching the flame because there was no evident correlation between solvent viscosity and absorption (Table III). Perhaps a hotter or a more reducing condition was created in the flame with the result that the vaporization and dissociation of the metal compound was increased. It was also evident from Table III that the addition

TABLE II

EFFECT OF ORGANIC SOLVENTS ON BERYLLIUM ABSORPTION

(Beryllium = 30 p.p.m.)

Organic solvent (10%)	*Percentage absorption*	*Organic solvent (10%)*	*Percentage absorption*
None	7.6	Diethylene glycol	22.6
Acetone	7.8	Formaldehyde (37% by wt.)	7.6
Ethanol	11 8	Isopropyl alcohol	11.8
Methanol	9.0	Methyl ethyl ketone	8.6
1,4-Dioxane	10.6		

TABLE III

EFFECT OF VARIOUS GLYCOLS ON BERYLLIUM ABSORPTION

(Beryllium = 20 p.p.m.)

Sample uptake (ml/min)	*Glycol added (10%)*	*Percentage absorption*
4.5	None	5.0
3.3	Ethylene glycol monoethyl ether	11.8
3.2	Ethylene glycol monomethyl ether	11.9
3.3	Ethylene glycol dimethyl ether	9.7
2.5	Diethylene glycol monobutyl ether	14.7
3.3	Diethylene glycol monoethyl ether	17.6
3.5	Diethylene glycol	14.2
3.3	Diethylene glycol diethyl ether	24.0

of 10 ml of diethylene glycol diethyl ether for every 100 ml of the sample resulted in a 5-fold enhancement of beryllium absorption. Further experiments to evaluate the optimum solvent–water ratio indicated that a 10% diethylene glycol diethyl ether in water was sufficient to obtain maximum sensitivity; a more concentrated solution produced no significant enhancement. The sensitivity of the procedure was found to be 0.9 p.p.m. for 1% absorption.

Interference studies

The interfering effect of the substances listed in Table IV on the absorption of beryllium was investigated using the procedure indicated above. In these investigations the concentration of beryllium was 20 mg/l and that of the interfering substance, 250 mg/l. In each case, 10 ml of diethylene glycol diethyl ether were added before diluting to 100 ml with double-distilled water. The effect of acid was examined by adding 5 ml of appropriate concentrated acid before making up to volume.

TABLE IV

INTERFERENCE STUDIES

Group I.	Li^+, Na^+, K^+, Rb^+, Cs^+, Cu^{2+}, Ag^+.
Group II.	Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Hg_2^{2+}, Hg^{2+}.
Group III.	$B_4O_7^{2-}$, Al^{3+}, Ce^{4+}.
Group IV.	HCO_3^-, CO_3^{2-}, SiO_3^{2-}, Ti^{4+}, Zr^{4+}, Sn^{2+}, Sn^{4+}, Pb^{2+}.
Group V.	NH_4^+, NO_3^-, HPO_4^{2-}, VO_3^-, $HAsO_4^{2-}$, Sb^{5+}, Bi^{3+}.
Group VI.	SO_3^{2-}, SO_4^{2-}, Cr^{3+}, SeO_3^{2-}, MoO_4^{2-}, TeO_3^{2-}, WO_4^{2-}, UO_4^{2-}.
Group VII.	F^-, Cl^-, Br^-, I^-, Mn^{2+}.
Group VIII.	Fe^{3+}, Co^{2+}, Ni^{2+}, Pd^{2+}.
Miscellaneous substances: citrate, tartrate, oxalate, EDTA and detergent (Dreft), hydrochloric acid, sulfuric acid, nitric acid, perchloric acid and acetic acid.	

With the exception of aluminum and acetic acid, none of the substances listed in Table IV interfered in the beryllium determination. Aluminum suppressed the absorption by about 25%, but the interference was readily overcome by the addition of about 1.5 g/l of fluoride. Acetic acid enhanced the sensitivity by about 20%. However, significant amounts of acetic acid are not likely to be present in air or water samples, but correction must be made if its presence is suspected.

Nitrous oxide–acetylene flame

Although Willis[7] reported the use of nitrous oxide–acetylene flames for the determination of many refractory metals including aluminum and beryllium, detailed information for various metals with this flame has not yet been reported. An investigation was therefore undertaken to develop methods for the determination of aluminum or beryllium with nitrous oxide–acetylene flames and to examine several potential interferences in the method developed.

Sensitivities of other lines

Table V lists the sensitivities obtained for various other absorption lines useful for aluminum determination. It is evident that the 3691 Å line has approximately the same sensitivity as that at 3092 Å (actually a doublet 3092.7 Å and 3092.8 Å). Although the present investigation was confined to the 3092 Å resonance line, other, less sensitive lines should be preferred for more concentrated samples.

TABLE V

SENSITIVITIES OF VARIOUS ALUMINUM RESONANCE LINES

Wavelength (Å)	*Sensitivity (p.p.m./1% absorption)*	*Wavelength (Å)*	*Sensitivity (p.p.m./1% absorption)*
3092	1.2	2373	3.5
3961	1.0	2575	7.0
3082	1.8	2652	8.5
3944	2.2		

In the case of beryllium, high sensitivity was noticed only in the case of the atomic resonance line at 2349 Å. No absorption was observed using the resonance lines of ionized beryllium at 3130 Å and 3131 Å. The line at wavelength 3321 Å denoting transition between the 2P triplet and 2S singlet was examined. No absorption was detected using a beryllium solution of 1000 p.p.m. concentration. This was in contrast to the work reported by GOLEB who used transitions from triplet to singlet states to determine noble gases[8].

Interference studies

The method developed was studied in the presence of the potential interfering substances listed in Table IV. The concentrations of aluminum and beryllium were 20 mg/l and 1 mg/l respectively. The concentration of interfering ions was 200 mg/l in the case of aluminum and 100 mg/l in the case of beryllium. The effect of acids was examined by adding 5 ml of appropriate concentrated acid before diluting to 100 ml with water.

With the exception of titanium(IV) and acetic acid in the case of aluminum, and acetic acid alone in the case of beryllium, none of the substances listed in Table IV interfered. Acetic acid (5%) solution enhanced the absorption by 10% in the case of aluminum and 20% in the case of beryllium. Titanium also enhanced the aluminum absorption by 25%, and therefore if its presence is suspected it is essential to incorporate some titanium both in standards and samples. Further studies on the effect of titanium(IV) on 20 p.p.m. of aluminum indicated that 80 p.p.m. of Ti(IV) is sufficient to produce maximum enhancement. Higher concentrations, up to 300 p.p.m., showed no further noticeable change in aluminum absorption. A similar observation was made in the case of the determination of vanadium with nitrous oxide–acetylene flame where both titanium and aluminum caused enhancement[9]. It is probable that these refractory metals compete with one another for oxide formation, which results in the production of a greater number of atoms of those metals which have a tendency to form less stable oxides. The increase in the absorption due to vanadium in the presence of titanium and aluminum, and the increase in the absorption due to aluminum in the presence of titanium and none in the presence of vanadium, suggests that the stabilities of the metal oxides are most probably in the order $Ti > Al > V$. This order of relative stability has been reported by GAYDON[10].

Effect of glycols

Investigations of the absorption by beryllium using oxy–acetylene flames showed that the addition of glycols considerably enhanced the sensitivity. A similar observation was noted in the case of aluminum and beryllium when a series of solutions containing the same amounts of aluminum or beryllium and 5% of various glycols (Table III) was sprayed into nitrous oxide–acetylene flames. The effect was more pronounced in aqueous solutions of diethylene glycol diethyl ether with each metal, as was previously observed with beryllium in oxy–acetylene flames. The sensitivity was increased by 30% in the case of aluminum and by 25% in the case of beryllium. Further experiments with aluminum and beryllium on the effect of diethylene glycol diethyl ether indicated that 5% of the glycol was adequate to obtain maximum sensitivity. Although the increase in sensitivity obtained in the presence of the glycol was not great, it could be helpful in some applications. Of course, in such instances it is essential to construct calibration curves from solutions containing similar concentrations of glycols.

Precision

The precision of the procedure was checked by carrying out 6 replicate determinations on each of the solutions, containing 5 p.p.m. of aluminum and 0.5 p.p.m. of beryllium, under the established conditions. The average recovery was 4.9 p.p.m. and 0.50 p.p.m. for beryllium, with standard deviations of 0.1 and 0.01 respectively.

CONCLUSION

An investigation of the determination of aluminum and beryllium by means of atomic absorption spectroscopy has shown that each metal can be determined using nitrous oxide–acetylene flames down to 1 p.p.m. and 0.025 p.p.m. respectively. An oxy–acetylene flame may be used for beryllium with an aqueous solution containing 10% diethylene glycol diethyl ether, but the sample should contain more than 1 p.p.m. of beryllium to make satisfactory absorption measurements. Both metals were essentially free from the interference of several ions and compounds and consequently the method should be of value for routine analysis of air or water samples. When the nitrous oxide–acetylene flame is used, the calibration curve for aluminum is linear over the range 5–60 mg/l, and for beryllium, 0.1–2.5 mg/l. The less sensitive procedure for beryllium with oxy–acetylene flame obeys Beer's law over the range 5–50 mg/l of beryllium.

RECOMMENDED PROCEDURES

Oxy–acetylene flame

Transfer a suitable aliquot containing beryllium to a 100-ml volumetric flask and add 10 ml of diethylene glycol diethyl ether. Make up to volume with double-distilled water. The final concentration of beryllium in this solution should be 5–50 mg/l. Measure the percentage absorption under conditions described in EXPERIMENTAL. Convert the percentage absorption to optical density and determine the concentration of beryllium using a standard curve prepared under identical conditions for 5–50 mg/l of beryllium.

Nitrous oxide–acetylene flame

The working range with nitrous oxide–acetylene flame is 0.1 to 2.5 mg/l for beryllium and 5–50 mg/l for aluminum in pure aqueous solution as well as in 5%

diethylene glycol diethyl ether. With the instrument set under optimum conditions for the nitrous oxide–acetylene flame as given under EXPERIMENTAL, measure the percentage absorption for aluminum or beryllium. The concentration of each of these metals is determined from the appropriate respective calibration curve. If the presence of titanium is suspected in aluminum samples, it is essential to add 100 mg/l of titanium(IV) to both standards and samples before subjecting to the atomization process.

This investigation was supported by the U. S. Public Health Service Research Grant AP 00128, Division of Air Pollution, Bureau of State Services.

SUMMARY

The use of atomic absorption spectroscopy for the determination of aluminum and beryllium has been studied. The nitrous oxide–acetylene flame was found to be useful for the determination of trace amounts of either aluminum or beryllium. Beryllium can also be determined in an oxy–acetylene flame at the 1 p.p.m. level and upwards if the aqueous solution contains 10% of diethylene glycol diethyl ether. The determinations were essentially free from interferences.

RÉSUMÉ

On a examiné l'emploi de la spectroscopie par absorption atomique pour le dosage de l'aluminium et du béryllium. La flamme oxyde nitreux–acétylène convient au dosage de traces d'aluminium ou de béryllium. Ce dernier peut également être dosé dans une flamme oxy–acétylène. Ces déterminations sont tout à fait exemptes d'interférences.

ZUSAMMENFASSUNG

Es wurde die Eignung der Flammenabsorptionsspektroskopie zur Bestimmung von Aluminium und Beryllium untersucht. Die Stickstoffoxid–Acetylen-Flamme war für die Bestimmung von Spuren beider Elemente brauchbar. Mehr als 1 p.p.m. Beryllium können auch mit der Sauerstoff–Acetylen-Flamme bestimmt werden, wenn die wässrige Lösung 10% Diäthylenglykoldiäthyläther enthält. Die Bestimmungen waren völlig frei von Störungen.

REFERENCES

1 C. L. CHAKRABARTI, J. W. ROBINSON AND P. W. WEST, *Anal. Chim. Acta*, 34 (1964) 269.
2 T. V. RAMAKRISHNA, J. W. ROBINSON AND P. W. WEST, *Anal. Chim. Acta*, 36 (1966) 57.
3 T. V. RAMAKRISHNA, J. W. ROBINSON AND P. W. WEST, *Anal. Chim. Acta*, 37 (1967) 20.
4 C. L. CHAKRABARTI, G. R. LYLES AND F. B. DOWLING, *Anal. Chim. Acta*, 29 (1963) 489.
5 W. SLAVIN AND D. C. MANNING, *Anal. Chem.*, 35 (1963) 253.
6 M. D. AMOS AND P. E. THOMAS, *Anal. Chim. Acta*, 32 (1965) 139.
7 J. B. WILLIS, *Nature*, 207 (1965) 715.
8 J. A. GOLEB, *Fifth National Meeting, Society for Applied Spectroscopy, Chicago, June 13–17, 1966.*
9 S. L. SACHDEV, J. W. ROBINSON AND P. W. WEST, *Anal. Chim. Acta*, 37 (1967) 12.
10 A. G. GAYDON, *Dissociation Energies*, 2nd Edn., Chapman and Hall, London, 1953.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE DETERMINATION OF TRACES OF IRIDIUM IN RHODIUM BY NEUTRON ACTIVATION ANALYSIS

R. GIJBELS* AND J. HOSTE
Institute for Nuclear Sciences, Ghent University, Ghent (Belgium)

(Received February 20th, 1967)

The most important impurities in refined rhodium are Ir, Pd, Fe, Ni and Si, and Pt, Ru, Au, Ag, Cu, Sn, Pb, Zn and Co[1]. Since the complete separation of rhodium from iridium is very difficult, the iridium content of rhodium is a good measure of its purification. Small amounts of iridium (a few per cent) cannot be determined accurately in rhodium by wet chemical analysis: 2 independent analyses often differ by a factor of 5. Spectrographic techniques have been described by GERLACH *et al.*[2,3], BABAEVA AND LAPIR[4] and LEWIS *et al.*[1], but the sensitivity is insufficient in many cases, *ca.* 0.25% Ir only for 25 mg rhodium sponge or black. KURANOV *et al.*[5] developed a special spectrographic technique and attained a sensitivity of 0.1%, but matrix and third-element effects limit the accuracy of the analysis.

Several authors have applied neutron activation to this problem[6-11]. MORRIS *et al.*[11] used an addition method to avoid neutron-shielding differences between samples and standards. No other analytical methods, such as colorimetry, polarography or X-ray fluorescence, are described in the literature[12,13].

Neutron activation is very favourable in this case, because no chemical separation is necessary, the periods of the produced rhodium isotopes being 4.4-min (^{104m}Rh) and 42-sec (^{104}Rh) only. Owing to the very high specific activity of iridium (72-d ^{192}Ir; 19-h ^{194}Ir) a rhodium sample of only a few mg is sufficient for iridium trace analysis. Other impurities are not likely to interfere with the iridium determination for the same reason, the more so as iridium is one of the most important impurities.

Because of the high absorption cross-section of rhodium (100% ^{103}Rh) for thermal neutrons (156 barns), the problem of self-absorption must be considered. If 19-h ^{194}Ir is to be measured, its specific activity can also be affected by the resonance absorption of rhodium, as the resonance peaks coincide[14] (Rh: $E_r = 1.257$ eV, resonance integral 655 b; ^{193}Ir: $E_r = 1.303$ eV and others, total resonance integral 1370 b), although it can be shown that the latter effect is at least 20 times less important, even for irradiation positions where the cadmium ratio for gold is only 5.5.

The thermal self-absorption is, however, very high and will lower the specific activity of ^{192}Ir and of ^{194}Ir. According to ZWEIFEL[15] it can be calculated that for only 10 mg of rhodium powder, the self-absorption is already as high as 20%, assuming an apparent density of 3 and treating the powder as an equivalent sphere. An analogous result has been found by the method of KENNA AND VAN DOMELEN[16].

In an earlier paper it has been shown experimentally, that standards prepared

---

* Research fellow of the I.I.K.W.

by spotting microgram amounts of iridium on filter paper, are not likely to give rise to self-absorption[17]. Hence it can be expected that classical activation analysis will give too low iridium contents, as will be shown further (method A). Once the iridium content of a given homogeneous sample has been determined accurately (see method B), it can be used as a standard for further analyses, so that there is no longer any problem of neutron-shielding differences between samples and standards (method C).

EXPERIMENTAL AND RESULTS

Method A: "Classical" determination of iridium in spectrographically pure rhodium sponge

Samples of 10 mg were accurately weighed, wrapped in mylar foil and placed in aluminium "saucers" (15 mm diameter, 2 mm height). Standards were prepared by spotting and evaporating 100 μl of an iridium standard solution[17], containing 0.1 or 1 μg Ir on Whatman no. 1 paper. After irradiation for 2 days at a thermal neutron flux of $4 \cdot 10^{11}$ n $\cdot$ cm$^{-2} \cdot$ sec^{-1}, the γ-spectrum of the rhodium sponge showed the presence of ^{192}Ir + ^{194}Ir and of ^{24}Na. After *ca.* 1 week (decay of 15-h ^{24}Na and of 19-h ^{194}Ir) a pure ^{192}Ir spectrum remained (Fig. 1). The iridium content could be calculated from the 317, 468 and 610 keV photopeaks. If the same result is found for the 3 peaks, this indicates that interference from other long-lived impurities is unlikely to occur. The following results were found for spectrographically standardized rhodium: 17.15 p.p.m. (317 keV photopeak), 16.7 p.p.m. (468 keV) and 17.2 p.p.m. (610 keV); average value 17.0 p.p.m.

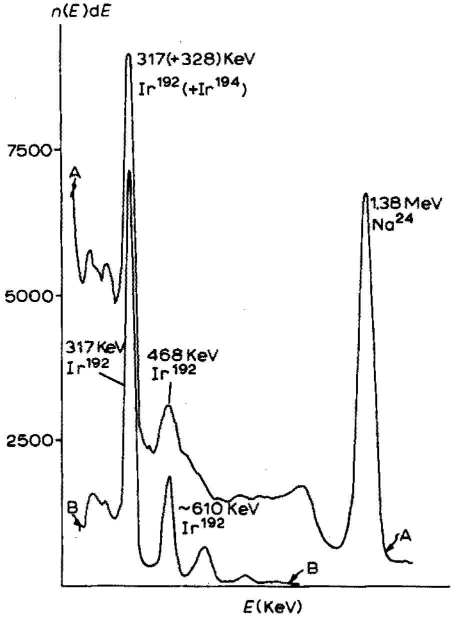


Fig. 1. γ-Spectrum of neutron irradiated rhodium. (A) 15 h after the end of irradiation; (B) 3 weeks after the end of irradiation.

Method B: Addition method. Determination of iridium in spectrographically pure rhodium sponge.

Seven samples of 10 mg of spectrographically standardized rhodium sponge were accurately weighed (within ±1%) into silica tubes (length 5–6 cm; internal diameter 4 mm; wall thickness 1 mm). To 3 samples 100 μl of an iridium standard solution, containing 0.20 μg Ir (corresponding to 20 p.p.m. Ir) was added and carefully evaporated to dryness. At least 150 μl of concentrated hydrochloric acid and a few drops of concentrated nitric acid were added and the contents of the silica tubes solidified by partly immersing them in liquid nitrogen. After quick sealing, the silica ampoules were placed in a Carius oven at 200–215° for several hours to dissolve the samples[18]. Too high a temperature, *e.g.* 250°, and too small a volume of reagent had to be avoided, otherwise an insoluble anhydrous chloride could be formed. The samples were then irradiated in the conditions mentioned above, together with a "blank" silica tube. Two weeks after the end of the irradiation the silica tubes were cleaned, placed in counting vials and directly counted in the same geometry on a flat 3×3″ NaI(Tl) detector. The background was determined with the "blank" silica tube as the quartz was not radiochemically pure (^{122}Sb + ^{124}Sb).

