# 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. 51, No. 3, 349–572, September 1970
Published monthly
Completing Volume 51

## Publication Schedule for 1971

In the interests of rapid publication it has been found necessary to schedule 5 volumes for appearance in 1971. Since monthly publication will be maintained, this implies that 2 of the volumes will each consist of three issues, while 3 of the volumes will each consist of only 2 issues. The following provisional schedule applies:

| | | |
|---|---|---|
| Vol. 53, No. 1 | January 1971 | |
| Vol. 53, No. 2 | February 1971 | **(completing Vol. 53)** |
| Vol. 54, No. 1 | March 1971 | |
| Vol. 54, No. 2 | April 1971 | |
| Vol. 54, No. 3 | May 1971 | **(completing Vol. 54)** |
| Vol. 55, No. 1 | June 1971 | |
| Vol. 55, No. 2 | July 1971 | **(completing Vol. 55)** |
| Vol. 56, No. 1 | August 1971 | |
| Vol. 56, No. 2 | September 1971 | |
| Vol. 56, No. 3 | October 1971 | **(completing Vol. 56)** |
| Vol. 57, No. 1 | November 1971 | |
| Vol. 57, No. 2 | December 1971 | **(completing Vol. 57)** |

Subscription price: $17.50 or Dfl. 63.— per volume plus postage. Total subscription price for 1971: $87.50 or Dfl. 315.— plus postage. Additional cost for copies by airmail available on request. For subscribers in the U.S.A. and Canada, 2nd class postage paid at New York, N.Y. For advertising rates apply to the publishers.

Subscriptions should be sent to:

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

---

## 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 B15 2TT (Great Britain)

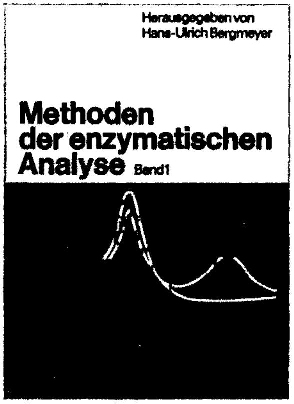
*Reprints*

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.

*Im Oktober erscheint in Neuauflage - jetzt in 2 Bänden:*

# Methoden der enzymatischen Analyse

## Herausgeber Hans-Ulrich Bergmeyer


Herausgegeben von
Hans-Ulrich Bergmeyer

Methoden der enzymatischen Analyse Band 1

37 Mark sparen Sie durch unser Subskriptionsangebot!

Es lohnt sich also, die Bestellung sofort aufzugeben.

**Mit Beiträgen von 230 Autoren. 1970. 2., wesentlich erweiterte und neubearbeitete Auflage. 2 Bände. Ca. XXXII, 2400 Seiten mit ca. 215 Abbildungen und ca. 470 Tabellen. Leinen. Subskriptionspreis DM 248,–; endgültiger Ladenpreis DM 285,–. Die Subskriptionsfrist endet am 1. Oktober 1970. Beide Bände werden nur zusammen abgegeben.**

Die Entwicklung der enzymatischen Analytik ist so stürmisch verlaufen, die Neuerungen sind so umfangreich und vielseitig, daß es an der Zeit war, das Buch grundlegend zu überarbeiten. So ist, aufgebaut auf dem Konzept der Erstauflage, ein neues Werk entstanden. Der Umfang der Neuauflage hat sich verdoppelt. Aus diesem Grund erscheint das Werk jetzt in zwei Bänden. Jeder Band enthält das vollständige Register, das Abkürzungsverzeichnis und die gesamte Inhaltsangabe.

Die Vielzahl neuer enzymatischer Analysenmethoden, der Fortschritt in den verschiedenen Meßtechniken, grundsätzlich neue Meßprinzipien, Mechanisierung der Arbeitsplätze erforderten erhebliche Ergänzungen, die voll berücksichtigt sind. So mußte auch das Kapitel „Experimentelles" wesentlich erweitert werden.