γ-Spectrometric comparison of the rhodium samples with the iridium standards in the same geometry showed that integral counting was not advisable, as a foreign activity in the 0–250 keV region caused positive errors (calculated content: 21.7 p.p.m.). The results of the activities, counted under the photopeaks, are given in Table I.

TABLE I

DETERMINATION OF IRIDIUM IN SPEC-PURE RHODIUM BY THE ADDITION METHOD (ACTIVITIES IN c/3 min)

Ir added (p.p.m.)	*Act. 317 keV*	*Act. 468 keV*	*Act. 615 keV*
0	27.381	7.918	3.886
0	27.457	8.074	4.101
0	26.105	7.543	3.731
0	26.845	7.772	3.896
20	56.527	16.454	8.254
20	57.891	16.569	8.189
20	55.763	16.440	8.195
b_1 (c/3min/p.p.m.)	1490±30	433	215
b_0 (c/3min)	26,950±420	7827	3903
x (p.p.m.)	18.1±0.5	18.1	18.1

The parameters of the "calibration curve", the slope b_1, the intercept with the y-axis b_0 and the original iridium content in the sample without addition were calculated as described earlier[17]. From Table I, it appears that the classical method (A) introduced negative errors: (18.1–17.0)·100/18.1 = 6%. This value is lower than the calculated self-absorption effect (*ca.* 20%) because the apparent density of the rhodium powder in mylar wrapping is still lower than the assumed value of 3 and cannot be determined exactly.

Method C: Determination of iridium in a commercial rhodium sponge

The iridium content of spectrographically pure rhodium sponge having been determined accurately (18.1 p.p.m.), it can be used as a standard. The unknown sample was a commercial rhodium sponge.

From both, 5 samples of 10 mg were accurately weighed within ±1% (to allow direct comparison), wrapped in mylar foil and irradiated as described above. The problem of differences in self-absorption between samples and standards no longer exists. After irradiation and cooling for 2–3 weeks, all the samples were transferred to counting tubes (with mylar packing) and counted for 1.2 or 12 min at 5 cm distance from a 3×3″ flat NaI(Tl) crystal. The observed peak heights, normalized to 1.2 min, are given in Table II.

TABLE II

DETERMINATION OF IRIDIUM IN COMMERCIAL RHODIUM SPONGE, WITH SPECTROGRAPHICALLY PURE RHODIUM AS A STANDARD

Sample		*Height 317 keV*	*Height 468 keV*	*Height 615 keV*
Spectrographically pure	1	680.5	177.5	57.5
	2	683.4	178.2	54.5
	3	721.2	183.2	57.5
	4	691.5	179.7	55.2
	5	732.5	183.5	58.6
Commercial	1	2625	686	210
	2	2602	690	212
	3	2526	621	220
	4	(2989)	(800)	(241)
	5	2576	683	225

The ratio x of the iridium contents for both sponges is given by 2625/680.5; 2625/683.4; 2625/721.2 ... 2602/680.5; 2602/683.4 ... 686/177.5; 686/178.2; ... etc. Number 9 was discarded (Chaminet's rule). In that way 60 results are found, so that the standard deviation on the average value $\bar{x}$ can be estimated from

$$s^2(\bar{x}) = \Sigma(x_i - \bar{x})^2/n(n-1)$$

Calculation gives $\bar{x} = 3.74 \pm 0.02$. Hence the iridium content of commercial rhodium is given by $(18.1 \pm 0.5)(3.74 \pm 0.02) = 67.8 \pm 1.9$ p.p.m.

Sensitivity

The sensitivity of the described techniques is amply sufficient for iridium trace analysis in the purest rhodium samples now available (a few p.p.m. Ir). The sample weight can even be decreased, *e.g.* to 1 mg.

Grateful acknowledgement is made to the "Interuniversitair Instituut voor Kernwetenschappen" for financial support.

SUMMARY

Iridium traces were determined in rhodium by thermal neutron activation

for 2 days at a flux of $4 \cdot 10^{11}$ n·cm^{-2}·sec^{-1}. After cooling for at least 1 week, the samples were analysed by γ-spectrometry. No radiochemical separations were required. Special attention was paid to self-absorption phenomena in the rhodium samples.

RÉSUMÉ

Des traces d'iridium dans le rhodium peuvent être dosées par activation au moyen de neutrons thermiques, en irradiant 2 jours à un flux de $4 \cdot 10^{11}$ n cm^{-2} sec^{-1}. Après refroidissement pendant une semaine au minimum, les échantillons sont analysés par spectrométrie-γ. Aucune séparation radiochimique n'est nécessaire. On a examiné tout spécialement le phénomène d'autoabsorption dans les échantillons de rhodium.

ZUSAMMENFASSUNG

Es wird die Bestimmung von Spuren Iridium in Rhodium durch thermische Neutronenaktivierungsanalyse beschrieben. Nach zweitägiger Bestrahlung bei einem Fluss von $4 \cdot 10^{11}$ n cm^{-2} sec^{-1} und einwöchigem Abklingen wurden die Proben durch γ-Spektrometrie analysiert. Radiochemische Trennungen waren nicht erforderlich. Besondere Aufmerksamkeit wurde der Selbstabsorption in den Rhodiumproben gewidmet.

REFERENCES

1 C. L. Lewis, W. L. Ott and J. E. Hawley, *Can. Mining Met. Bull.*, 516 (1955) 208.
2 W. Gerlach and E. Riedl, *Phys. Z.*, 34 (1933) 516.
3 W. Gerlach and K. Ruthardt, *Siebert Festschr.*, (1931) 51.
4 A. V. Babaeva and E. S. Lapir, *Izv. Sektora Platiny i Drug. Blagorodn. Metal, Inst. Obshch. i Neorgan. Khim., Akad. Nauk SSSR*, 22 (1948) 145.
5 A. A. Kuranov, V. D Ponomareva and N. I. Chentsova, *Zh. Analit. Khim.*, 15 (1960) 476.
6 R. Döpel and K. Döpel, *Physik. Z.*, 44 (1943) 261.
7 G. H. Morrison, *Appl. Spectry.*, 10 (1956) 71.
8 A. A. Smales, *Proc. Isotope Techniques Conf., At. Res. Establishment, Oxford, July 16–20, 1951; Radioisotope Techniques*, Vol. 2, IV^x, Industrial and Allied Research Applications, H.M.S.O., London, 1952, p. 162–171.
9 G. W. Leddicotte *et al.*, *Progr. Nucl. Energy, Ser. IX*, 1 (1959) 123.
10 Y. Kamemoto, K. Shiba and Y. Onada, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 83 (1962) 57.
11 D. F. C. Morris, D. N. Slater and R. A. Killick, *Talanta*, 8 (1961) 373.
12 F. E. Beamish and W. A. E. McBryde, *Anal. Chim. Acta*, 9 (1953) 349; 18 (1958) 551.
13 F. E. Beamish, *Talanta*, 2 (1959) 244.
14 O. T. Høgdahl, *Radiochemical Methods of Analysis*, Proc. Symposium, Salzburg, 19–23 October, 1964, Vol. I, I.A.E.A., Vienna, 1965, p. 23.
15 P. F. Zweifel, *Nucleonics*, 18 (11) (1960) 174.
16 B. T. Kenna and B. H. Van Domelen, *Intern. J. Appl. Radiation Isotopes*, 17 (1966) 47.
17 R. Gijbels and J. Hoste, *Anal. Chim. Acta*, 32 (1965) 17.
18 E. Wichers, W. G. Schlecht and C. L. Gordon, *J. Res. Natl. Bur. Std.*, 33 (1944) 363, 451; C. L. Gordon, W. G. Schlecht and E. Wichers, *J. Res. Natl. Bur. Std.*, 33 (1944) 457.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE USE OF A DIGITAL COMPUTER FOR THE CALCULATION OF SUCCESSIVE COMPLEX FORMATION CONSTANTS

E. A. UNWIN, R. G. BEIMER AND QUINTUS FERNANDO
Systems Engineering Department and Department of Chemistry, University of Arizona, Tucson, Ariz. (U.S.A.)

(Received January 3rd, 1967)

SILLÉN[1] and INGRI AND SILLÉN[2] have discussed digital computer techniques for finding the values of equilibrium constants associated with complicated solution equilibria. The difficulties involved in these calculations are illustrated by considering one of the simpler problems, namely the calculation of the values of parameters, say θ_1 and θ_2, so that the function $y = g(x;\ \theta_1, \theta_2)$ "best" approximates the experimental data: $[(x_i, y_i): i = 1, 2, \ldots, n]$, where the function form of $g(x;\ \theta_1, \theta_2)$ is presumably known from the solution chemistry of the system. One must now answer the question: what does "best" mean? Traditionally, the answer has been: "best" in the sense that the sum of the squares of the errors over the data points is minimized. Although this is probably not the most meaningful answer, we also accept it for computational reasons. Thus, we must solve the problem:

$$\underset{\theta_1, \theta_2}{\text{minimize}} \sum_{i=1}^{N} [y_i - g(x_i;\ \theta_1, \theta_2)]^2 .$$

The general problem of estimating parameters so that the function $g(x;\ \theta_1, \theta_2)$ somehow best describes the data is known as the *regression problem*. The minimization problem arising by defining "best" to mean "in the sense of minimum of the squares of the errors" is one which has been discussed widely in the literature and several algorithms have been proposed for solving the problem. Each method has advantages and disadvantages which depend on the form of the function, *e.g.* MARQUARDT[3] has used a combination of techniques to obtain a "maximum neighborhood" method. In this paper a very unsophisticated, yet very effective, technique for solving the problem is proposed. The efficiency of the method relies upon having a reasonable *a priori* estimate for the parameter values which are of course readily available for successive complex formation constants from graphical methods.

THE REGRESSION PROBLEM

The regression problem is the problem of estimating values of parameters $\theta_1, \theta_2, \ldots, \theta_m$ so that it is possible to ascertain the value (actually the expected value) of a dependent variable y for a given value of one or more independent variables $x_1, x_2, \ldots x_k$. The form of the functional relationship is given (or assumed):

$$y = g(x_1, x_2, \ldots, x_k;\ \theta_1, \theta_2, \ldots, \theta_m)$$

The estimates of the parameters are to be made from experimental values. For simplicity, let us consider the case where there is only one independent variable x and two parameters θ_1 and θ_2.

If the functional form of $g(x;\theta_1,\theta_2)$ were known exactly and if it were possible to control the experiment perfectly, then there would be no problem since all the data points would fall on the curve $y = g(x;\theta_1,\theta_2)$ and the calculation of θ_1 and θ_2 would be trivial. However, the exact functional form of g is not usually known and it is not possible to obtain perfect experimental results. Thus, instead of a deterministic problem, one is essentially faced with a bivariate distribution $f(x, y)$ which associates probabilities with various values of x and y. With sufficient repetition of experiments it may be possible to determine $f(x,y)$ approximately, from which the conditional distribution $f(y|x)$ can be calculated. The graph of the mean (expected value) of $f(y|x)$ is, by definition, the curve of regression of y on x. Thus, theoretically, $g(x;\theta_1,\theta_2)$ can be determined in this way, or at least, it is possible to obtain a better understanding of what is meant by regression.

However, since the determination of $f(x,y)$ is quite tedious, it is reasonable to estimate θ_1 and θ_2 so that $y = g(x;\theta_1,\theta_2)$ in some sense "best" approximates the actual experimental results $[(x_i, y_i): i = 1, 2, \ldots, n]$. There are several choices for the meaning of "best", of which perhaps the most reasonable, statistically, is that which gives estimators which are unbiased and have minimal variance. Computationally, however, the most reasonable choice is probably that which minimizes the sum of squares between the curve $g(x;\theta_1,\theta_2)$ and the observed values y_i at the controlled or observed values of x_i.

SILLÉN[1] points out some necessary conditions for the least squares technique to result in maximum likelihood estimates. As a comparison and as an indication of the scope of the problem the following assumptions are necessary[4] for the method of least squares to yield estimators of θ_1 and θ_2 which are unbiased and have the smallest variance *in the linear case*, where $g(x;\theta_1,\theta_2) = \theta_1 + \theta_2 x$:

(*1*) the regression of y on x is linear; *i.e.*, the expected value of y given x_i is $\theta_1 + \theta_2 x_i$;

(*2*) the x_i values are controlled and/or observed without error;

(*3*) the deviations $y_i - (\theta_1 + \theta_2 x_i)$ are mutually independent;

(*4*) these deviations have the same variance whatever the value of x_i.

The last assumption is unnecessary if one knows how the variance varies as a function of x and if one then weights the data accordingly.

POSSIBLE REFORMULATIONS OF PROBLEM

The problem that has been chosen to solve is the least squares problem:

Problem I

Given $[(L_i, \bar{n}_i): i = 1, 2, \ldots, N]$, find the values of k_1 and k_2 which minimize

$$S(k_1, k_2) = \sum_{i=1}^{N}\left[\bar{n}_i - \frac{k_1 L_i + 2k_1 k_2 L_i^2}{1 + k_1 L_i + k_1 k_2 L_i^2}\right]^2$$

Necessary conditions for a solution to Problem I are that $\partial S/\partial k_1 = \partial S/\partial k_2 = 0$. This leads to the non-equivalent problem:

Problem II

Given $[(L_i, \bar{n}_i): i=1, 2, \ldots, N]$ with

$$S = \sum_{i=1}^{N}\left[\bar{n}_i - \frac{k_1 L_i + 2k_1 k_2 L_i^2}{1+k_1 L_i + k_1 k_2 L_i^2}\right]^2$$

find values of k_1 and k_2 which satisfy: $\partial S/\partial k_1 = 0 \qquad \partial S/\partial k_2 = 0$.
Since Problem II requires the solution of a non-linear system, another possible approach would be to consider quasi-linearization to give the problem:

Problem III

Given $[(L_i, \bar{n}_i): i = 1, 2, \ldots, N]$, let $F(k_1, k_2)$ be the linear (Taylor) approximation of $\dfrac{k_1 L_i + 2k_1 k_2 L_i^2}{1+k_1 L_i + k_1 k_2 L_i^2}$ about an estimate of (k_1, k_2). Find values of k_1 and k_2 to minimize

$$\left[T(k_1, k_2) = \sum_{i=1}^{N}[\bar{n}_i - F(k_1, k_2)]^2\right]$$

by solving the necessary linear equations $\partial T/\partial k_1 = \partial T/\partial k_2 = 0$. In this way, continue to generate a hopefully convergent sequence of (k_1, k_2) values.

Many other reformulations of the problem are possible but the ideas in the three stated problems will provide some insight. Problem I is *the* problem; the other problems arise by specifying techniques for solving problem I. However, the new problems generated are not equivalent to the original. In particular, even if problem I has a unique solution, problem II may have many solutions, *e.g.* local minima, maxima and saddle points. An iterative technique for problem II may converge to an answer which is not the solution of problem I.

Previous workers in this field have solved, with the aid of a digital computer,

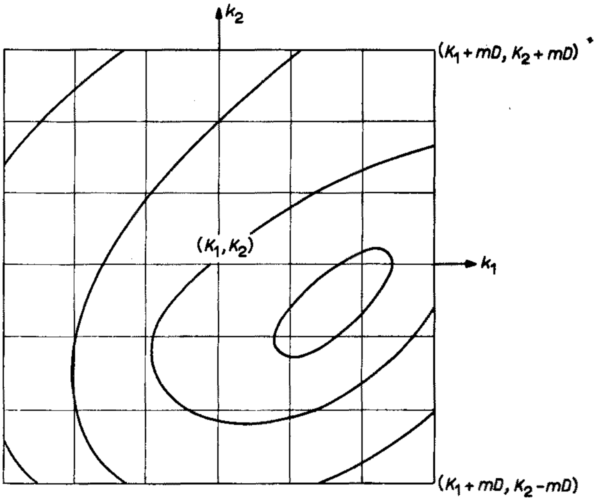
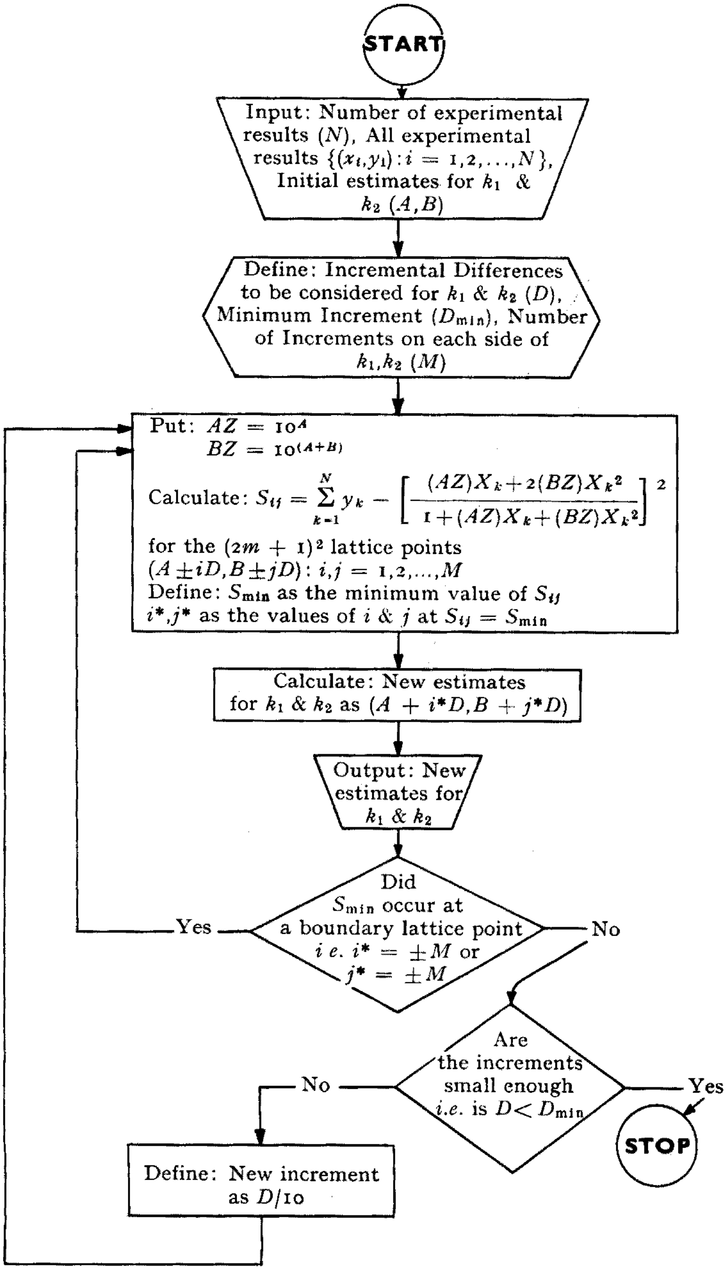


Fig. 1. The behaviour of the function S in the defined square lattice.

some reformulations of Problem I. From the preceding, it is apparent that this approach can lead to difficulties especially if the number of constants that has to be determined is greater than two. Therefore, in this work an attempt has been made to solve problem I directly by using the digital computer to evaluate $S(k_1, k_2)$ for various (k_1, k_2) and then actually choosing the minimum.

Fig. 2. Flow logic.



CALCULATION OF SUCCESSIVE COMPLEX FORMATION CONSTANTS

The problem to be solved is the determination of the successive complex formation constants k_1 and k_2 so that the function

$$\bar{n} = \frac{k_1 L + 2k_1 k_2 L^2}{1 + k_1 L + k_1 k_2 L^2}$$

"best" approximates the experimental data $[(L_i, \bar{n}_i):\ i=1,2,\ldots,N]$. Primarily for computational reasons, "best" is defined in the sense of least squares even though the estimates for k_1 and k_2 obtained in this way will not be smallest variance estimators. Thus the problem is:

$$\underset{k_1,k_2}{\text{minimize}}\ S(k_1, k_2) = \sum_{i=1}^{N} \bar{n}_i - \left[\frac{k_1 L_i + 2k_1 k_2 L_i^2}{1 + k_1 L_i + k_1 k_2 L_i^2}\right]^2$$

The surface S is reasonably well behaved in the (k_1, k_2) region concerned so that a simple, yet effective, search technique can be adopted to find the minimum. A square lattice is defined about an estimate for (k_1, k_2): $[(k_1 \pm iD, k_2 \pm jD):\ i,j = 1,2,\ldots,m$; D being the spacing$]$. Now, the function S is evaluated at each lattice point. This requires $(2m+1)^2$ evaluations of S. The minimum value calculated is stored along with the corresponding values for i and j. The coordinates of this minimum of S then become new estimates for (k_1, k_2). If the new point is a boundary point on the old lattice, the procedure is simply repeated starting with the new estimate for (k_1, k_2). If the new point is an interior point on the lattice, the incremental spacing of the lattice is reduced by a factor of 10 and the procedure repeated (see Fig. 1). The calculations are repeated until the spacing is small enough so that k_1 and k_2 have been determined to the required accuracy.

TABLE I

SILVER(I) COMPLEXES OF 4-AMINOBUTAN-1-OL

$\bar{n}$	*−log L*	$\bar{n}$	*−log L*	*log k_1*	*log k_2*	*Estimate number*	*Residual sum of squares*
0.065	4.656	0.980	3.666	2.60	4.70	Initial	$1.53 \cdot 10^{-1}$
0.130	4.429	1.045	3.628	3.20	4.10	I	$3.35 \cdot 10^{-2}$
0.195	4.293	1.110	3.590	3.40	3.90	II	$3.21 \cdot 10^{-3}$
0.261	4.198	1.174	3.549	3.44	3.86	III	$1.80 \cdot 10^{-3}$
0.325	4.121	1.238	3.516	3.44	3.86	Final	$1.59 \cdot 10^{-3}$
0.392	4.058	1.303	3.477				
0.458	4.000	1.429	3.389				
0.523	3.950	1.553	3.292				
0.589	3.906	1.671	3.173				
0.654	3.861	1.779	3.023				
0.719	3.818	1.862	2.824				
0.785	3.780	1.950	2.310				
0.850	3.740	1.965	2.119				
0.915	3.700						

Reported values[5]: log k_1 = 3.41 ± 0.05; log $k_1 k_2$ = 7.30 ± 0.02.

```
C     CALCULATION OF FORMATION CONSTANTS BY CONTRACTING GRIDS
C
      DIMENSION X(100),XL(100),Y(100),AK(13),S(13,13)
C
C     READ NUMBER OF DATA POINTS, OUTPUT CONTROL AND GRID SIZE
    5 READ 99,65,N,IP,M
   99 FORMAT (3I5)
      DO 10 I = 1,N
C
C     READ DATA
      READ 98,XL(I),Y(I)
   10 X(I) = EXPF(—XL(I))
   98 FORMAT(2F10.3)
C
C     READ INITIAL ESTIMATES FOR K1 AND K2
      READ 98,A,B
      K = 0
      KBND = 0
      MP = 2*M + 1
      PRINT 89,A
   89 FORMAT(//,25H1INITIAL ESTIMATE       K1 =,F9.6)
   12 PRINT 88,B
   88 FORMAT(21X,4HK2 =,F9.6,//)
      IF(IP—1)11,13,13
   13 PRINT 87
   87 FORMAT (4X,11HINPUT   DATA,10X,6HRESULT,6X,10HDIFFERENCE,/)
   11 ANEW = EXPF(A)
      BNEW = EXPF(A + B)
C
C     CALCULATE REGRESSION CURVE VALUES AND SUM OF SQUARES OF DIFFERENCES
      SUM = 0.0
      DO 15 I=1,N
      YF = (ANEW+2.*BNEW*X(I))*X(I)/(1.+(ANEW+BNEW*X(I))*X(I))
      DIFF = Y(I)—YF
      IF(IP—1)15,16,16
   16 PRINT  86,XL(I),Y(I),YF,DIFF
   86 FORMAT(2X,F6.3,3X,F6.3,6X,F9.6,4X,E15.7)
   15 SUM = SUM + DIFF*DIFF
      PRINT 85,SUM
   85 FORMAT(//,30X,23HRESIDUAL SUM OF SQUARES,E20.7,///)
C
C     SET UP GRID AND FIND COORDINATES OF MINIMUM POSITION
      IF(K—1)30,60,60
   30 IF(KBND)31,31,33
   31 K = K + 1
   33 KA = A + .5
      KB = B + .5
      A = KA
      B = KB
   32 ANEW = EXPF(A)
      BNEW = EXPF(A+B)
      FK = K
      DEL = EXPF(1.—FK)
      DO 35 J=1,MP
      GUY = J—M—1
   35 AK(J) = B + DEL*GUY
      IF(IP—1)36,36,37
   37 PRINT 84,(AK(J),J=1,MP)
   84 FORMAT(//,9H1 K1    K2,F6.3,2X,12F8.3,//)
   36 SMIN = 1000000.
      DO 40 I=1,MP
      EYE = I—M—1
      AKW = A + DEL*EYE
      AKX = EXPF(AKW)
```

```
      DO 45 J=1,MP
      GUY = J—M—1
      AKT = B + DEL*GUY
      AKZ = EXPF(AKT)*AKX
      S(I,J) = 0.0
      DO 50 L=1,N
      YF = (AKX+2.*AKZ*X(L))*X(L)/(1.0+(AKX+AKZ*X(L))*X(L))
      DIFF = Y(L)—YF
   50 S(I,J) = S(I,J) + DIFF*DIFF
      IF(S(I,J)—SMIN)55,55,45
   55 SMIN = S(I,J)
      IM = I
      JM = J
      ALN = AKW
      BLN = AKT
   45 CONTINUE
      IF(IP—1)40,40,47
   47 PRINT 83,AKW,(S(I,J),J=1,MP)
   40 CONTINUE
   83 FORMAT(2X,F6.3,13F8.5,/)
C
C     WHERE DID MINIMUM OCCUR
      IF(IM—1)70,71,70
C
C     MINIMUM ON BOUNDARY    DO NOT CHANGE GRID SIZE
   71 KBND = 1
      K = K — 1
      IF(K)72,78,72
   78 K = 1
      GO TO 72
   70 IF(IM—MP)73,71,73
   73 IF(JM—1)74,71,74
   74 IF(JM—MP)77,71,77
C
C     MINIMUM IN INTERIOR    CHANGE GRID
   77 KBND = 0
   72 A = ALN
      B = BLN
      IF(K—4)75,76,76
   75 PRINT 82,A
   82 FORMAT(//,25H   NEXT   ESTIMATE      K1 =,F9.6)
      GO TO 12
   76 PRINT 81,A
   81 FORMAT(//,25H FINAL   ESTIMATE      K1 =,F9.6)
      GO TO 12
   60 K = K+1
      IF(K—4)32,32,5
   65 STOP
      END
```

Fig. 3.

TABLE II

SILVER(I)–AMMINE COMPLEXES

$\bar{n}$	$-\log L$	$\bar{n}$	$-\log L$	$\log k_1$	$\log k_2$	*Estimate number*	*Residual sum of squares*
0.247	4.051	1.236	3.385	5.00	5.00	Initial	$8.02 \cdot 10^{-1}$
0.495	3.816	1.477	3.232	3.00	4.00	I	$6.77 \cdot 10^{-3}$
0.741	3.656	1.711	3.303	3.20	3.80	II	$3.38 \cdot 10^{-3}$
0.988	3.523	1.992	1.984	3.18	3.85	III	$9.69 \cdot 10^{-5}$
				3.18	3.85	Final	$9.47 \cdot 10^{-5}$

Reported values[6]: $\log k_1 = 3.20$; $\log k_2 = 3.83$.

Figure 2 shows the flow logic used in the computer program and Fig. 3 is a listing of the Fortran II program used in this work. The program was used to calculate the successive complex formation constants from more than one hundred sets of experimental ($\bar{n}$ *vs.* L) data that were available. The results obtained from this program in two typical computations are reported in Tables I and II. In both cases the values obtained agree quite well with the reported values.

Financial assistance from a National Science Foundation Institutional Grant is gratefully acknowledged.

SUMMARY

A simple digital computer technique is described for the calculation of the successive complex formation constants in systems in which only 2 types of complexes are formed. This method should prove useful for the calculation of equilibrium constants in more complicated systems.

RÉSUMÉ

On propose l'utilisation d'un "computer" digital pour le calcul des constantes successives de formation de complexe dans des systèmes où 2 types de complexes seulement se forment. Cette méthode pourrait être utile pour le calcul des constantes d'équilibre dans des systèmes plus compliqués.

ZUSAMMENFASSUNG

Es wird eine einfache, digitale Computor-Technik beschrieben zur Berechnung von sukzessiven Komplexbildungskonstanten in Systemen, in denen nur zwei Typen von Komplexen gebildet werden. Diese Methode sollte sich auch zur Berechnung von Gleichgewichtskonstanten in komplizierteren Systemen als geeignet erweisen.

REFERENCES

1 L. G. SILLÉN, *Acta Chem. Scand.*, 16 (1962) 159.
2 N. INGRI AND L. G. SILLÉN, *Acta Chem. Scand.*, 16 (1962) 173.
3 D. W. MARQUARDT, *J. Soc. Ind. Appl. Math.*, II (1963) 431.
4 N. L. JOHNSON AND F. C. LEONE, *Statistics and Experimental Design in Engineering and the Physical Sciences*, Vol. I, Wiley, New York, 1964, p. 377–436.
5 R. C. LANSBURY, V. E. PRICE AND A. G. SMEETH, *J. Chem. Soc.*, (1965) 1896.
6 J. BJERRUM, *Metal Ammine Formation in Aqueous Solution*, Haase, Copenhagen, 1941.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DETERMINATION OF TUNGSTEN IN SILICATES AND NATURAL WATERS

K. M. CHAN* AND J. P. RILEY
Department of Oceanography, the University, Liverpool 3 (Great Britain)

(Received December 7th, 1966)

Comparatively little is known of the geochemical distribution of tungsten. Reviews of its occurrence have been given by GOLDSCHMIDT[1] and by RANKAMA AND SAHAMA[2]. Many of the earlier figures appear to be much too high, owing to the use of unsatisfactory analytical techniques. More recent work by JEFFERY[3] suggests that its average abundances in granitic rocks and sediments are *ca.* 1.4 and 3.9 p.p.m. respectively.

The concentrations of the element present in most rocks and sediments are below the limits of detection by direct spectrographic methods. Highly sensitive neutron activation techniques for the determination of traces of tungsten in terrestrial materials have been described by ATKINS AND SMALES[4] and by AMIRUDDIN AND EHMAN[5]. The photometric determination of the element is made difficult by the necessity for separating it from the numerous elements, particularly molybdenum, which interfere in most photometric procedures for tungsten. Several photometric procedures have been described for its determination in soils[6-9], stream sediments[9] and ores[10]. However, most of these methods do not possess sufficient sensitivity for the determination of the low concentration of tungsten present in silicate rocks (average *ca.* 1 p.p.m.)[11].

Techniques for the analysis of silicate rocks have been described by SANDELL[12], and JEFFERY[13]. In the former procedure, iron, titanium, etc. are removed by a double precipitation with sodium hydroxide and molybdenum is precipitated by hydrogen sulphide using antimony sulphide as a carrier. Tungsten is determined visually by the tin(II) chloride–thiocyanate procedure after extraction with ether. In the method of JEFFERY[13] the sample is opened by fusion with sodium hydroxide and sodium nitrate. Tungsten and molybdenum are leached from the fused residue and separated by chloroform extraction of their α-benzoinoxime complexes. The elements are determined simultaneously after extraction with dithiol by measuring the absorbances of the extract at 630 and 680 nm. If, as is usually the case, the ratio of molybdenum to tungsten exceeds *ca.* 4:1 it is necessary to separate the elements by selective extraction with dithiol.

The occurrence of tungsten in sea water was first reported by BARDET *et al.*[14] in 1938. ISHIBASHI *et al.*[15,16] determined the element in sea water by coprecipitating it with iron(III) hydroxide; the precipitate was fused with fusion mixture and tungsten and molybdenum were recovered by leaching the fused residue with water. Most of the molybdenum was removed by precipitation as sulphide in the presence of citric acid. Tungsten was determined photometrically with dithiol after making

---

* Present address: Department of Agriculture and Fisheries, Aberdeen, Hong Kong.

allowance for traces of molybdenum remaining. When this procedure was tested using radioactive tracer techniques it was found that *ca.* 12% of the tungsten present could not be leached from the residue after the fusion. A further loss of *ca.* 5% occurred during the precipitation of molybdenum.

The present paper describes an investigation into the determination of traces of tungsten in silicate rocks, marine sediments and natural waters, particularly sea water.

Concentration of tungsten

Since the abundance of tungsten in silicates and natural waters is low, it is necessary to concentrate the element before determination. Experience of the coprecipitation of molybdenum, and a review of previous work, suggested that coprecipitation would be useful for this purpose. The coprecipitation of tungsten by metal hydroxides has been extensively studied[17-21], and complete recovery with iron(III) hydroxide has been claimed. Organic cocrystallizing agents such as 8-hydroxyquinoline[22] and methylene blue+tannin[23] have also been employed for concentration of tungsten in rock analysis.

An investigation was therefore made of the coprecipitation of tungsten by hydrous metallic oxides. Aliquots (2 l) of filtered sea water were acidified with hydrochloric acid and spiked with 15 μc of tungsten-185 and 15 μg of inert tungsten, each as tungstate. The samples were then treated with iron(III) chloride solution (equivalent to 40 mg of iron) and adjusted to a range of pH values by cautious addition of ammonia. After the precipitate of iron(III) hydroxide had settled it was collected by centrifugation and the recovery of tungsten was determined radiometrically. In agreement with the findings of ISHIBASHI *et al.*[24], tungsten was coprecipitated completely in the pH range 4–7.5; both above and below these limits the efficiency of coprecipitation declined markedly (*viz.* to 85% and 88% at pH values of 2.0 and 8.5 respectively). Analogous experiments were carried out with the hydroxides of aluminium and titanium. These gave much lower recoveries of tungsten at all pH values; thus, aluminium hydroxide (40 mg Al) carried 56% and 70% at pH values of 6.5 and 7.8 respectively, titanium hydroxide (from 30 mg Ti^{3+}) carried 68% at pH 3.8 and only 10% at pH 7.2.

Since the closely related element molybdenum is quantitatively coprecipitated by hydrous manganese dioxide[25,26] experiments were carried out to study the coprecipitation of tungsten with this compound. Aliquots (2 l) of filtered sea water were acidified to pH 2, spiked with tungsten-185 as tungstate and treated with 8 ml of 0.5 *N* potassium permanganate (*ca.* 40 mg Mn) and 4 ml of ethanol. The samples were immediately adjusted to a range of pH values by addition of hydrochloric acid or ammonia solution and well mixed. On the following day the precipitated hydrous manganese dioxide was filtered off and the tungsten-185 which it contained was estimated radiometrically. The results of these experiments (Table I) indicate that

TABLE I

PERCENTAGE COPRECIPITATION OF TUNGSTEN WITH MANGANESE DIOXIDE AS A FUNCTION OF pH

pH	0.9	2.1	4.4	5.1	6.5	7.2	8.5
W coprecipitated (%)	84	98	97	95	88	78	62

tungsten can be recovered in 97–98% yield in the pH range 2.0–4.9. A further investigation showed that at pH 2–3, 15 mg of manganese per litre sufficed for the coprecipitation of at least 50 µg of tungsten/l from sea water. Similar results were also found with fresh waters.

Tests were also carried out to ascertain whether tungsten could be concentrated from sea water by cocrystallization with either thionalide or 5,7-dibromo-8-hydroxyquinoline. However, in neither instance could recoveries of more than 30 % be obtained.

Although the coprecipitation of tungsten by iron(III) hydroxide is slightly more complete than that by manganese dioxide, the latter is considerably more selective in its action. In addition, attempts to use hydroxide precipitation in the analysis of silicate sediments would result in the formation of very bulky precipitates. For these reasons coprecipitation at pH 2.5 with manganese dioxide (*ca.* 20 mg MnO_4^-–Mn/l) was adopted for the concentration of tungsten. The precipitated dioxide is subsequently dissolved in an acidified sulphur dioxide solution.

Separation of tungsten

Although manganese dioxide is a selective coprecipitating agent for tungsten, it will also carry down quantitatively a number of other elements such as vanadium, molybdenum, bismuth, selenium, antimony and tin, together with traces of iron.^{7} Some of these elements, *e.g.* tin, iron, and particularly molybdenum, must be separated before photometric determination of the tungsten since they cause serious interference.

A number of anion-exchange procedures have been described for the separation of tungsten from other elements including molybdenum. Mixtures of hydrofluoric and hydrochloric acids$^{27-32}$ and of hydrochloric acid with organic acids^{33} have been used for selective elution of tungsten from columns of strongly basic anion exchangers.

TABLE II

ELUTION OF 3 µg OF TUNGSTEN FROM DEACIDITE FF BY SUCCESSIVE ELUTION WITH 25-ml ALIQUOTS OF MIXTURES OF HYDROFLUORIC AND HYDROCHLORIC ACIDS

Eluant number		*Percentage of tungsten contained in eluant*		
	HF normality	*1*	*2.5*	*2*
	HCl normality	*9*	*5*	*9*
1		14	62	71
2		12	11	12
3		4	5	3
4		1	3	2
Total		31	81	88

Attempts were made to separate 3 µg of tungsten from 50 µg of molybdenum by elution from a 6 × 0.8 cm column of Deacidite FF (8% cross-linked, 52–100 mesh) using mixtures of various strengths of hydrochloric and hydrofluoric acids (see Table II). It was observed that molybdenum was not eluted. Although the bulk of the tungsten was removed in the first 25 ml of eluant, *ca.* 20% was tenaciously retained by the column and even 250 ml of 2 *N* hydrofluoric–2 *N* hydrochloric acid only eluted *ca.* 95% of the tungsten. Attempts to elute microgram amounts of tungsten with 3 N hydrochloric acid solutions 0.5 N, 0.1 N or 0.05 N with respect to oxalic, citric or ethylenediamine tetraacetic acid respectively were even less successful since 100 ml of these mixtures eluted less than 25%.