Die bewährte Aufteilung des Werkes in vier Abschnitte ist unverändert geblieben. Auch der Aufbau der einzelnen Kapitel ist im wesentlichen beibehalten worden. Das Meßprinzip wird durchweg, auf einen Blick überschaubar, als Formel dargestellt. Das Kernstück jeder Methode, das Pipettierschema, ist als Tabelle mit Angabe der „Konzentration in Test" besonders hervorgehoben. Neu ist die Angabe der Zusammensetzung der Tests für Enzymaktivitäten im Abschnitt „Die biochemischen Reagentien".

Die 2., wesentlich erweiterte und neubearbeitete Auflage des großen Laboratoriumsbuches wird auch Ihre Arbeit erleichtern und Ihnen Zugang zu den neuesten Arbeitsmethoden verschaffen.

Ein Sonderprospekt steht zur Verfügung.

# Laboratory Techniques in Biochemistry and Molecular Biology

Editors:
T. S. WORK, *National Institute for Medical Research, Mill Hill*
E. WORK, *Imperial College, London*

---

The three separate parts of the first volume of this series are now available in

**handy inexpensive paperback editions**

especially designed for use at the laboratory bench

## Electrophoresis of Proteins in Polyacrylamide and Starch Gels

By A. H. GORDON, *National Institute for Medical Research, Mill Hill*
1969. 150 pages. Hfl. 15.— (35 s.) ISBN 7204 4202 8

CONTENTS: Applicability of starch and acrylamide zone electrophoresis. Acrylamide gel. Apparatus and techniques. Methods allowing recovery of separated materials (preparative methods). Starch gel. Appendix. References. Subject index.

## An Introduction to Gel Chromatography

By L. FISCHER, *Pharmacia Fine Chemicals AB, Uppsala*
1969. 246 pages. Hfl. 25.— (58 s.) ISBN 7204 4203 6

CONTENTS: What is gel chromatography? Basic concepts. Gels for chromatography. Equipment for gel chromatography in columns. Experimental technique in column gel chromatography. Some applications of gel chromatography. Thin-layer gel chromatography. Special techniques. Some notes on the mechanism of gel chromatography. Appendices. References. Subject index.

## Immunochemical Techniques for the Identification and Estimation of Macromolecules

By J. CLAUSEN, *The Neurochemical Institute, Copenhagen*
1969. 176 pages. Hfl. 15.— (35 s.) ISBN 7204 4204 4

CONTENTS: Introduction. Immunodiffusion in gels. Antisera. Techniques of immunodiffusion. Techniques of immunoelectrophoresis. Visualization and interpretation of precipitates in gels. Radio-immunochemical techniques. Difficulties and artifacts arising in gel diffusion and in immunoelectrophoresis. Immunochemical reactions in free buffer systems. Appendices. References. Subject index.

*The cloth-bound edition of the complete volume I of this series is still available:*
*1969. 580 pages. Many illustrations and graphs. Hfl. 90.— (210 s.; $ 25.20)*
*Volume II is in preparation.*

AMSTERDAM
P.O. BOX 3489
**NORTH HOLLAND**
PUBLISHING CO.
NETHERLANDS

*Sole distributors for the U.S.A. and Canada:*
*American Elsevier Publishing Company, Inc., 52 Vanderbilt Avenue, New York, N.Y. 10017*

427 G

# SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 51, No. 3, September 1970

## AN X-RAY FLUORESCENCE SPECTROSCOPIC METHOD FOR THE DETERMINATION OF TOTAL MANGANESE IN ROCKS AND MARINE SEDIMENTS

A method for the determination of manganese by X-ray fluorescence is described. By using scattered X-rays as an internal standard, a linear calibration plot is obtained for standard rocks that agrees with the chemical data. The scattered X-ray method, compared with a widely used net-intensity method, shows improvement in accuracy especially at higher concentrations.

L. A. WOLFE AND H. ZEITLIN,
*Anal. Chim. Acta*, 51 (1970) 349–354

## ATOMIC ABSORPTION AND FLUORESCENCE SPECTROSCOPY WITH A CARBON FILAMENT ATOM RESERVOIR

### PART II. USE OF THE ATOM RESERVOIR IN ATOMIC FLUORESCENCE SPECTROSCOPY

The design and operation of an improved carbon filament atom reservoir is described. The improvements incorporated are: a rigid metal base, a system of water cooling the electrode supports, introduction of a laminar gas flow through the cell, improved electrical contact between the filament and its supports and the use of calibrated micropipettes to apply the sample. Optimum conditions for determination by atomic fluorescence of a number of metals are described and limits of detection are reported. The latter generally appear to be somewhat better than those obtained by flame methods, but it is the absolute size of the amount determined which is most significant. The coefficient of variation for a single determination with the improved cell is less than 3%.

R. G. ANDERSON, I. S. MAINES AND T. S. WEST,
*Anal. Chim. Acta*, 51 (1970) 355–363

## ATOMIC ABSORPTION AND FLUORESCENCE SPECTROSCOPY WITH A CARBON FILAMENT ATOM RESERVOIR

### PART III. A STUDY OF THE DETERMINATION OF CADMIUM BY ATOMIC FLUORESCENCE SPECTROSCOPY WITH AN UNENCLOSED ATOM RESERVOIR

A modified filament atom reservoir cell is described which permits atomic fluorescence measurements to be made without surrounding the electrically heated graphite element with a glass dome. The fluorescence behaviour of cadmium in this atom reservoir is described. At 228.8 nm, cadmium exhibits resonance fluorescence more strongly in argon than in nitrogen, but at 326.1 nm cadmium exhibits much stronger "stepwise fluorescence" in nitrogen than in argon. Nitrous oxide, carbon dioxide and hydrogen atmospheres show very strong quenching action at 228.8 nm and no luminescence is shown at 326.1 nm. Various interference effects and their elimination are discussed. The detection limits for cadmium are $1.5 \cdot 10^{-13}$ g (0.00015 p.p.m.) at 228.8 nm in argon and $3 \cdot 10^{-13}$ g (0.0003 p.p.m.) in nitrogen.

J. F. ALDER AND T. S. WEST,
*Anal. Chim. Acta*, 51 (1970) 365–372

# OXIDATION AND COMBUSTION REVIEWS

edited by **C. F. H. TIPPER,** *Senior Lecturer in the Department of Inorganic, Physical and Industrial Chemistry, University of Liverpool, England*

## Volume 1

APPLICATION OF THE THEORY OF BRANCHED CHAIN REACTIONS IN LOW-TEMPERATURE COMBUSTION. **R. Ben–Aim and M. Lucquin**
OXIDATION REACTIONS INDUCED BY IONISING RADIATION. **G. Hughes**
GAS PHASE PHOTO-OXIDATION. **G. R. McMillan and J. G. Calvert**
OXIDATION REACTIONS INVOLVING NITROGEN DIOXIDE. **J. H. Thomas**
OXIDATIVE DEGRADATION OF HIGH POLYMERS. **W. L. Hawkins**
THE HETEROGENEOUS SELECTIVE OXIDATION OF HYDROCARBONS. **R. J. Sampson and D. Shooter**

**6 x 9″, vii + 344 pages, 29 tables, 45 illus., 815 lit. refs., 1966 hardbound only, US$ 15,00 plus $0.50 postage**

## Volume 2

THERMAL EXPLOSION THEORY. **P. Gray and P. R. Lee**
SOME FUNDAMENTALS OF COMBUSTION INSTABILITY. **R. F. Salant and Tau–Yi Toong**
THE USE OF ADIABATIC COMPRESSION AND MASS SPECTROMETRY IN THE STUDY OF COMBUSTION. **A. Martinengo and K. H. Homann**
TRAPPED RADICALS AND COMBUSTION. **A. Thomas**