More satisfactory elution was attained with 1 N hydrochloric acid containing 88 g of ascorbic acid/l; 100 ml of this solution eluted 75% of the tungsten present on the column, but a further 50 ml only removed another 2%. Attempts to use anion-exchange methods for the separation of tungsten were abandoned, since it appeared that although such procedures gave recoveries of over 98% with amounts of tungsten of 100 μg or more, they failed at the microgram level owing to tenacious retention of *ca.* 1 μg of the element by the anion exchanger.

It has been known for some time[34,35] that tungsten can be separated from many of the commoner elements by elution from a cation exchanger with hydrogen peroxide. Experiments were therefore carried out in order to determine the elution pattern of tungsten from a 10 × 1.2 cm column of Zeo-karb 225 (8% D.V.B., 52–100 mesh) using various strengths of hydrogen peroxide. It was observed that tungsten could be satisfactorily eluted by means of *ca.* 120 ml of 0.3% hydrogen peroxide solution. Molybdenum and vanadium were eluted with this reagent at practically the same rate as tungsten, and even with much longer columns no separation of these elements was feasible. However, since this ion-exchange procedure gave a clean separation of tungsten from all other elements coprecipitated by manganese dioxide it was incorporated in the analysis scheme.

Since molybdenum interferes in most sensitive photometric methods for the determination of tungsten it was still necessary to separate these two elements. ISHIBASHI *et al.*[16] have employed precipitation of molybdenum as sulphide for removal of the bulk of molybdenum during the determination of tungsten in sea water. However, tests showed that at the microgram level less than half of the molybdenum could be removed in this way. SANDELL[36] has suggested the use of antimony(V) sulphide as a carrier for molybdenum sulphide; when this procedure was tested with *ca.* 0.5 μg of tungsten in the presence of 50 μg of molybdenum and 2 mg of antimony, *ca.* 10% of the tungsten was coprecipitated with the molybdenum.

Solvent extraction separation of tungsten and molybdenum

Solvent extraction procedures using dithiol have been used by a number of workers for separation of molybdenum from tungsten. In these methods, the molybdenum–dithiol complex is extracted by means of an organic solvent from a solution of high acidity, alone[37,38], or in the presence of citric acid[39]. Under these conditions tungsten is not extracted. Radiochemical tests were made to determine the effect of both acidity and citric acid concentration on the extraction of the tungsten–dithiol complex.

Effect of acidity on extraction of tungsten. Aliquots (5 ml) of sodium tungstate solution (*ca.* 12 μg W) containing *ca.* 5 μc of tungsten-185 were acidified with various amounts of hydrochloric acid, diluted to 25 ml, and treated with 5 ml of 0.5% dithiol solution. After 1 h the solution was extracted with 5 ml of butyl acetate and the tungsten contained in the organic phase was estimated by scintillation counting. The results of these experiments (Table III) indicated that the percentage extraction of tungsten decreased rapidly as the acidity increased, but that even at an acidity of 5 N appreciable amounts of tungsten were extracted. Analogous experiments showed that molybdenum was quantitatively extracted over the whole range of acid concentrations studied.

Effect of citric acid concentration on extraction of tungsten. Since increase in the acidity alone did not completely prevent extraction of tungsten, the complexing effect of citric acid was investigated in a similar manner at 2 different hydrochloric acid concentrations. It was observed that 0.05 g and 0.01 g of citric acid completely prevented the extraction at acidities of 0.2 N and 2.4 N respectively. Molybdenum was extracted quantitatively even in the presence of 0.2 g of citric acid. In the method adopted, molybdenum was extracted from a solution having an acidity of 2.4 N, in the presence of 0.1 g of citric acid and could, if desired, be determined photometrically. The recovery of tungsten in this process was 98–100%. These conditions are similar to those used by BICKFORD, JONES AND KEENE[39].

TABLE III

EFFECT OF ACIDITY ON EXTRACTION OF TUNGSTEN AS ITS DITHIOL COMPLEX

Final acid normality	0.2	0.8	1.6	2.4	3.4	4.8
Percentage extraction	85	77	32	13	4	2

Photometric determination of tungsten

A review of the literature suggested that only the dithiol procedure[40,41] would provide the sensitivity necessary for the determination of 0.5–2 μg of tungsten. Techniques based on this reagent have been used for the determination of tungsten in silicate rocks[13], biological materials[37] and stream sediments[9]. The methods are all based on photometry of organic extracts of the blue complexes formed between dithiol and tungsten.

The formation of the tungsten–dithiol complexes may be carried out under 2 quite different sets of conditions:

(*1*) in a hot strongly acidic medium in the presence of a powerful reducing agent such as tin(II)[42] or titanium(III)[43] chloride. According to SANDELL[44] the reactions involved are obscure and may involve the formation of tungsten(V);

(*2*) in a hot weakly acidic medium[38].

Experiments carried out to compare these 2 sets of conditions showed that similar results were obtained if the tungsten dithiolate was formed at 90° in either *ca.* 0.3 N hydrochloric acid medium containing *ca.* 0.8% (w/v) of hydroxylamine hydrochloride, or *ca.* 6 N hydrochloric acid medium containing titanium(III) chloride (1% (w/v)Ti) or tin(II) chloride (1.1%, (w/v) Sn).

It was decided to carry out the reaction at low acidity since both tin(II) and titanium(III) chlorides oxidise and hydrolyse readily. When the reaction is carried out at low acidity it is not essential to use a reducing agent. However, hydroxylamine hydrochloride was employed in the working method because it speeded up the reaction and also helped to stabilize the reagent.

Effect of acidity on extraction of tungsten dithiolate. The principal factor controlling the formation of the tungsten dithiolate is the acidity of the solution. In order to find the optimum acidity for the reaction, 5-ml aliquots of tungsten-185 tracer containing 7 μg of inert tungsten were acidified with various amounts of 5 N

TABLE IV

EFFECT OF ACIDITY ON EXTRACTABILITY OF TUNGSTEN–DITHIOLATE

Acid normality before addition of dithiol	0.04	0.12	0.20	0.28	0.36	0.80	1.6
Tungsten extracted (%)	86	100	100	100	100	90	62
Acid normality before addition of dithiol	2.4	3.5					
Tungsten extracted (%)	36	12					

hydrochloric acid and diluted to 25 ml. To each solution was added 1 ml of 10% hydroxylamine hydrochloride solution and 5 ml of 0.5% dithiol reagent (see EXPERIMENTAL). The solutions were heated in a water bath to 80° for 20 min and then cooled. The tungsten dithiolate was extracted with 5 ml of *n*-butyl acetate and the percentage extraction was assessed by scintillation counting. It was observed (Table IV) that the extraction of tungsten was complete with solutions having acidities (before addition of the dithiol reagent) lying within the range *ca.* 0.1–0.4 *N*, corresponding to the addition of 3–10 ml of 1 *N* hydrochloric acid. In all subsequent work 5 ml of 1 *N* hydrochloric acid was used.

Effect of dithiol concentration on reaction. The amount of dithiol used in the reaction is of less importance than the acidity; complete extraction of tungsten was achieved with 3 ml or more of the 0.5% reagent. In order to ensure an excess, 5 ml of this reagent was employed.

Choice of solvent for extraction. Both polar and non-polar solvents can be used for the extraction of tungsten–dithiolate and previous workers have employed petroleum ether, *n*-amyl acetate, *n*-butyl acetate or chloroform. Comparative tests showed that all these solvents are equally effective; *n*-butyl acetate was selected for use because of its comparatively low volatility and its not unpleasant smell.

Beer's law and reproducibility. In order to determine how well the system adhered to Beer's law, determinations were made on amounts of tungsten ranging from 1–10 µg. The observed optical densities showed a linear relationship to the amount of tungsten taken, with an optical density increment of $0.0978 \pm 0.0011/\mu g$ tungsten (extract volume 5 ml; 4 cm cell). Replicate determinations made at the 2 µg and 4 µg levels gave coefficients of variation of 1.0% and 0.8% respectively. The tungsten dithiolate extracts showed no change in optical density for at least 24 h.

Interferences. The influence of foreign metal ions in the determination of tungsten with dithiol has been studied by a number of workers[37,41,42,45], who have shown that the reagent is comparatively specific in its action.

Since a combination of the selective procedures coprecipitation, ion exchange and solvent extraction is used in the present work for the isolation of tungsten, it is unlikely that significant amounts of interfering elements will reach the final photometric stage.

It was shown that no interference was caused by manganese (100 mg), or by vanadium(V), titanium, tin(II), iron(III), or copper (100 µg each).

Storage of sea water samples

Tests were carried out in order to determine the optimum conditions of storage of sea water samples for tungsten determination. Aliquots (500 ml) of filtered sea water, spiked with carrier-free tungsten-185 in the form of tungstate, were stored in the dark at room temperature in a series of 1-l bottles made of different materials. After storage for 2 weeks, tungsten was coprecipitated with hydrous manganese dioxide, and the recovery of tungsten-185 was assessed radiometrically. It was found, after correcting for radioactive decay, that 7%, 1% and 4% of the activity had disappeared from the water samples in soda glass, Pyrex glass and polyethylene bottles respectively. In a similar experiment in which the water sample was acidified to 0.1 *N* with respect to hydrochloric acid before storage in a polyethylene bottle, no loss of tungsten occurred. It is recommended therefore that samples be filtered and stored in the acidified condition in polyethylene bottles.

EXPERIMENTAL

Ion-exchange column

Digest Zeo-karb 225 resin (8% cross linked, 52–100 mesh) 3 times with 3 *N* hydrochloric acid. Wash the resin thoroughly with water and fill a 1.2 cm diameter exchange column to a depth of 10 cm with it. Regenerate the column after use by passing *ca.* 100 ml of 3 *N* hydrochloric acid through it, and then wash with water until the pH of the washings is greater than 3.

Reagents

Hydrogen peroxide, 0.3%. Dilute 10 ml of 30% (w/v) hydrogen peroxide to 1 l.

Dithiol reagent. Dissolve 5 g of toluene-3,4-dithiol in a cold solution of 28 g of potassium hydroxide in *ca.* 500 ml of water. Dilute to 1 l. Store the solution in a polyethylene bottle at 0°. This reagent is stable for at least 3 weeks if stored at −10°, but if stored at room temperature gives high blanks in less than 3 days.

Standard tungsten solution. Dissolve 0.1794 g of sodium tungstate dihydrate in distilled water and dilute to 1 l. Prepare from this solution, which contains 100 µg W/ml, a working standard solution containing 2 µg W/ml.

Determination of tungsten in sea water

Filter the sample through a 0.5 µ membrane filter as soon as possible after collection. Place 10 l of the filtered water in an Erlenmeyer flask and bring to pH 2 by cautious addition of 1 *M* hydrochloric acid. Add 20 ml of ethanol and 40 ml of 0.5 *N* potassium permanganate solution and stir vigorously. Cover the flask and allow it to stand overnight.

When the precipitate of hydrous manganese dioxide has settled, siphon off the supernatant liquid through a glass-fibre filter (Whatman GF/B). Separate the precipitate remaining in the flask by centrifugation and wash it once with water. Dissolve the precipitate on the filter in *ca.* 20 ml of a saturated solution of sulphur dioxide in *ca.* 0.2 *M* hydrochloric acid. Add this solution to the centrifuge bottle containing the main bulk of the precipitate and stir until the latter has dissolved. Transfer the solution quantitatively to a small beaker and heat on the water bath until the sulphur dioxide has been removed. Cool, and dilute to *ca.* 50 ml.

Pass the solution through the Zeo-karb 225 column, wash the column with 20 ml of water and reject the washings. Elute tungsten with 100 ml of 0.3% hydrogen peroxide solution. Place the eluate in a platinum basin and evaporate to 2–3 ml. Destroy the last traces of hydrogen peroxide by addition of a few drops of sulphur dioxide solution. Quantitatively transfer the solution to a 50-ml separating funnel using not more than 10 ml of water. Add 5 ml of concentrated hydrochloric acid, 5 ml of 2% (w/v) citric acid and 5 ml of dithiol reagent and mix well. After 10 min extract the green molybdenum complex with two 10-ml aliquots of *n*-butyl acetate. Discard these extracts unless it is desired to determine molybdenum, in which case they should be combined, diluted to 25 ml and the absorbance measured at 670 nm in a 4-cm cell[26].

Transfer the aqueous layer to a 50-ml silica beaker, add 5 ml of concentrated nitric acid and evaporate slowly. When the majority of the organic matter has been destroyed, add 2–3 ml of 60% perchloric acid and heat on a hot plate until dense white fumes are evolved. Take up in 10 ml of water, add a slight excess of ammonium hydroxide and boil off any excess ammonia. Add 5 ml of 1 *M* hydrochloric acid, 1 ml of 10% (w/v) hydroxylamine hydrochloride and 5 ml of dithiol reagent. Warm to 80–90° on the water bath for 20 min. Cool to room temperature and then transfer the solution to a separating funnel. Extract the tungsten–dithiol complex with 5 ml of butyl acetate and measure the absorption of the extract in a 4-cm cell at 630 nm.

Determine the reagent blank by carrying out the above procedure on sea water from which tungsten has been removed by coprecipitation with manganese dioxide. The reagent blank normally corresponds to *ca.* 0.3 μg of tungsten. Calibrate the method by analyzing sea water samples which have been stripped of their tungsten and then spiked with 1 μg or 4 μg of tungsten per 10 l. Multiply the determined concentration of tungsten by 1.06 in order to make allowance for losses occurring during the separation procedure.

Determination of tungsten in sediments and silicate rocks

Weigh out *ca.* 2 g of the finely ground sample into a platinum basin. Add 8 ml of 60% perchloric acid and 30 ml of hydrofluoric acid. Cover the basin and heat overnight on a water bath. On the following morning remove the cover and allow the bulk of the liquid to evaporate. Continue the evaporation almost to dryness under an infrared heater. After cooling, add 4 ml of perchloric acid, stir with a platinum rod and again evaporate almost to dryness. Repeat the fuming with a further 4 ml of perchloric acid in order to remove all traces of fluoride. Add 2 ml of perchloric acid and 40 ml of water and heat the basin on the water bath until dissolution of the solids is complete.

Transfer the solution to a 500-ml Erlenmeyer flask and dilute to *ca.* 250 ml with water. Adjust to *ca.* pH 2 by cautious addition of 4 *N* ammonium hydroxide. Add 2 ml of ethanol and 4 ml of 0.5 *N* potassium permanganate solution. After allowing the solution to stand overnight, separate the precipitated hydrous manganese dioxide by centrifugation. Wash the precipitate with water and dissolve it in *ca.* 20 ml of a saturated solution of sulphur dioxide in 0.05 *N* hydrochloric acid. Heat the solution to expel sulphur dioxide, dilute to *ca.* 50 ml and pass it through a 10 × 1.2 cm column of Zeo-karb 225. Elute tungsten along with the molybdenum and vanadium present in the sample using 100 ml of 0.3% hydrogen peroxide. Continue the analysis as described above for sea water. Carry out a reagent blank in the same manner but omitting the sample. Evaluate the results from photometric calibration runs made using 1 and 2 µg of tungsten, multiplying the results by 1.05 to make allowance for the 95% recovery obtained in the separation process (see below).

RESULTS

Sea water

Replicate analyses were carried out on 10-l aliquots of 3 samples of surface water from the Irish Sea collected during June and July 1966. These showed an average tungsten content of 0.116 µg/l (at a chlorinity of 19‰), with a standard deviation of 0.010 µg/l. This figure is in excellent agreement with the average concentration of 0.12 µg/l reported by ISHIBASHI *et al.*[15,16] for Pacific Ocean water from off the coast of Japan.

In order to test the accuracy of the procedure, tungsten was stripped from a sample of sea water by coprecipitation with manganese dioxide; 10-l aliquots of this water were then spiked with 1 µg of tungsten as tungstate and analyzed. Recoveries of 0.94 and 0.96 µg were obtained. In a similar experiment 10-l portions of the stripped sea water were analyzed after treatment with *ca.* 15 µc of ^{185}W containing 6 µg of inert tungsten as carrier. The recoveries of tungsten were assessed both photometrically and radiochemically and were found to be 93–95% and 93–94% respectively. The separation procedure thus gives a high and reproducible recovery. The results obtained in the photometric analysis should be multiplied by a factor of 1.06 in order to correct for these losses of tungsten.

Sediments and silicate rocks

In order to test the reproducibility of the proposed scheme, replicate analyses were carried out on dried (105°) red clay samples from Discovery Stations 2896 and 2911 (locations 01° 06′N 85° 36′E depth 4464 m and 35° 55′N, 17° 29′E, depth 3956 m respectively). These samples were found to contain 1.05±0.07 and 0.50±0.03 µg/g respectively. Samples (1 g) of sediment from Discovery Station 2896 were analysed after being spiked with 10 µg of inert tungsten and *ca.* 10 µc of tungsten-185. The recovery of tungsten was assessed both photometrically and radiochemically and in both instances the recovery was 95±1.3%.

SUMMARY

Coprecipitation with hydrous manganese dioxide is used for the concentration of tungsten from natural waters (including sea water) and from solutions prepared from silicate rocks and sediments by hydrofluoric acid attack. After dissolution of the hydrous manganese dioxide precipitate in acidified sulphur dioxide solution, cation exchange is used to separate tungsten and molybdenum from other coprecipitated elements, hydrogen peroxide being used as eluant. Molybdenum is separated from tungsten by extraction of its dithiol complex from 2.4 *N* hydrochloric acid medium containing citric acid and can be determined photometrically. After destruction of citric acid, tungsten is determined photometrically with dithiol. The overall chemical yield of the analytical process is 94±1%. The standard deviation of the method is ±0.010 µg for sea water (0.116 µg W/l) and *ca.* 0.05 µg/g for siliceous sediments containing 0.5–1.0 µg W/g.

RÉSUMÉ

On propose une coprécipitation avec dioxyde de manganèse hydrate pour concentrer le tungstène dans les eaux (y compris l'eau de mer) et dans des solutions préparées à partir de roches silicatées et de sédiments, avec attaque à l'acide fluorhydrique. Après dissolution du précipité, on procède à une séparation du tungstène et du molybdène d'avec d'autres éléments coprécipités, au moyen d'un échangeur de cations. On utilise l'eau oxygénée comme éluant. Le molybdène est séparé du tungstène par extraction de son complexe dithiol, en milieu HCl 2.4 *N* contenant de l'acide citrique et dosé photométriquement. Le tungstène est dosé ensuite photométriquement après destruction de l'acide citrique.

ZUSAMMENFASSUNG

Die Mitfällung mit wässrigem Mangandioxid wird für die Anreicherung von Wolfram aus natürlichen Wässern benutzt; ebenso für Lösungen, die durch Behandlung von Silikaten und Sedimenten mit Flusssäure hergestellt wurden. Nach dem Auflösen der wässrigen Mangandioxid-Fällung in saurer Schwefeldioxidlösung wird zur Abtrennung des Wolframs und Molybdäns von anderen mitgefällten Elementen ein Ionenaustauscher benutzt; Wasserstoffperoxid wird zum Eluieren verwendet. Molybdän wird vom Wolfram abgetrennt durch Extraktion seines Dithiol-Komplexes aus 2.4 *N* salzsaurem Medium, das Zitronensäure enthält, und wird photometrisch bestimmt. Nach der Zerstörung der Zitronensäure wird Wolfram photometrisch mit Dithiol bestimmt. Die Ausbeute des analytischen Verfahrens beträgt 94±1%. Die Standardabweichung der Methode liegt bei ±0.010 μg für Seewasser (0.116 μg W/l) und bei etwa ±0.05 μg/g für silikatische Sedimente mit 0.5–1.0 μg W/g.

REFERENCES

1 V. M. Goldschmidt, *Geochemistry*, Oxford University Press, 1958.
2 K. Rankama and T. G. Sahama, *Geochemistry*, University of Chicago Press, 1949.
3 P. G. Jeffery, *Geochim. Cosmochim. Acta*, 16 (1959) 278.
4 D. H. F. Atkins and A. A. Smales, *Anal. Chim. Acta*, 22 (1960) 462.
5 A. Amiruddin and W. D. Ehman, *Geochim. Cosmochim. Acta*, 26 (1962) 1011.
6 T. G. Matsaberidze, *Ezhegodnik Kavkazask. Inst. Mineral'n Syrya*, (1957) 51.
7 J. H. Watkinson, *New Zealand J. Sci.*, 1 (1958) 201.
8 F. N. Ward, *U.S. Geol. Surv. Circ.*, 119 (1951) 1.
9 P. Bowden, *Analyst*, 89 (1964) 771.
0 H. Grillot, J. Beginnot, M. Boucetta, C. Rouquette and S. Sima, *Franc. Rep. Bur. Rech. Geol. Minieres Mem.*, No. 30 (1964) 1.
11 E. B. Sandell, *Am. J. Sci.*, 244 (1946) 643.
12 E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, 18 (1946) 163.
13 P. G. Jeffery, *Analyst*, 81 (1956) 104.
14 J. Bardet, A. Tchakirian and R. Lagrange, *Compt. Rend.*, 206 (1938) 450.
15 M. Ishibashi, *Records Oceanog. Works Japan*, 1 (1953) 88.
16 M. Ishibashi, T. Shigematsu and Y. Nakagawa, *Bull. Inst. Chem. Res. Kyoto Univ.*, 32 (1954) 199.
17 M. Ishibashi, T. Fujinaga, T. Kuwamoto, M. Kori and S. Sugibayashi, *J. Chem. Soc. Japan*, 81 (1960) 392.
18 A. N. Zelikman and N. N. Goronits, *Zavodsk. Lab.*, 24 (1958) 940.
19 A. P. Degtarenko, R. I. Libina and A. D. Miller, *Gidrokhim. Materialy*, 29 (1959) 264.
20 M. Ishibashi, *Records Oceanog. Works Japan*, 6 (1962) 215.

21 A. F. NEMIROVSKAYA, L. N. KEREMEDZHIDI AND N. I. YASHIMA, *Tr. Novochersk. Politekh. Inst.*, 143 (1963) 55.
22 R. NIERICKER AND W. D. TREADWELL, *Helv. Chim. Acta*, 29 (1946) 1472.
23 A. B. ISAEVA, *Tr. Inst. Okeanol.*, 47 (1961) 159.
24 M. ISHIBASHI, T. FUJINAGA AND T. KUWAMOTO, *Records Oceanog. Works Japan*, 6 (1962) 215.
25 M. TANAKA, *Mikrochim. Acta*, (1958) 204.
26 K. M. CHAN AND J. P. RILEY, *Anal. Chim. Acta*, 36 (1966) 220.
27 K. A. KRAUSE, F. NELSON AND G. E. MOORE, *J. Phys. Chem.*, 58 (1954) 11.
28 K. A. KRAUSE, F. NELSON AND G. E. MOORE, *J. Am. Chem. Soc.*, 77 (1955) 3972.
29 D. H. WILKINS, *Talanta*, 2 (1959) 355.
30 E. J. DIXON AND J. B. HEADRIDGE, *Analyst*, 89 (1964) 185.
31 J. L. HAGUE, E. D. BROWN AND H. A. BRIGHT, *J. Res. Natl. Bur. Std.*, 53 (1954) 261.
32 K. F. SUGAWARA, *Anal. Chem.*, 36 (1964) 1373.
33 W. R. BANDI, E. G. BUYOK, L. L. LEWIS AND L. M. MELRICK, *Anal. Chem.*, 33 (1961) 1275.
34 D. J. RYABCHIKOV AND V. E. BUKHTIAROV, *Zh. Analit. Khim.*, 15 (1960) 242.
35 F. W. E. STRELOW, *Anal. Chem.*, 35 (1963) 1279.
36 E. B. SANDELL, *Ind. Eng. Chem., Anal. Ed.*, 18 (1946) 163.
37 S. H. ALLEN AND M. B. HAMILTON, *Anal. Chim. Acta*, 7 (1952) 483.
38 C. S. PIPER AND R. S. BECKWITH, *J. Soc. Chem. Ind.*, 67 (1948) 374.
39 C. F. BICKFORD, W. S. JONES AND J. S. KEENE, *J. Am. Pharm. Assoc., Sci. Ed.*, 37 (1948) 255.
40 J. H. HAMENCE, *Analyst*, 65 (1940) 152.
41 C. C. MILLER AND A. J. LOWE, *Analyst*, 69 (1944) 109.
42 B. BAGSHAWE AND R. J. TRUMAN, *Analyst*, 72 (1947) 189.
43 P. GREENBERG, *Anal. Chem.*, 29 (1957) 896.
44 E. W. SANDELL, *Colorimetric Determination of Traces of Metals*, 3rd Edn., Interscience, New York, 1959.
45 E. W. HOBART AND E. P. HURLEY, *Anal. Chim. Acta*, 27 (1962) 144.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

1,1'-BIS(6-CHLOROANTHRAQUINONYL)AMINE AS A REAGENT FOR TRACE AMOUNTS OF BORON†

ROBERT L. GROB, JOHN COGAN*, JOHN J. MATHIAS**, SAMUEL M. MAZZA AND ALLAN P. PIECHOWSKI
Chemistry Department, Villanova University, Villanova, Penn. (U.S.A.)

(Received January 17th, 1967)

The analysis of materials containing small amounts of boron has become increasingly important in recent years. Previously, plant and biological systems were the most widely investigated[1-4] but recent work has involved semiconductors[5,6], isotope technology[7], organoboron chemistry, steel and alloys[8,9] and detergents. Early work has been reviewed by GOWARD AND WIEDERKEHR[10].

Some years ago, colorimetric methods for the determination of boron based on the use of substituted 1,1'-bis(anthraquinonyl)amines, were described[4,11]. Further work on this general type of reagent for determination of boron has shown that 1,1'-bis(6-chloroanthraquinonyl)amine is useful.

EXPERIMENTAL

Equipment

A Perkin-Elmer 220 Recording Spectrophotometer and a Beckman DU Spectrophotometer were used with 1-cm pyrex cells.

All glassware was pyrex brand. The distillation apparatus for the separation of the methyl ester of boric acid was made from Corning alkali-resistant glassware No. 7280; this is essentially free of boron (maximum boron oxide, 0.2%).

Synthesis of the reagent

Heat a mixture of 0.2 mole of 2-chloroanthraquinone (Eastman Organic Chemicals), 48 g of 22% oleum, and 0.5 g of mercury(II) sulfate to 120° during 60–90 min, and then hold at this temperature for 3 h. Precipitate the 1-potassium sulfonate-6-chloroanthraquinone by the addition of concentrated potassium chloride solution to the cooled reaction mixture (yield, 60%)[14]. Convert the potassium salt to the 1,6-dichloroanthraquinone by reacting with sodium chlorate and hydrochloric acid in a 10% sulfuric acid solution. Add the 30% hydrochloric acid slowly over a 6-h period to the actively boiling mixture[15]***. A quantitative yield of the 1,6-dichloro derivative (m.p. 202–204°) results.

---

† Presented at the First Middle Atlantic Regional Meeting of the American Chemical Society; Philadelphia, Pa., February 4, 1966.

* Smith, Kline and French Laboratories, Philadelphia, Penn. (U.S.A.).

** Department of Biochemistry, Pennsylvania State University, University Park, Penn. (U.S.A.).

*** This is a modification of the reference directions. It was found that adding the HCl slowly to the actively boiling solution gave better results. The addition of sulfuric acid raised the boiling point of the solution, so that the reaction proceeded at a faster rate.

To make the 1-amino-6-chloroanthraquinone, treat 0.2 mole of 2-chloroanthraquinone with concentrated nitric acid in concentrated sulfuric acid; the yield of the nitration product is 60% (m.p. 274–275°). A quantitative yield of the 1-amino-6-chloroanthraquinone (m.p. 210–211°) is obtained by reduction of the nitro derivative with an aqueous alkaline sodium sulfide solution.

Prepare the reagent by reacting equimolar amounts of the 1,6-dichloro- and 1-amino-6-chloro-9,10-anthraquinone derivatives, in the presence of sodium bicarbonate and copper(II) acetate, using nitrobenzene or naphtha as the solvent[16]. The yield for this reaction is essentially quantitative.

The reagent is a deep red solid (melting range 305–315°). It forms a greenish-yellow solution on dissolution in 96% sulfuric acid, which becomes pink on heating above 125°.

Standard solutions

Boron solution. Dissolve 5.7162 g of orthoboric acid in 100 ml of 96% sulfuric acid. This solution contains 1.0 mg of boron per ml. Dilute to prepare solutions containing 100, 10 and 1 μg of boron per ml.

Reagent solution. Dissolve 49.834 mg of reagent in sufficient 96% sulfuric acid to make 100 ml of solution. This solution is $10^{-3}M$; $10^{-4}M$ solution is made by dilution with 96% sulfuric acid.

Diverse ion solutions. Reagent-grade compounds were used for all solutions. Stock solutions were made up in 96% sulfuric acid and contained 1 mg of the desired ion per ml.

Procedure

Select a sample size which will give a boron concentration of 1–5 μg in the final solution. Dissolution of the sample may be performed by any technique which is compatible with the sample. If the boron must be separated because of interfering ions, several techniques are available; *e.g.*, distillation of the methyl ester[4], or ion exchange[12,13]. Whichever technique is employed, the boron must be present finally as orthoboric acid or its salt; this can be assured by a final evaporation of the boron-containing solution in the presence of a slight excess of a strong base, *e.g.* sodium or calcium hydroxide.

Add 1.0 ml of 96% sulfuric acid and 1.0 ml of $10^{-4}M$ reagent solution and develop the color at 125° for 5 h. Dilute to 10 ml with 96% sulfuric acid and measure the absorbance at 641 nm *versus* a reagent blank. Determine the boron content of the solution by reference to a calibration graph.

RESULTS AND DISCUSSION

Absorption spectra

Absorption spectra of the reagent solution and of solutions of the boron complex are shown in Fig. 1. Under the conditions used, there is very little absorption of the reagent at the wavelength of maximum absorption of the complex.

Rate of formation of the complex

The formation of a stable complex between the boron and these anthraquino-

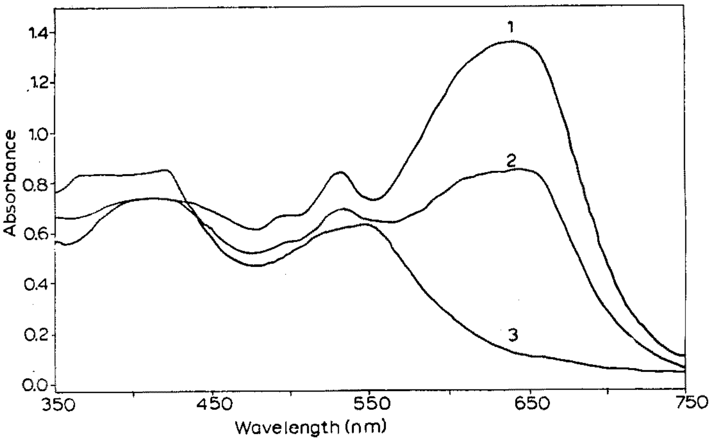


Fig. 1. Absorption spectra of the reagent and the boron complex. (3) Reagent ($7 \cdot 10^{-6}\,M$) *versus* 96% sulfuric acid. (2) Complex (excess reagent; 5 μg boron) *versus* 96% sulfuric acid. (1) Complex (excess boron; 100 μg boron) *versus* 96% sulfuric acid.

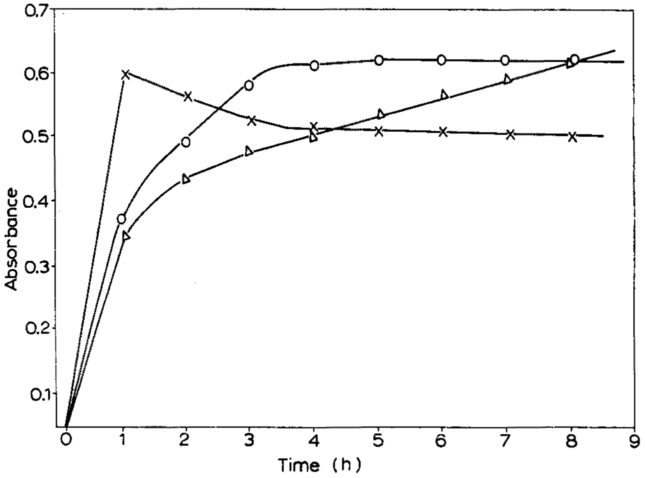


Fig. 2. Time–temperature study for the formation of the boron complex. △ 100°, ○ 125°, × 150°.

nylamines is very slow and may take days to reach equilibrium. The rate of the reaction can be increased by heating. A time–temperature study was made with solutions containing 1.0 ml of $1 \cdot 10^{-4}\,M$ reagent and 10.0 μg of boron; at various time intervals, the solutions were removed from the oven, cooled and diluted to 10 ml with 96% sulfuric acid, and the absorbances were measured at 641 nm *versus* a reagent blank. The results (Fig. 2) showed that the maximum absorbance occurred after 5 h of heating at 125°. These conditions were therefore chosen for all later work.

Effect of sulfuric acid concentration

Solutions containing 10 μg of boron and varying weight percentages of sulfuric acid were heated for the required time and then the absorbances were measured at 641 nm *versus* the appropriate reagent blank. A large decrease in absorbance (Table I) was noted as the weight percent of sulfuric acid decreased; below 90% (w/w) sulfuric acid the reagent began to separate from the solution, thus destroying the complex. Clearly, at least 96% sulfuric acid is needed to insure precision; no tests were made with stronger sulfuric acid. The data are consistent with published results[4,11].

TABLE I

EFFECT OF SULFURIC ACID CONCENTRATION ON THE FORMATION OF THE BORON COMPLEX

μg Boron	*% H_2SO_4 (by weight)*	*Absorbance*
10	90	0.238
10	92	0.455
10	94	0.514
10	96	0.610

Composition of the complex

The methods used to evaluate the ratio of boron to reagent in the complex were the mole ratio method[17], the method of continuous variations[18] as modified by VOSBURGH AND COOPER[19], and the slope ratio method[20,21]. For the mole ratio technique, the reagent concentration was kept constant (3.0 ml of $1 \cdot 10^{-4}$ *M* reagent) while the volume of boron solution ($1 \cdot 10^{-4}$ *M*) was varied from 1 to 7 ml; all solutions had a final volume of 10 ml. For the continuous variations method, both the reagent solution and the boron solution were $1 \cdot 10^{-4}$ *M* and the total volume was kept at 10 ml. For the slope ratio method, two sets of data were obtained. In one, the reagent was maintained constant ($1 \cdot 10^{-4}$ *M*) and in excess while the boron concentration was varied from 1 to 5 μg; in the other the boron was in excess (100 μg) while the volume of reagent solution ($1 \cdot 10^{-4}$ *M*) was varied from 1 to 5 ml.

All 3 methods showed unequivocally that the complex contained one atom of boron to one molecule of reagent. Some extrapolation was necessary to determine the relationship because of the dissociation of the complex.

Stabilities of reagent solution and of the boron complex

To study the stabilities of solutions containing the reagent and containing the boron complex, the absorption spectra of both solutions were checked at various time intervals; a change of 0.01 in the absorbance was taken as a significant change in the solution. A $1 \cdot 10^{-3}$ *M* solution of the reagent did not register any noticeable change until after 30 days. A $1 \cdot 10^{-3}$ *M* solution of the boron complex registered a change after 120 days. These time intervals are more than adequate for any analytical system.

Beer's law

The boron–1,1′-bis(6-chloroanthraquinonyl)amine complex obeyed Beer's law over the concentration range 1–5 μg of boron per 10 ml of solution. Larger amounts could probably have been determined with smaller cells or greater dilution. The optimum concentration range was 1.0–3.5 μg of boron per 10 ml of solution. The sensitivity of this system was 0.0005 μg B · cm^{-2} calculated by SANDELL's method[22]. Comparison of this method with other methods clearly shows that the proposed method is more sensitive than the 3 previous methods[4,11] based on substituted 1,1′-bis(anthraquinonyl)amine. It is also much more sensitive than methods based on curcumin, quinalizarin, etc. The method presented here has an absorptivity of 2000.

Effect of diverse ions

To determine the interference by diverse ions, solutions were prepared containing 2 μg of boron, 1.0 ml of reagent solution, and 100 μg of each ion to be tested. A change of 0.010 in absorbance was arbitrarily chosen to represent an interference, and tolerance limits were established by varying the concentration of the diverse ion. When the diverse ion was rather insoluble, *e.g.*, $SrCO_3$ and TiO_2, saturated solutions were used, the concentration being estimated by some suitable procedure. Table II shows the tolerances of the diverse ions investigated and the compounds employed in their preparation.

TABLE II

EFFECT OF DIVERSE IONS

Ion	*Added as*	*Limiting concentration (μg)*	*Ion*	*Added as*	*Limiting concentration (μg)*
Al^{3+}	$Al_2(SO_4)_3$	3.0	Fe^{2+}	$Fe(NH_4)_2(SO_4)_2$	11.0
AsO_4^{3-}	Na_3AsO_4	188.0	F^-	CaF_2	0.0
Ba^{2+}	BaO	6.0	Ge^{4+}	GeO_2	20.0
Cd^{2+}	$CdSO_4$	10.0	IO_4^-	KIO_4	1.0
Ca^{2+}	$CaSO_4$	10.0	Mg^{2+}	$MgSO_4$	10.0
ClO_4^-	$KClO_4$	133.0	Mn^{2+}	$MnSO_4$	10.0
Cl^-	$NaCl$	11.0	Ni^{2+}	$NiSO_4$	12.0
$Cr_2O_7^{2-}$	$Na_2Cr_2O_7$	13.0	NO_3^-	KNO_3	0.0
Cr^{3+}	$Cr_2(SO_4)_3$	110.0	NO_2^-	KNO_2	10.0
Co^{2+}	$CoSO_4$	68.0	$Sb_2O_7^{4-}$	$K_2H_2Sb_2O_7$	18.0
Cu^{2+}	$CuSO_4$	10.0	Sr^{2+}	$SrCO_3$	78.0
$C_2O_4^{2-}$	$Na_2C_2O_4$	234.0	Ti^{4+}	TiO_2	20.0
Fe^{3+}	$FeNH_4(SO_4)_2$	10.0	Zn^{2+}	$ZnSO_4$	6.0

Precision of the method

A synthetic medium containing boron, was analyzed and the reproducibility of color development was studied with a standard solution of orthoboric acid. For the statistical study, an aliquot of solution containing 10 μg B/ml was mixed with 1.0 ml of reagent solution ($1 \cdot 10^{-3} M$), diluted to 25 ml and taken through the color development and absorbance measurement steps. Fifteen replicate analyses showed a standard deviation of 0.002 absorbance units, the average reading being 0.758.