**6 x 9″, vii + 301 pages, 19 tables, 64 illus., 311 lit. refs., 1967, hardbound only, US$15.00 plus $0.50 postage**

## Volume 3

THE MECHANISM OF COMBUSTION OF DROPLETS AND SPRAYS OF LIQUID FUELS. **A. Williams**
THE LOW TEMPERATURE GAS-PHASE OXIDATION OF LOWER ALIPHATIC ALDEHYDES. **J. F. Griffiths and G. Skirrow**
IONIZATION IN COMBUSTION PROCESSES. **W. J. Miller**
AMMONIUM PERCHLORATE AS AN OXIDIZER. **A. R. Hall and G. S. Pearson**

**1968, two issues, US$12.50 plus US$0.50 postage**

## Volume 4

PERCHLORATE OXIDIZERS. **G. S. Pearson**
FORMATION AND BEHAVIOUR OF CHEMI-IONS IN FLAMES. **J. Peeters, C. Vinckier and A. van Tiggelen**
THE USE OF ISOTOPES IN THE STUDY OF OXIDATION AND COMBUSTION PROCESSES. **D. Gál**
GAS PHASE REACTIONS OF THE HYDROXYL RADICAL. **D. D. Drysdale and A. C. Lloyd**

**1969, two issues, US$12.50 plus US$0.50 postage**

For 1970. One volume, two issues. Subscription price: US$12.50 plus $0.50 postage per volume

A free specimen copy will be sent on request
Orders should be sent to: Dept. OXCOM

---

**Elsevier**

P.O. Box 211
Amsterdam – The Netherlands
**107Ea**

## MULTI-ELEMENT ATOMIC FLUORESCENCE SPECTROSCOPY

### PART II. A DUAL-ELEMENT ARSENIC–ANTIMONY ELECTRODELESS DISCHARGE TUBE SPECTRAL LINE SOURCE FOR ATOMIC FLUORESCENCE AND ATOMIC ABSORPTION SPECTROSCOPY

The preparation and operation of a dual-element arsenic–antimony microwave-excited electrodeless discharge tube is described; it can be applied to atomic fluorescence and atomic absorption spectroscopy. The dual source is as stable as the corresponding single-element sources, and the sensitivities in atomic absorption and detection limits in fluorescence are similar to those obtained for individual electrodeless discharge tubes. Interference studies with a selected number of other ions show that there is no extra interference introduced by use of the multi-element source. In addition, bismuth can be determined by direct-line fluorescence at 302.5 nm by spectral-overlap excitation from the 206.163-nm iodine line which is emitted by the As–Sb–I source. Arsenic–cadmium spectral-overlap excitation also permits the fluorimetric or absorptiometric determination of cadmium at 228.802 nm by means of the 228.81-nm arsenic line from the dual-element source; in this case the sensitivities obtained by both techniques are much inferior to those obtained with a cadmium electrodeless discharge tube.

A. FULTON, K. C. THOMPSON AND T. S. WEST,
*Anal. Chim. Acta*, 51 (1970) 373–380

## INTERFERENCES OF ACIDS IN ATOMIC ABSORPTION SPECTROPHOTOMETRY

Hydrochloric, perchloric, nitric and phosphoric acids were examined to elucidate the mechanism of their interferences on the atomic absorption spectrophotometry of copper, iron and chromium. The interferences were complex in nature and varied for different elements and for different acids. The mechanism of the interferences is discussed.

T. MARUTA, M. SUZUKI AND T. TAKEUCHI,
*Anal. Chim. Acta*, 51 (1970) 381–385

## A NEW METHOD FOR THE NEBULIZATION OF SOLID SAMPLES FOR ATOMIC ABSORPTION SPECTROSCOPY

A dispersion system for the nebulization of solid samples for atomic absorption spectrophotometry is described. Compared to the conventional method of nebulization, the proposed method has the advantages of avoiding any preliminary dissolution step, and of requiring less sample. Absorbance measurements show good sensitivity and stability. Powdered samples ($<$ 200 mesh) are dispersed in methanol with a special vibrating stirrer and the suspension is sucked directly into the flame. The method is applied to the determination of cobalt and molybdenum in alumina catalysts.

M. KASHIKI AND S. OSHIMA,
*Anal. Chim. Acta*, 51 (1970) 387–392

## CATHODE-RAY-EXCITED EMISSION SPECTROSCOPIC ANALYSIS OF TRACE RARE EARTHS

### PART IV. DETERMINATION OF THULIUM IN ZINC SULFIDE

The method of analysis for trace amounts of rare earths in a matrix by cathode-ray-excited emission spectroscopy has been extended to the determination of thulium in a zinc sulfide matrix, with lithium added as a charge-compensating ion. If the 478-nm emission from thulium is used as the detection wavelength, one p.p.b. can be readily determined, with an estimated detection limit of the order of 0.01 p.p.b. Thulium determinations by this means are compared with those from solid-state mass spectrometry. Effects of sample firing parameters and interferences are discussed.

S. LARACH, R. E. SHRADER AND R. A. KAUFFUNGER,
*Anal. Chim. Acta*, 51 (1970) 393–398

# 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, £10.0.0.**

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.

OM REVIEWS OF THE NEW EDITION

... As we have come to expect, Professor FEIGL has once more provided an outstanding service to the chemical community ...

Analytica Chimica Acta

... C'est pourquoi le livre du professeur FEIGL est extrêmement précieux pour le chimiste comme le montre la succession des éditions ...

Bulletin de la Société Chimique de France

... This volume, together with its companion on "Spot Tests in Inorganic Analysis" (5th ed., 1958), is a useful and authoritative source of information not only to analytical chemists but also to organic chemists, pharmaceutical chemists, and biochemists. Advanced students and research workers in analytical chemistry will find these two volumes stimulating and helpful ...

Analytical Chemistry

... As each successive edition of this book appeared, it was greeted with ever increasing praise. It is difficult, therefore, to find adequate superlatives to describe this new, completely revised edition ...
... The astonishing range of applications of the tests makes this book essential for every chemist concerned with organic compounds ...

Chemistry in Britain

Elsevier
Publishing
Company AMSTERDAM LONDON NEW YORK

147E

# THE DETERMINATION OF SCANDIUM AND GOLD IN METEORITES, TEKTITES AND STANDARD ROCKS BY NEUTRON ACTIVATION ANALYSIS WITH AN INTERNAL-REFERENCE METHOD

An internal-reference method has been established for the determination of scandium and of gold by neutron activation analysis, with calcium and platinum, respectively, as the reference elements; the method has been applied to the determination of both elements in several materials of geochemical origin. The composite $\gamma$-ray spectra of scandium and gold activities arising from scandium and gold in a sample and from the element used as reference by the $(n,\gamma)$ reaction followed by $\beta^-$-decay are measured. The results can be calculated on the basis of the activity ratio of the two species in terms of the photopeak areas. The success of the method depends on chemical separations and on the high resolving power of a lithium-drifted germanium detector. Sensitivity and accuracy were assessed by analyzing synthetic mixtures of known composition. The proposed method was verified to be accurate for both elements even at p.p.b. levels. The Bruderheim and Canyon Diablo meteorites, Indochinite tektite, and standard rocks, G-1, W-1 and JG-1 were tested.