A synthetic medium was made up to contain the ions listed in Table III. The boron was separated by distillation of its methyl ester[11]. Ten replicate analyses of solutions containing 2.0 and 4.0 μg of boron gave an average percentage recovery of 98.45% with a standard deviation from the mean of 1.55%.

TABLE III

SYNTHETIC MEDIUM

Ion	*Added as*	*Concentration (p.p.m.)*	*Ion*	*Added as*	*Concentration (p.p.m.)*
BO_3^{3-}	H_3BO_3	4.0	Cd^{2+}	$CdSO_4$	15.0
Zn^{2+}	$ZnSO_4$	20.0	Ba^{2+}	BaO	5.0
Mg^{2+}	$MgSO_4$	10.0	Fe^{3+}	$FeNH_4(SO_4)_2$	25.0
Ge^{4+}	GeO_2	5.0	Al^{3+}	$Al_2(SO_4)_3$	10.0
Cr^{3+}	$Cr_2(SO_4)_3$	30.0			

APPLICATION OF THE METHOD

The performance of the method for some vegetation samples was evaluated. In some cases the boron was separated from the ashed sample of vegetation by distillation, and in others, the colorimetric procedure was applied directly to the sample of vegetation. Two types of vegetation were analyzed, *i.e.*, spinach and carrot tops; in both cases the samples were dried in an oven at 110° and then ground to a large homogeneous sample. When boron was not separated from the sample, the ashing procedure was similar to that described by ELLIS *et al.*[23].

Wet digestion

Add 2 ml of concentrated sulfuric acid to a 25-mg sample of dried leaf in a small porcelain casserole. Add 50 mg of calcium hydroxide and 1 drop of 30% hydrogen peroxide. Heat the mixture gently at first and then more vigorously until fumes of sulfur trioxide appear. Cool and repeat the peroxide-fuming process until the solution becomes clear (usually 3–4 times). Add 1.0 ml of the reagent solution and heat in an oven at 125° for 5 h. Cool and transfer with 96% sulfuric acid to a 10.0-ml volumetric flask. Mix well and read the absorbance at 641 nm *versus* a reagent blank.

The technique for separating the boron from the leaf sample has been described previously[4].

Table IV gives the results obtained, which show very little difference between the performance of the distillation technique and the wet digestion technique. For this type of sample, at least, separation of the boron by distillation of its methyl ester seems unnecessary; the same may be true for other types of vegetation.

TABLE IV

COMPARISON OF BORON DETERMINATIONS UNDER TWO SETS OF CONDITIONS

Leaf type and sample no. Spinach	*Boron found (μg)*		*Leaf type and sample no. Carrot tops*	*Boron found (μg)*	
	Distillation 50-mg samples	*Wet digestion 25-mg samples*		*Distillation 50-mg samples*	*Wet digestion 25-mg samples*
1	4.00	2.05	1	2.10	1.02
2	3.96	2.00	2	2.05	1.00
3	4.05	1.98	3	2.08	1.05
4	4.00	2.00	4	1.98	1.00
5	3.95	2.05	5	2.05	1.03
	s.d. = 0.04	s.d. = 0.03		s.d. = 0.05	s.d. = 0.02

SUMMARY

A new reagent, 1,1'-bis(6-chloroanthraquinonyl)amine, has been synthesized and applied to the determination of trace amounts of boron. A blue complex is formed on heating with orthoboric acid in 96% sulfuric acid medium. Oxidizing agents and some cations interfere with the method; separation of the boron either by distillation of the methyl ester or by ion exchange removes such interferences. The method is very sensitive *i.e.*, 0.0005 μg B/cm^2, and can be used for the analyses of vegetation.

RÉSUMÉ

Un nouveau réactif, la 1,1'-bis(6-chloroanthraquinolyl)amine, est synthétisé et appliqué au dosage de traces de bore. Un complexe bleu est formé par chauffage avec l'acide orthoborique en milieu acide sulfurique 96%. En présence d'oxydants et de quelques cations, il est nécessaire de séparer le bore soit par distillation de l'ester méthylique ou à l'aide d'échangeurs d'ions. Cette méthode est très sensible (0.0005 μg B/cm^2) et peut s'appliquer à l'analyse des végétaux.

ZUSAMMENFASSUNG

Ein neues Reagenz, 1,1'-bis(6-Chloroanthraquinonyl)amin, wurde synthetisiert und für die Bestimmung von Spuren Bor verwendet. Durch Erhitzen von Orthoborsäure in 96%iger Schwefelsäure mit dem Reagenz wird ein blauer Komplex gebildet. Störungen durch Oxydationsmittel und einige Kationen können durch Abtrennung des Bors durch Destillation als Methylester oder durch Ionenaustausch beseitigt werden. Die Methode ist mit 0.0005 μg B/cm^2 sehr empfindlich und kann für die Analyse von Pflanzenmaterial verwendet werden.

REFERENCES

1 J. E. Brown and H. G. Gauch, *Am. Fern J.*, 55 (1965) 67.
2 H. G. Gauch and W. M. Dugger, *Univ. of Md. Agr. Expt. Sta., Bull. A-80*, Dec. 1954.
3 G. Bertrand, *Rec. Trav. Chim.*, 57 (1938) 569.
4 R. L. Grob and J. H. Yoe, *Anal. Chim. Acta*, 14 (1956) 253.
5 G. H. Morrison and R. L. Rupp, *Anal. Chem.*, 29 (1957) 892.
6 S. S. Flaschen and C. L. Luke, *Anal. Chem.*, 30 (1958) 1406.
7 A. W. Wenzel and C. E. Pietri, *Anal. Chem.*, 36 (1964) 2083.
8 L. C. Pastzor and J. D. Bode, *Anal. Chem.* ,32 (1960) 1530.
9 L. C. Pastzor, J. D. Bode and Q. Fernando, *Anal. Chem.*, 32 (1960) 277.
10 G. W. Goward and V. R. Wiederkehr, *Anal. Chem.*, 35 (1936) 1542.
11 J. H. Yoe and R. L. Grob, *Anal. Chem.*, 26 (1954) 1465.
12 A. W. Wenzel and C. E. Pietri, *Anal. Chem.*, 36 (1964) 2083.
13 J. D. Callicoat, J. D. Wolszon and J. R. Hayes, *Anal. Chem.*, 31 (1959) 1437.
14 U. S. FIAT 1313, Vol. II, p. 52–56 (PB 85172).
15 U. S. FIAT 1313, Vol. II, p. 36–37.
16 F. Ullman and H. Bincer, *Ber.*, 49 (1916) 747.
17 J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 111.
18 P. Job, *Ann. Chim. (Paris)*, 9 (1928) 113.
19 W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, 63 (1941) 437.
20 A. E. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, 72 (1950) 4488.
21 A. E. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, 74 (1952) 4744.
22 E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Edn., Interscience, New York, 1959, p. 83.
23 G. H. Ellis, E. G. Zook and O. Baudisch, *Anal. Chem.*, 21 (1949) 1345.

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SHORT COMMUNICATIONS

Spectrophotometric determination of 2,5-hexanedione

In recent work in this laboratory, it became necessary to determine micro amounts of γ-dicarbonyl compounds formed as oxidation products of proteins. Methods for determining dicarbonyl compounds are available[1,2], but these are not specific for γ-dicarbonyl compounds. A semimicro qualitative test for 1,4-diketones has been described[3].

A micro method for the determination of γ-dicarbonyl compounds, based on the qualitative test for γ-dicarbonyl compounds of MAREK AND LERCH[4], is described below. The method involves the quantitative conversion of the γ-dicarbonyl compounds with ammonia to pyrroles; the latter are then determined by treatment with *p*-dimethylaminobenzaldehyde.

2,5-Hexanedione (acetonylacetone) was used in the development of this method as a representative γ-dicarbonyl compound.

Apparatus

A Beckman DU spectrophotometer was used.

Reagents

2,5-Hexanedione (Fisher "Highest Purity") was purified by repeated partial freezing and thawing. All other chemicals used were reagent grade.

p-*Dimethylaminobenzaldehyde reagent.* Dissolve 1 g of *p*-dimethylaminobenzaldehyde in 69 ml of 91.3% formic acid and 31 ml of 85% orthophosphoric acid. This reagent will remain usable for one week if stored in a refrigerator.

Procedure

Into a series of 25-ml tubes place 0.1–0.6 ml aliquots of aqueous 0.001 *M* solution of 2,5-hexanedione (or an aqueous solution containing about 10–70 μg of 2,5-hexanedione in up to 8.5 ml). To each tube add 7 ml of 6 *N* ammonia solution and sufficient water to obtain a total volume of 15.5 ml. After heating for 30 min in a boiling water bath, remove the tubes, and add 3 ml of *p*-dimethylaminobenzaldehyde reagent. After cooling, read the absorbance at 525 nm. Determine the absorbance of a reagent blank with water in place of the hexanedione. Correct all results for the reagent blank.

Results and discussion

The agreement of the visible absorption spectrum of the colored substance obtained as the product of the reaction with the spectrum obtained by treatment of *p*-dimethylaminobenzaldehyde with 2,5-dimethylpyrrole indicates that the product obtained by reaction of 2,5-hexanedione with ammonia is the expected 2,5-dimethylpyrrole. The absorption maximum of the colored product depends, obviously, on the pyrrole formed, which in turn depends on the particular γ-dicarbonyl compound originally present.

The effects of the amount of ammonium hydroxide solution, the type of *p*-dimethylaminobenzaldehyde reagent, and the heating time were studied to determine the optimum conditions for the reaction.

The absorbance at 525 nm of the final solution varied with the amount of 6 *N* ammonium hydroxide used for the formation of the pyrrole. Maximum color was obtained with 7 ml; with 6 ml, 13% less color was obtained, while 9 ml gave 6% less color. Use of *n*-propylamine in place of ammonia did not increase the sensitivity of the method.

The absorbance of the final solution was less if acetic acid or hydrochloric acid was used in place of formic acid in the *p*-dimethylaminobenzaldehyde reagent, the decreases being about 31% and 58%, respectively. A range of 4–6% of 85% orthophosphoric acid in the final solution (v/v) is required for maximum color development.

Maximum color development was obtained with a heating time of 30 min in boiling water. With heating periods of 5 min, 15 min, and 45 min, the absorbances were 47%, 11%, and 7% below the maximum, respectively. Periods in the dark after heating of up to 60 min did not increase the absorbance of the solution.

The color produced in the reaction was stable for at least 2 h. The effect of possible interfering substances was determined. Neither tryptophan nor tyrosine increased the absorbance of the solutions at 525 nm, even when the amino acids were present in molar concentrations that were 300 times that of the dione. The presence of unoxidized protein did not interfere in the determination; for example, 0.5 ml of a 1% gelatin solution used in place of the 2,5-hexanedione solution in the analysis gave a final solution whose absorbance did not differ from that of the reagent blank.

The absorbance *vs.* concentration plots were linear in the range 10–70 μg of 2,5-hexanedione. The standard deviation of the method was ±1.6%.

The authors express appreciation to the Nopco Chemical Co. Scholarship Fund and to the Ernest Griess Fellowship Fund.

Dept. of Basic Science in Tanning Research,
University of Cincinnati,
Cincinnati, Ohio (U.S.A.)
C. L. DEASY
Dept. of Chemistry,
College of Mount St. Joseph on the Ohio,
Mount St. Joseph, Ohio (U.S.A.)
ANN E. STITZEL

1 C. NEUBERG AND E. STRAUSS, *Arch. Biochem.*, 7 (1945) 211.
2 C. S. WISE AND C. L. MEHLTRETTER, *Anal. Chem.*, 30 (1958) 174.
3 W. G. LEACH, *Analyst*, 67 (1942) 53.
4 B. MAREK AND E. LERCH, *J. Soc. Dyers Colourists*, 81 (1965) 481.

(Received February 2nd, 1967)

A transistorised linear-to-logarithmic signal converter for use with recording spectrophotometers

Most double-beam recording spectrophotometers which are suitable for use with external recorders, present their output as a potential which varies linearly to represent the variation of transmission with wavelength. In analytical spectrophotometry it is frequently advantageous to record the variation in absorbance of a sample rather than its transmission. This is usually accomplished mechanically in commercially available potentiometric recorders by application of the linear signal to an instrument that has its slide-wire wound with logarithmic spacing, or whose pen carriage is driven through logarithmic gearing. In both systems the resolution decreases as absorbance increases, and mechanical systems of this type are frequently subject to fatigue and non-reproducibility. This paper describes a simple and inexpensive electronic unit which has been constructed to enable absorbance to be displayed against wavelength on any standard recorder with a linear slide-wire. It is necessary for such a device to exhibit rapid, accurate and reproducible response to variation in the input signal; these conditions are fulfilled over a wide range of input voltage with the unit described.

Previous work on a similar device has been described by THOMPSON[1], who produced a unit for use with a single-beam spectrophotometer where the unit was linked directly to the output of the photomultiplier on a commercial instrument. DAVEY[2] has also used a system involving constant photomultiplier output on a single-beam instrument, in which the change in dynode voltage required to compensate for changes in light intensity was measured.

Converter unit

The unit was constructed for use with the Beckman DB recording spectrophotometer to enable absorbance readings to be displayed directly on a Honeywell Electronic recorder. The logarithmic conversion depends on the characteristics of a

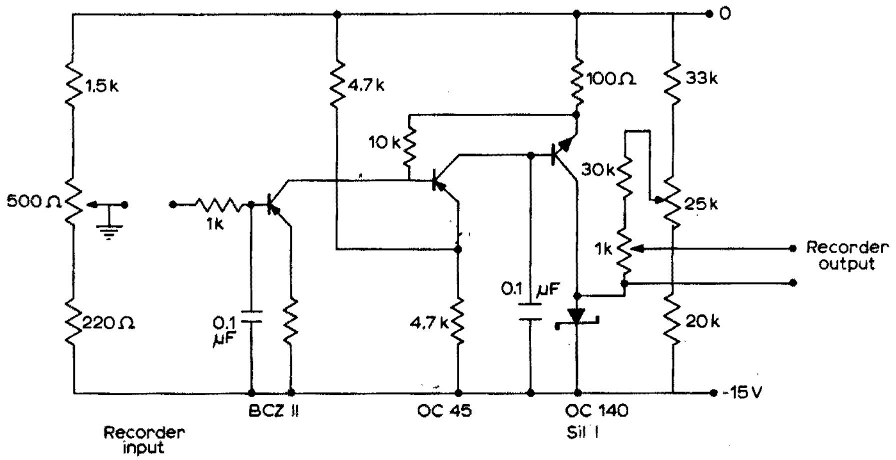


Fig. 1. Circuit diagram of Logarithmic Conversion Unit.

particular Zener diode (Standard Telephones and Cables, Type SIL I.) that has been manufactured so that the Zener voltage is a logarithmic function of the Zener current. Figure 1 shows the circuit employed in the converter unit. The input is taken from the recorder terminals of the spectrophotometer, whose maximum output is 100 mV (200 μA through 500 ohms). This corresponds to an absorbance of zero on the spectrophotometer scale. The output is amplified by a three-stage semiconductor amplifier with a current gain of 50, the last stage of which has the Zener diode as a collecter load. The voltage developed across the diode is compared with a reference voltage derived by potential dividing of the supply voltage. The difference is then applied to the recorder input via a simple attenuator which is adjusted to give full-scale deflection at the recorder for an absorbance of 1.0. The output from the spectrophotometer has one terminal common to earth, so that the highly stabilised 15-V power supply must be floating with respect to earth potential. The 15-V D.C. supply was taken from a Coutant type ELV50-15 power pack.

Evaluation of characteristics of converter unit

Figure 2 shows a block diagram of the arrangement used to evaluate the utility of the signal converter unit.

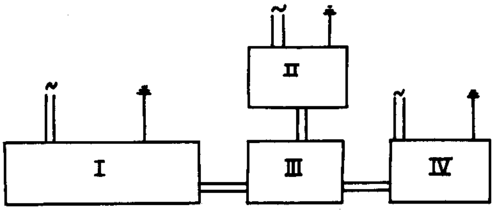


Fig. 2. Block diagram of apparatus used to test converter unit. (I) Double-beam spectrophotometer. (II) Stabilised 15-V power supply. (III) Linear-logarithmic Converter unit. (IV) Recorder with linear slide-wire.

Accuracy. The unit was interposed between the spectrophotometer and strip chart recorder. A 0.2 *M* solution of nickel sulphate in distilled water was employed as the sample and distilled water as the reference solution. The manual wavelength scan facility was employed to adjust the spectrophotometer output to 100% transmission (zero absorbance) and the reading on the recorder was noted. The output was then decreased in steps equivalent to 10% transmission by adjustment of the wavelength used, and at each step the recorder reading and the absorbance reading on the spectrophotometer scale were observed. Figure 3 shows the results obtained. The converted absorbance is plotted against the spectrophotometer scale absorbance and the unconverted signal obtained without the unit in use is also shown.

The response from the unit is linear up to absorbance values of 0.7, and up to this value the converted signal is reproducibly within 3% of the expected absorbance. The accuracy is even better than this at absorbance values between 0.3 and 0.6, in which range the values obtained lie within 1–2% of the expected absorbance. Owing to the deviation from linearity of the output of the Zener diode for very low currents, at absorbance values greater than 0.7 the converted signal becomes increasingly inaccurate (low) with reference to the true absorbance value. Thus at an expected absorbance of 0.8 the value obtained, 0.75, is 6.25% low.

Results similar to those obtained above for the accuracy check using the nickel absorption spectrum at different wavelengths were also produced when calibration graphs of nickel concentration against absorbance were constructed at the wavelength of maximum absorbance.

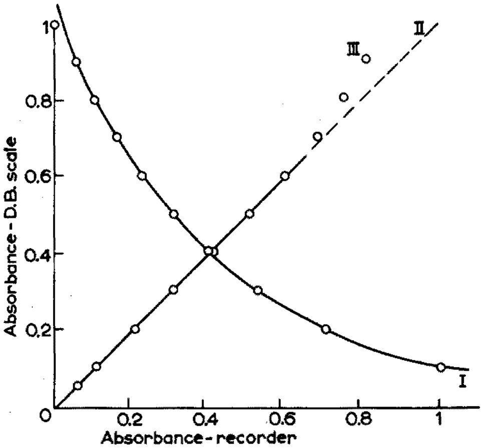


Fig. 3. Linearity of absorbance response for unit under test. (I) Response of recorder (abscissa) to equal decrements in absorbance measured on the DB scale without unit in operation. (II) Ideal linear conversion of transmission to absorbance. (III) Conversion obtained, showing deviation from linearity at high absorbance values.

TABLE I

TEST OF REPRODUCIBILITY OF UNIT

Solution concn. (Ni^{2+} molarity)	*Absorbance (390 nm)*	*Standard deviation (%)*
0.15	0.712	
	0.714	
	0.710	
	0.714	
	0.712	0.24
0.10	0.514	
	0.509	
	0.514	
	0.510	
	0.513	0.46
0.05	0.261	
	0.264	
	0.261	
	0.265	
	0.262	0.70

Reproducibility. In order to obtain an estimate of the reproducibility of the absorbance values after conversion, standard solutions of nickel sulphate of different concentrations were prepared, and their absorption spectra were recorded using the spectrophotometer, converter and recorder. The absorption spectrum of each solution was taken repetitively, and the results for the standard deviation in the absorbance produced at the wavelength of maximum absorbance are shown in Table I. The concentrations of the nickel solutions were selected to produce absorbance values at the two extremities, and at the centre, of the range of values for which good photometric accuracy is obtained, and which are normally encountered in calibration curves in quantitative solution spectrophotometry.

Conclusion

The unit described permits rapid and reproducible presentation of absorbance at recorders fitted with linear slide-wires. The device stabilises immediately and remains stable during many hours continuous use. Changes in laboratory temperature up to 5° cause less than 1% variation in output voltage. Deviation from linear response at high absorbance values results from the inability of the Zener diode to respond strictly logarithmically to extremely low currents. The upper limit of linearity of absorbance may be found to vary very slightly from diode to diode (manufacturers tolerance is 7%). Logarithmic scale contraction is avoided, and it is possible to read an absorbance of 0.7 with the same accuracy as an absorbance of 0.1. On the recorder used it is possible to read absorbances to ±0.001 at any value without difficulty.

Chemistry Department,
Imperial College,
London, S.W.7 (Great Britain)

D. ALGER
G. F. KIRKBRIGHT
M. D. MAYHEW
T. S. WEST

1 A. E. THOMPSON, *Unicam "Spectrovision"*, (15) (1966) 7.
2 S. C. B. DAVEY, *Hilger J.*, 8 (1963) 2, 30.

(Received February 11th, 1967)

Oximidobenzotetronic acid: a new reagent for the gravimetric determination of cobalt

The most commonly used reagents for the gravimetric determination of cobalt are anthranilic acid[1], α-nitroso-β-naphthol[2], ammonium phosphate[3] and potassium nitrite[4]. WILLIAMS[5] and more recently FOSTER AND WILLIAMS[6] critically re-investigated these reagents in order to assess their relative values as quantitative precipitants for cobalt; they recommended the phosphate method with certain modifications, including a rapid spectrophotometric determination of cobalt in the filtrate with nitroso-R salt. LINGANE[7] has improved the potassium cobaltinitrite method by the use of boiling solutions for the precipitation of $K_3Co(NO_2)_6$ but various common metals interfere.

Oximidobenzotetronic acid (α-isonitrosobenzotetronic acid) has already been used for the spectrophotometric determination of iron[8] and cobalt[9]. When a freshly prepared solution of the reagent in alcohol is added to an aqueous solution of cobalt(II), a brownish-red precipitate is formed; with an excess of sodium hydroxide a deep red solution is formed, so that a spectrophotometric determination is possible. In the present work, it was found that the precipitation of the cobalt–oximidobenzotetronic acid complex was quantitative between pH 3.0 and 6.0; the precipitate could be weighed after drying or converted to cobalt sulphate. The complex contained a metal : ligand ratio of 1:3.

Preparation of oximidobenzotetronic acid

Of the various methods available for the synthesis of 4-hydroxycoumarin, that recommended by STAHMANN *et al.*[10] was used. The coumarin was readily converted to α-isonitrosobenzotetronic acid by the method described by ANSCHÜTZ[11] and was further crystallised from cold chloroform.

A 1.5–2.0% solution of the reagent in ethanol was used.

Reagents

Cobalt sulphate solution was prepared from $CoSO_4 \cdot 7H_2O$ (BDH, AnalaR) and standardised by means of anthranilic acid[1] as well as by conversion to $CoSO_4$ after precipitation with α-nitroso-β-naphthol[2].

All other salts were of either BDH AnalaR or Merck Pro Analysi quality. Dilute solutions of hydrochloric acid and ammonium hydroxide were used for the adjustment of pH. The pH measurements were made with a Beckman pH-meter Model H-2 using a suitable glass electrode.

Procedure

To about 100 ml of an aqueous solution of cobalt(II) sulphate (containing about 3.75 mg of cobalt(II)), add 2–3 g of ammonium chloride or nitrate and heat to 40–50°. Add the reagent solution slowly with constant stirring. The initially dark green solution gradually changes and a greenish brown precipitate is formed. Add the reagent until no more precipitate forms; then add a slight excess (the total amount of the reagent required is 2–3 times the theoretical amount). Leave the solution for 10–15 min at room temperature so that the supernate becomes clear yellow-green. Filter through a weighed G3 sintered glass crucible and wash with hot 1% NH_4NO_3 solution until the washings are free from chloride and sulphate; then wash with hot water until the washings give no color with Nessler's reagent. Dry the complex at 140° and weigh as $Co(C_9H_4NO_4)_3$.

TABLE I

DETERMINATION OF DIFFERENT QUANTITIES OF COBALT USING OXIMIDOBENZOTETRONIC ACID

Co taken (by α-nitroso-β-naphthol method) (mg)	*Co found by new method (mg)*	*Difference (mg)*
1.733	1.723	0.010
3.768	3.758	0.010
7.536	7.496	0.040
15.07	14.97	0.10
18.84	18.76	0.08

TABLE II

EFFECT OF pH ON THE PRECIPITATION OF COBALT–OXIMIDOBENZOTETRONIC ACID COMPLEX
(Weight of cobalt taken = 3.768 mg)

pH	0.6	2.0	2.5	3.0	4.0	5.0	6.0	6.6	7.8
Co found (mg)	1.985	2.970	3.131	3.762	3.754	3.758	3.750	2.093	—

TABLE III

DETERMINATION OF COBALT IN PRESENCE OF FOREIGN IONS

Co taken (mg)	*Foreign ion added*	*Amount added (mg)*	*Co found (mg)*	*Error (mg)*
3.466	Ni^{2+} as $NiSO_4 \cdot 7H_2O$	1.875	3.454	0.012
		3.750	3.464	0.002
		3.750	3.474	0.008
		5.525	2.264	1.202
		7.50	1.657	1.809
	Zn^{2+} as $ZnSO_4 \cdot 7H_2O$	4.61	3.454	0.012
		7.86	3.474	0.008
	Cd^{2+} as $CdCl_2 \cdot 2H_2O$	4.28	3.454	0.012
		16.18	3.474	0.008
		39.70	3.459	0.007
	Al^{3+} as potash alum	3.65	3.454	0.012
		8.65	3.474	0.008
		35.90	3.464	0.002
	Cr^{3+} as chrome alum	3.58	3.459	0.007
		17.05	3.445	0.021
		34.38	3.469	0.003
	Cu^{2+} as $CuSO_4 \cdot 5H_2O$	4.52	4.809	1.343
	Tartrate	5.69	3.633	0.167
		19.09	3.656	0.190
		39.65	3.676	0.210
	Oxalate	12.21	3.062	0.404
	Phosphate as $(NH_4)_2HPO_4$	8.78	3.075	0.391
4.512	Mn^{2+} as $MnSO_4$	4.52	4.540	0.028
		22.21	4.540	0.028
		44.21	4.536	0.024
	Acetate	4.65	4.931	0.419
	Zn^{2+} as $ZnSO_4 \cdot 7H_2O$	43.23	4.540	0.028
2.256	Cd^{2+}	24.08	2.261	0.005
	Zn^{2+}	22.76		
	Al^{3+}	21.61		
	Cr^{3+}	20.79		
	Mn^{2+}	22.10		

The complex is quite stable in the temperature range 120–170°. It is soluble in organic solvents such as ethanol, ether and chloroform, but is insoluble in acetone, dilute hydrochloric acid or nitric acid (pH $>$ 3), hot water or hot water containing not more than 10% ethanol.

Effect of pH on the precipitation of the complex

As can be seen from Table II, cobalt can be accurately estimated in the pH range 3.0 to 6.0. At lower pH the precipitation is incomplete while at pH 7.8 and above, the complex is soluble.

Separation of cobalt from other metal ions

With oximidobenzotetronic acid, cobalt could be separated and determined in presence of zinc(II), cadmium(II), manganese(II), aluminium(III) and chromium(III) even when these were present in quantities 10 times that of cobalt(II) (see Table III). Iron(II) at the p.p.m. level gives a deep blue water-soluble complex with the reagent; in larger amounts it was precipitated and thus interfered. Copper(II) was coprecipitated while nickel(II) interfered in amounts more than equal to that of cobalt. Bismuth(III) salts were hydrolysed at the pH used and hence interfered. Anions such as phosphate, tartrate, citrate, oxalate and acetate interfered.

Further studies regarding the nature of cobalt–oximidobenzotetronic acid complex are in progress.

Department of Chemistry,
University of Delhi,
Delhi-7 (India)

G. S. MANKU
A. N. BHAT
B. D. JAIN

1 A. I. VOGEL, *A Text Book of Quantitative Inorganic Analysis including Elementary Instrumental Analysis*, 3rd Edn., Longmans, Green & Co., 1962, p. 530.
2 N. H. FURMAN, *Scott's Standard Methods of Chemical Analysis*, Vol. I, D. Van Nostrand, New York, 1959, p. 314.
3 N. H. FURMAN, *Scott's Standard Methods of Chemical Analysis*, Vol. I, D. Van Nostrand, New York, 1959, p. 330.
4 N. H. FURMAN, *Scott's Standard Methods of Chemical Analysis*, Vol. I, D. Van Nostrand, New York, 1959, p. 312.
5 W. J. WILLIAMS, *Talanta*, 1 (1958) 88.
6 W. J. WILLIAMS AND A. G. FOSTER, *Anal. Chim. Acta*, 24 (1961) 20.
7 J. J. LINGANE, *Anal. Chim. Acta*, 31 (1964) 315.
8 A. N. BHAT AND B. D. JAIN, *Anal. Chim. Acta*, 25 (1961) 343.
9 A. N. BHAT AND B. D. JAIN, *J. Ind. Chem. Soc.*, 38 (1961) 779.
10 M. A. STAHMANN, I. WOLF AND K. P. LINK, *J. Am. Chem. Soc.*, 65 (1943) 2285.
11 R. ANSCHÜTZ, *Ann. Chem.*, 367 (1909) 169.

(Received November 28th, 1966)

Neutron activation analysis for gold in osmium

The determination of ruthenium and iridium in osmium has been described[1], but that procedure does not allow a simultaneous determination of gold, because gold is partly volatilized (*ca.* 7%) during the peroxide–sulfuric acid treatment[2]. It was therefore recommended to distill Os + Ru simultaneously from boiling bromate–sulfuric acid mixture[3], where gold remains quantitatively in the residue, together with other impurities (mainly iridium), as was found by radioactive tracer techniques. Gold-198 can be determined in the presence of $^{192(194)}$Ir by γ-spectrometric analysis without further chemical separation, for its γ-energy (411 keV) differs sufficiently from that of $^{192(194)}$Ir (mainly 317 + 328, 468, ... keV).

Chemical separation can also be carried out. After the quantitative distillation of osmium (>99.997%)[3], the residual ^{191,193}Os activity is negligible compared to those of ^{198}Au and ^{192,194}Ir. Hence, the problem is practically reduced to the separation of gold from iridium, these elements being the most highly activated impurities in osmium. Gold is easily extracted with ethyl acetate from hydrochloric acid medium of various strengths[4]. One must, however, determine the acid concentration at which the iridium contamination of the organic phase is at a minimum; and the influence of sulfuric acid and salts must be considered.

The preparation of ^{192}Ir tracer has been described[1]. Gold-198 tracer was prepared by dissolving 1 mg of irradiated gold wire in aqua regia and diluting with 6 *N* hydrochloric acid to the desired specific activity per ml.

Radiochemical study of the separation Au/Ir

To 15 ml of water, 10 ml of 18 *N* sulfuric acid and 15 ml of 20% sodium bromate solution, 0.1–1 ml tracer solution was added; the solution was boiled for 1–3 h at *ca.* 100° in the distillation flask, while an air current was drawn through, as described previously[5]. During the heating, *ca.* 15 ml of the bromate solution was added per hour. Without interrupting the air current, concentrated hydrochloric acid was then carefully added to destroy the bromate. When no further chlorine developed, sufficient acid was added to obtain the desired HCl concentration, *e.g.* 2 *N*. The solution was then transferred to a separatory funnel and extracted with the same volume of pre-equilibrated ethyl acetate. The aqueous phase was separated and the organic phase washed 3 times with 5-ml portions of pre-equilibrated hydrochloric acid of the same normality. At 4 *N* HCl, *ca.* 4.5% of the ^{192}Ir activity was found in the organic phase, whereas at 2 *N* HCl the iridium extraction could be reduced to 0.1–0.2% or even less, if washing of the organic phase was repeated. In the latter condition, 99–99.5% of the ^{198}Au was recovered in the organic phase.

Practical procedure for neutron activation analysis

Samples of osmium can be dissolved by sodium peroxide fusion after irradiation, but this introduces large amounts of salts, which could interfere during further separations. The 10-mg samples of commercial osmium were therefore dissolved before irradiation in small sealed silica tubes (length: 5 cm, internal diameter: 3 mm) with 100 μl of concentrated hydrochloric acid and a few drops of concentrated nitric acid under pressure at a temperature of *ca.* 150° (*cf.* ref. 6). An addition method was followed. A preliminary analysis indicated that the gold content of commercial osmium was a few p.p.m. Standards were thus prepared by evaporating in a silica tube 100 μl of a standard solution, containing 0.01 μg Au, on osmium sponge, after which the sponge and the gold addition were dissolved as described above. Gold and iridium standards for γ-spectrometric corrections were prepared by pipetting 100 μl of standard solutions into silica tubes. Samples and standards were irradiated for 3 days at a thermal flux of $4 \cdot 10^{11}$ n $\cdot$ cm^{-2} $\cdot$ sec^{-1}. After the irradiation, the silica ampoules were immersed in liquid nitrogen to reduce the internal pressure and opened. Both halves were then placed in the distillation flask described previously[5]. After addition of 20 ml of water, 10 ml of 18 *N* sulfuric acid and 15 ml of 20% sodium bromate solution, distillation was carried out at *ca.* 100° for 2–3 h, *ca.* 15 ml of bromate solution being added per hour.

Determination of gold without chemical separation from iridium

The distillate, which was absorbed in 2 × 5 ml of 9 *N* sodium hydroxide was discarded (99.997% of the osmium activity: ^{191}Os, ^{193}Os, ^{185}Os). The residue was transferred to 100-ml measuring flasks, diluted to the same volume, and counted with a 3 × 3″ NaI(Tl) detector of good resolution coupled to a multichannel analyzer (*ca.* 2 days after the end of the irradiation).

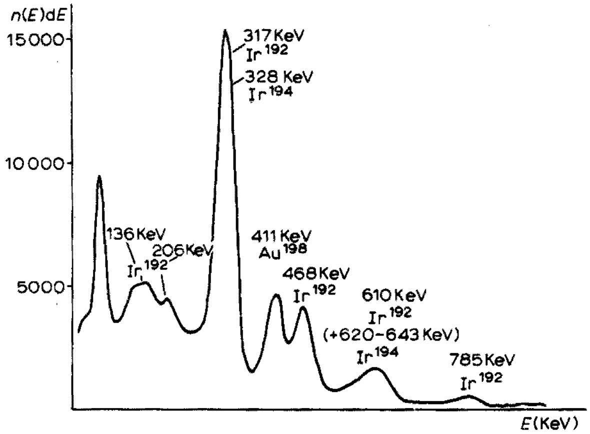


Fig. 1. γ-Spectrum of residue, after bromate distillation (on second day from end of irradiation). This sample contains 21 ± 2 p.p.m. Ir and 3.4 ± 0.6 p.p.m. Au.

A γ-spectrometric study of the residue showed the presence of ^{198}Au and of ^{192}Ir + ^{194}Ir (Fig. 1). Gold-198 could be determined without further chemical separations and its net activity calculated from the following equation:

$$A_{1,\mathrm{Au}} = \frac{k_{\mathrm{Ir}} A_1 - A_2}{k_{\mathrm{Ir}} - k_{\mathrm{Au}}} \qquad (1)$$

where: A_1 = the activity in the energy region of 411 keV; A_2 = the activity in the energy region of 468 keV; $k_{\mathrm{Au}} = A_{2,\mathrm{Au}}/A_{1,\mathrm{Au}}$; and $k_{\mathrm{Ir}} = A_{2,\mathrm{Ir}}/A_{1,\mathrm{Ir}}$.

The factors k_{Au} and k_{Ir} were determined by means of $^{192+194}$Ir and ^{198}Au standards, which were produced during a simultaneous irradiation, and counted in the same geometry.

The net ^{198}Au activity could also be directly determined by visual peel-off of the ^{192}Ir + ^{194}Ir contribution from the total γ-spectrum (468 keV→0). Some typical results are summarised in Table I.

The gold content was calculated by the least squares method[1]. "Classical" calculation from the specific activity of the gold standard (1 p.p.m. = 10,962 c/6 min) gave 3.1 p.p.m. and 2.9 p.p.m. Au for the results in columns 5 and 6 respectively.

TABLE I

DETERMINATION OF GOLD IN COMMERCIAL OSMIUM, WITHOUT CHEMICAL SEPARATION FROM IRIDIUM
(Counted for 6 min, 2.5 days after end of irradiation)

Sample	*p.p.m. Au added*	A_1	A_2	$A_{1,\mathrm{Au}}$ *(eq. (1))*	$A_{1,\mathrm{Au}}$ *(peel-off)*
Au-stand.	(0.966)	10,589	982	($k_{\mathrm{Au}} = 0.093$)	—
Ir-stand.	—	6,905	20,788	($k_{\mathrm{Ir}} = 3.011$)	—
1	—	48,919	44,175	35,298	33,593
2	—	43,763	35,003	33,125	32,152
3	—	44,480	39,350	32,375	30,780
4	0.966	55,363	37,559	44,207	42,417
5	0.966	55,058	43,462	41,870	40,349
Au content	—	—	—	3.4 ± 0.6 p.p.m.	3.4 ± 0.5 p.p.m.

TABLE II

DETERMINATION OF GOLD IN COMMERCIAL OSMIUM AFTER CHEMICAL SEPARATION FROM IRIDIUM
(Counted for 5 min, 8 days after end of irradiation)

Sample	*p.p.m. Au added*	*net* ^{198}*Au* *(eq. (1))*	*net* ^{198}*Au* *(peel-off)*
1	—	7,496	7,481
2	—	7,076	7,026
3	—	6,584	6,600
4	0.966	9,789	9,806
5	0.966	8,744	8,721
Au content		3.1 ± 0.7 p.p.m.	

Determination of gold after chemical separation from iridium

The contents of the measuring flask were transferred to a beaker and evaporated to *ca.* 50 ml; concentrated hydrochloric acid was added to destroy the excess of bromate, and to adjust the final acidity to 2 *N* before extraction with pre-equilibrated ethyl acetate. The aqueous phase was discarded and the organic phase washed with 5-ml portions of pre-equilibrated 2 *N* acid (3 times). Finally the organic phase was transferred to a 100-ml measuring flask and diluted with ethanol. The measurements and the determination of the net ^{198}Au activity (corrections for small iridium contaminations) were performed as described above (see Table II).

"Classical" calculation by means of the specific activity of the Au standard gave 2.8 p.p.m.

Sensitivity of the method

The limiting factor for the determination of gold in osmium by the method described is not due to the background activity, but to the presence of $^{192}Ir + ^{194}Ir$.

It is estimated that without chemical separation gold can be determined in the presence of a 25-fold amount of iridium (*e.g.* 1 p.p.m. Au/25 p.p.m. Ir). After chemical separation, this ratio may be as high as 100, provided that the organic phase is thoroughly washed to decrease the iridium contamination.

This work is sponsored by the "Interuniversitair Instituut voor Kernwetenschappen" whose financial support is gratefully acknowledged.

Institute for Nuclear Sciences,
Ghent University, Ghent (Belgium)

R. Gijbels*
J. Hoste

1 R. Gijbels and J. Hoste, *Anal. Chim. Acta*, 32 (1965) 17.
2 R. Gijbels and J. Hoste, *Anal. Chim. Acta*, 36 (1966) 230.
3 R. Gijbels and J. Hoste, *Proc. Intern. Conf. Modern Trends in Act. Anal., College Station, Texas, U.S.A., April 19–22, 1965*, p. 121.
4 E. B. Sandell, *Colorimetric Determination of Traces of Metals*, Interscience, New York, 1959.
5 R. Gijbels and J. Hoste, *Anal. Chim. Acta*, 29 (1963) 289.
6 E. Wichers, W. G. Schlecht and C. L. Gordon, *J. Res. Natl. Bur. Std.*, 33 (1944) 363, 451; C. L. Gordon, W. G. Schlecht and E. Wichers, *J. Res. Natl. Bur. Std.*, 33 (1944) 457.

(Received February 20th, 1967)

---

* Research fellow of the I.I.K.W.

The determination of dysprosium in the presence of aluminum

To control the homogeneity of aluminum–dysprosium alloys a rapid and reasonably accurate method for the determination of dysprosium in the presence of aluminum was needed. As in the case of the determination of lutetium in Al–Lu alloys[1] the compleximetric analysis of dysprosium using xylenol orange as an indicator was adopted. Aluminum was masked with sulfosalicylic acid[1]. The Al–Dy alloys that had to be analysed were prepared from high-purity dysprosium (99.9%) and aluminum (99.99%) so that no interference from other elements was expected.

Apparatus and reagents

A calibrated burette of 10 ml capacity was used; the pH measurements were made with combined glass–calomel electrode. All reagents used in this procedure were of reagent-grade quality.

Standard dysprosium solution. Dissolve dysprosium oxide in 6 *N* hydrochloric acid and dilute to obtain a solution containing 0.5 mg Dy/ml.

Standard aluminum solution. Prepare a solution containing 25 mg or 50 mg Al/ml by dissolving aluminum metal (99.99%) under reflux in 6 *N* hydrochloric acid.

Procedure

Quantities of 3 mg, 5 mg and 10 mg Dy were titrated in the presence of 100 mg, 200 mg, 300 mg, 500 mg and 1000 mg Al. The procedure described below is that for 10 mg Dy in the presence of 200 mg Al.

The standard dysprosium solution (20 ml) and 8 ml of the aluminum solution were mixed with 20 ml of 50% (w/v) sulfosalicylic acid solution and the volume was brought to about 150 ml with water. Concentrated ammonia solution (d = 0.9) was added to give pH *ca.* 5.5, and the pH was adjusted to 6.0 (pH meter) with a dilute (1:99) ammonia solution. Xylenol orange indicator was added as a solid mixture with KCl (1:99) and the titration was made with standard EDTA solution[1], taking the sharp color change from red to yellow-orange as the end-point. The results obtained with the described procedure are shown in Fig. 1. S% indicates the coefficient of variation, for 9 single determinations for each concentration. This Figure shows how much alloy has to be dissolved to obtain a specific precision.

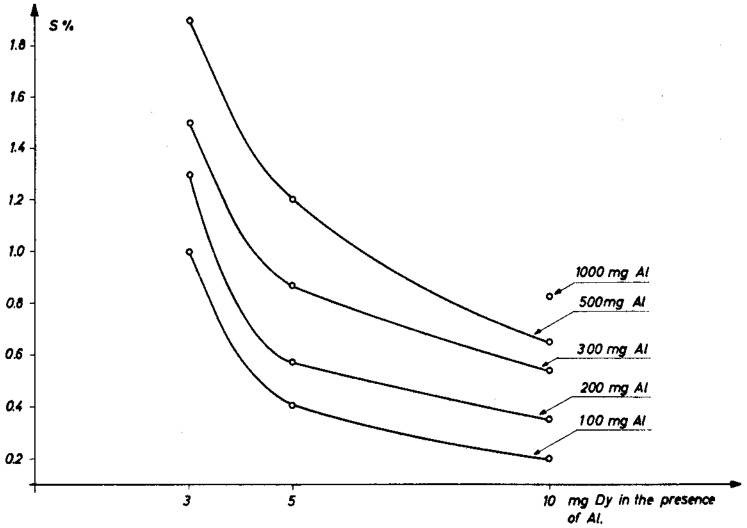


Fig. 1. Results obtained for the compleximetric titration of Dy in the presence of Al.

To obtain a sharp end-point and reproducible results the following points are essential:

(1) the pH of the solution at the start of the titration must be adjusted with ammonia solution to a value of 6.0±0.3 (pH meter);

(2) for 100 mg Al present per titration, 10 ml of the sulfosalicylic acid solution should be added.

The authors are indebted to M. CUYVERS for much of the practical work done.

Central Bureau for Nuclear Measurements,
Euratom,
Geel (Belgium)

A. BRÜCK
K. F. LAUER

1 A. BRÜCK AND K. F. LAUER, *Anal. Chim. Acta*, 33 (1965) 338.

(Received February 20th, 1967)

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

BOOK REVIEWS

G. CHARLOT, *Les Méthodes de la Chimie Analytique: Analyse Quantitative Minérale,* 5ème Edition entièrement refondue, Masson et Cie, Paris, 1966, 1024 pp., Cartonné toile frs 135.—.

La dernière édition de ce traité est de 1961. Le succès qu'il a remporté est remarquable et s'explique par le fait que l'auteur est en même temps un analyste distingué et un pédagogue de grande valeur. Il est un des premiers à avoir introduit, par exemple, les courbes de polarisation, ce qui lui a permis de présenter de façon logique et claire les diverses méthodes d'électro-analyses. De même, grâce à l'étude des variations de concentrations au cours des réactions, base de toutes les méthodes utilisant le titrage, il a pu faire une synthèse des méthodes de titration et en rendre l'étude théorique plus aisée, plus claire.

La nouvelle édition qui vient de paraître a été remaniée. La bibliographie, qui est une partie importante de cet ouvrage, a été complétée, puisque les références vont jusqu'en 1964, et dans certains cas, un nouveau choix a été fait.

Le chapitre de radiochimie est supprimé, l'auteur a sans doute estimé que, vu le développement de cette discipline, il n'était plus possible, en quelques pages, d'en présenter les notions essentielles. Par contre les méthodes statistiques ont été revues et complétées ainsi que le chapitre concernant l'analyse en milieu non aqueux qui renferme maintenant une table très complète des valeurs de k_{H_2O} pour des complexes acide–base variés. L'électroanalyse a subi aussi quelques modifications. De nouvelles méthodes de dosage des éléments, choisies avec soin, ont été introduites.

Nous recommandons donc vivement cet ouvrage à tous ceux qui désirent acquérir de solides bases théoriques en chimie analytique.

D. MONNIER (Genève)

Methods of Biochemical Analysis. Edited by DAVID GLICK, Vol. 14, Interscience Publishers — J. Wiley & Sons, Inc., New York, 1966, ix+562 pp., price 113 s.

The latest volume in this series deals with the following topics: — the estimation of magnesium in biological materials (N. W. ALCOCK AND I. MACINTYRE), the microbiological assay of vitamin B_{12} (H. R. SKEGGS), the fluorimetric analysis of corticoids (R. H. SILBER), the preparation and analysis of basic proteins (N. O. LINDH AND B. L. BRANTMARK), the determination of nucleic acids (H. N. MUNRO AND A. FLECK), the determination of amino acids by ion exchange chromatography (S. JACOBS), the separation and determination of amino acids and peptides by gas–liquid chromatography (B. WEINSTEIN), newer developments in determination of bile acids and steroids by gas chromatography (A. KUKSIS) and gel electrophoresis in buffers containing urea (M. D. POULIK).

It would be invidious to select any of these contributions for special consideration in the limited space available. All the articles maintain the high standard set by those in earlier volumes. Full experimental details of the procedures described are in general given and each contributor provides an extensive list of references.

H. G. BRAY (Birmingham)

Treatise on Analytical Chemistry, Edited by I. M. KOLTHOFF AND P. J. ELVING with the assistance of E. B. SANDELL, Part II, Vol. 4, Interscience–J. Wiley and Sons, Inc., New York, 1966, 452 p., price 130 s.

Ce nouveau fascicule a pour objet l'analyse systématique de l'argent, de l'or et des métaux alcalino-terreux (sauf Mg et Be déjà traités). I. M. KOLTHOFF ET P. J. ELVING se sont assurés le concours de 8 spécialistes distingués. On peut se demander pour quelles raisons l'or et l'argent font partie du même fascicule que l'aluminium et une partie des alcalino-terreux. La bibliographie, restreinte, va jusqu'en 1962. Si nous examinons par exemple le chapitre concernant le calcium, nous remarquons qu'il comprend 5 parties: une introduction tout d'abord où les milieux dans lesquels le calcium est fréquemment dosé sont décrits, puis les propriétés de ce dernier: isotopes stables et radioactifs, structure électronique et dimensions de l'ion et de l'atome, les composés, les produits de solubilité, les constantes de stabilité et les méthodes d'identification de cet élément. Une troisième partie a pour objet les séparations: précipitations, échanges d'ions et extraction. La détermination du calcium est traitée dans une quatrième partie: gravimétrie, titrimétrie, spectrophotométrie de flamme et d'absorption atomique, spectroscopie, colorimétrie, fluorescence X, activation aux neutrons. Enfin les auteurs proposent un certain nombre de méthodes, judicieusement choisies et décrites avec soin, en tenant compte de la concentration dans l'échantillon de la substance à doser.

On peut toujours discuter sur le choix des méthodes, il semble avoir été fait avec discernement.

Ce nouveau fascicule, comme les précédents, est un précieux guide pour les chimistes analystes. Il renferme beaucoup de renseignements utiles.

D. MONNIER (Genève)

Anal. Chim. Acta, 39 (1967) 138

J. W. EMSLEY, J. FEENEY AND L. H. SUTCLIFFE, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon Press, Oxford, 1966, Vol. I, l + 663 pp., price 105 s.; Vol. II, ix + 491 pp., price 105 s.

Only a few years ago, it was generally agreed that many years would pass before the standard work on N.M.R. by POPLE, SCHNEIDER AND BERNSTEIN could be replaced. However, the authors of the present volumes have succeeded in this task, which has been made the more formidable by the rapid growth of the subject.

The book is produced in two volumes. The first deals with the theoretical aspects of N.M.R., while the second volume gives a detailed account of chemical shift and coupling constants of different nuclei. Many parts of the first volume are highly mathematical and the second volume will be more useful to analytical chemists. One of the best sections of Vol. I gives an extensive discussion of the analysis of high-resolution spectra. There are also sound chapters on the calculation of shielding parameters, coupling constants, and chemical and conformational equilibria.

The volumes are well presented and seem to contain very few errors. In general, the text is of such a high standard that it should be available in all laboratories that employ the N.M.R. technique.

E. F. MOONEY (Birmingham)

Anal. Chim. Acta, 39 (1967) 138

R. S. YOUNG, *The Analytical Chemistry of Cobalt.* (International Series of Monographs in Analytical Chemistry, Vol. 27), Pergamon Press, Oxford, 1966, vii+170 pp., price 45s.

The increasing importance of cobalt in the industrial field renders the publication of a work devoted to the analytical chemistry of the element of prime importance.

A number of brief review sections contributes greatly to the value of the volume. These are devoted to occurrence, nature, properties and uses of cobalt compounds in industrial and biological contexts; adequate descriptions of sampling techniques and reduction of ores and metals to the assay condition, together with some indication of classical and instrumental detection and identity tests are also given. Even though sampling methods relating to trace analysis are briefly dismissed, the data presented on normal concentration levels in the various systems considered is more than adequate. Experimental details of separations and analytical procedures including gravimetric, colorimetric, electrometric, volumetric and a variety of instrumental methods applicable on the macro and semimicro scales, are provided.

Differentiation of occurring forms is summarised and a final chapter defines procedures for a number of applications within specific areas of endeavour and so forms a rounding up of an excellent monograph.

R. SAWYER (London)

Anal. Chim. Acta, 39 (1967) 139

Fluorescence and Phosphorescence Analysis: Principles and Applications, Edited by DAVID M. HERCULES, Interscience–J. Wiley and Sons, New York, 1966, xiii+258 pp., price 90 s.

This book is a "self-tutor" text, designed to introduce the uninitiated analyst to the world of fluorescence and phosphorescence spectroscopy, and to dwell on its achievements and potential as an analytical technique. It is a written account of a summer school held for this purpose by the American Chemical Society in Chicago, in 1964.

Chapters 1 and 2 (by D. M. HERCULES AND D. W. ELLIS) introduce the "student" to the basic theory of the excitation and decay of luminescence in polyatomic molecules, and to the experimental techniques and instrumentation necessary for the quantitative observation of fluorescence and phosphorescence. Snags which can arise in relating practical observation to theoretical description are emphasized. The basic theory is extended in Chapter 3 by E. C. WEHRY AND C. B. ROGERS, who give a very well documented review of the present state of research in the field. In Chapters 4 and 5, W. E. OHNESORGE AND J. D. WINEFORDNER describe the advantages and disadvantages of exploiting fluorescence in metal chelates for the quantitative determination of the metal ions, and phosphorescence in frozen solutions for the determination of trace amounts of the phosphorescent solute. Chapter 6, by J. P. PARIS, is a brief review of chemiluminescent reactions, *i.e.*, exothermic reactions producing electronically excited molecules. B. L. VAN DUUREN describes applications of fluorimetry in biological systems, *e.g.*, in the investigation of protein structure by "labelling" the protein with fluorescent dyes (Chapter 7). G. WEBER, who has had much to do with the development of this application, provides the final chapter; this is a clear, theoretical account of the origins of the polarization of fluorescence, and of the information regarding the excited molecule and its interaction with its surroundings, that can be gained from measuring the polarization.

The book as a whole maintains an even balance between theory and application, and can be recommended to all interested analysts, though the price will tend to discourage personal acquisition.

J. P. SIMONS (Birmingham)

Anal. Chim. Acta, 39 (1967) 139–140

J. INCZÉDY, *Analytical application of ion exchangers*. (Translated from the Hungarian by A. PALL. Ed. by I. BUZAS AND M. WILLIAMS). Pergamon Press, Oxford, 1966. Pp. xi+443. Price 105s.

This book is a translation of a text originally published in Hungary in 1962. It is therefore out of date to some extent, though this does not materially detract from the value of what is without doubt a most useful work. The basic guide lines for utilization of ion exchange in analytical studies had been laid some years previously and the text remains sufficiently comprehensive as a working tool. Of the newer developments, cation exchange in concentrated mineral acids has come too recently to gain inclusion at all and the rapidly expanding field of liquid ion exchangers receives only a cursory mention.

Theoretical principles, experimental techniques and practical applications are covered in a balanced manner and a wealth of data on the now prolific output of analytical separations is incorporated in tabular form giving ready access to the literature which is covered to the extent of over 1200 references. Inclusion of conditions under which separations have been achieved enhances the value of the tabulations and they are likely to prove of real utility as a working reference source. A number of practical examples, presented in small print, are well chosen for teaching and demonstration purposes.

In a concise text which has suffered little from the translation process, a few shortcomings are evident; in particular the treatment of weak acid cation exchange is inadequate and somewhat misleading. The quality of production has apparently been geared to an economic selling price and it is unfortunate that many of the diagrams are poorly presented and are lacking in clarity.

J. K. FOREMAN (London)

Anal. Chim. Acta, 39 (1967) 140

VOL. 39 NO. 1 ANALYTICA CHIMICA ACTA SEPTEMBER 1967

CONTENTS

Short communications

PRINTED IN THE NETHERLANDS

SPOT TESTS IN ORGANIC ANALYSIS

Seventh English Edition, completely revised and enlarged

by FRITZ FEIGL in collaboration with VINZENZ ANGER

6 x 9″, xxiii + 772 pages, 19 tables, over 2000 lit.refs., 1966, Dfl. 85.00, £8.10.0, $30.00

This 7th edition has involved complete revision and reorganisation of the subject in order to present a still clearer picture of the multitudinous applications open to organic spot test analysis. The amount of new work which is appearing has certainly necessitated expansion, but the author has kept this to a minimum by omitting the chapter on spot test techniques (which are covered in the companion volume *Spot Tests in Inorganic Analysis*) and by limiting the number of tables and structural formulae.
Comparison with the 6th edition reveals the following differences:

	Number in	
	6th Edn.	7th Edn.
Preliminary tests	32	45
Functional group tests	70	109
Individual compound tests	133	148
Detection of particular structures and types of compounds	0	74
Differentiation of isomers etc.	0	54
Applications in the testing of materials etc.	111	131

In total the book now gives in 561 sections information on more than 900 tests compared with 600 tests in 346 sections in the preceding edition.

An important feature is the inclusion of a large number of recently developed tests and comments which have not hitherto been published in any form.

It is the author's hope that this work will help to correct the widespread impression that physical instrumentation is always superior to chemical methods for solving analytical problems. Each of the chapters presents instances of problems for which no solutions by physical means have yet been developed, or for which the rapid spot tests are equal or superior to the expensive instrumental procedure.

CONTENTS: 1. Development, present state and prospects of organic spot test analysis. 2. Preliminary (exploratory) tests. 3. Detection of characteristic functional groups in organic compounds. 4. Detection of structures and certain types of organic compounds. 5. Identification of individual organic compounds. 6. Application of spot tests in the differentiation of isomers and homologous compounds. Determination of constitutions. 7. Application of spot reactions in the testing of materials, examinations of purity, characterization of pharmaceutical products, etc... Appendix: Individual compounds and products examined. Author index. Subject index.

FROM REVIEWS OF THE SIXTH EDITION

... This new book, like its author, is unquestionably a giant on the analytical scene...
Journal of the Royal Institute of Chemistry

... Die Tatsache, dass Feigls klassisch gewordenes Werk, welches überall mit Begeisterung aufgenommen wurde, bereits in 6. Auflage erscheint, ist an sich Empfehlung genug... Es ist also eine wahre Fundgrube für neue Experimentaluntersuchungen... *Chimia*

... Even in these days of physical instrumentation there is ample room for the techniques described in this book which were originated and largely developed by Prof. Feigl. They are mostly very quick and very economical on materials. They sometimes present solutions to problems so far insoluble by expensive physical methods...
Laboratory Practice

ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK

147E