K. Nomura, A. Mikami, T. Kato and Y. Oka,
*Anal. Chim. Acta*, 51 (1970) 399–408

# DIRECT DETERMINATION OF FLUORIDE IN MISCELLANEOUS FLUORIDE MATERIALS WITH THE ORION FLUORIDE ELECTRODE

The Orion fluoride electrode was used to measure major concentrations of fluoride in samples containing aluminum, calcium and silicon without prior separation. Liquid samples were mixed with a total ionic strength buffer and direct potentiometric readings were compared to a calibration curve. Samples of $AlF_3$, $Na_3AlF_6$, $CaF_2$, and $SiO_2$ (containing 20% fluoride) were fused with sodium carbonate and dissolved in water or a total ionic strength buffer. For samples containing alumina which may not be rendered soluble by a carbonate fusion, a borate–carbonate fusion was used. Interferences were masked by the addition of equal concentrations of the interfering ion during the preparation of the standards. Results are shown for various samples analyzed by this technique and by the Willard–Winter distillation and titration. The direct method is accurate to within ± 3% of the amount present.

R. T. Oliver and A. G. Clayton,
*Anal. Chim. Acta*, 51 (1970) 409–415

# APPLICATION OF SILICONE RUBBER-BASED GRAPHITE ELECTRODES FOR CONTINUOUS FLOW MEASUREMENTS

## PART I. GENERAL RELATIONSHIPS

The behaviour of the silicone rubber-based graphite electrode was studied. The relationship between the surface area of the electrode and the voltammetric current constant was established. The applicability of the silicone rubber-based graphite electrode in the continuous analysis of electrolyte flows was also investigated. At constant potential, the current exhibited a linear dependence on the concentration of the depolarizer and on the square root of the flow rate.

E. Pungor, Zs. Fehér and G. Nagy,
*Anal. Chim. Acta*, 51 (1970) 417–424

# Photoluminescence of Solutions

With Applications to Photochemistry and Analytical Chemistry

by C. A. Parker, Royal Naval Scientific Service, Head of Chemistry Division of the Admiralty Materials Laboratory, Holton Heath, Poole, Dorset, England

**× 9″, xvi + 544 pages, 53 tables, 188 illus., 443 lit. refs., 1968, Dfl. 85.00, £11.10.0.**

Contents: Basic principles, definitions and kinectics of fluorescence, phosphorescence and delayed fluorescence; polarisation; light scattering; monochromators; light sources; filters; photodetectors; actinometry; recording systems; inner filter effects; specimen compartments; correction of spectra; measurement of photoluminescence efficiency and lifetime; purity of materials; parameters of singlet and triplet states; equilibria in the excited state; excited dimers; solvent effects; fluorescence and phosphorescence analysis.

# Comprehensive Analytical Chemistry

edited by C. L. Wilson, Professor of Inorganic and Analytical Chemistry, University of Belfast (Northern Ireland)
and D. W. Wilson, Head of the Chemistry Department, Sir John Cass College, London (England)

**VOLUME IIB: Physical Separation Methods**

**6 × 9″, xvi + 445 pages, 30 tables, 116 illus., 897 lit.refs., 1968, Dfl. 70.00, £8.10.0.**

Volume Two, Part B is devoted to physical separation methods. After an account of the theory and practise of liquid chromatography in columns, the volume continues with a lengthy treatment of gas chromatography.
The next chapter, on ion exchangers, is notable for the account it gives of analytical applications, while distillation (theory and technique) is the last topic to be treated in the present volume.

Contents: I. *Liquid Chromatography in Columns*. 1. Introduction. 2. Theory. 3. Apparatus and operation. II. *Gas Chromatography*. 1. Introduction and general principles. 2. Theoretical aspects. 3. Apparatus. 4. The partitioning phases. 5. Absorbents and gas-solid chromatography. 6. Gas-liquid chromatography. 7. Analytical methods. 8. Applications. III. *Ion Exchangers*. 1. Foreword. 2. Introduction. 3. The constitution of ion exchangers. 4. The mechanism of ion exchange. 5. Technique. 6. Analytical applications. Appendix 1: Ion-exchanger data. Appendix 2: Methods of testing ion exchangers. Appendix 3: Bibliography. IV. *Distillation*. 1. Introduction. 2. Theoretical background. 3. Experimental techniques.

# Atomic-Absorption Spectroscopy

and Analysis by Atomic-Absorption Flame Photometry

by J. Ramírez-Muñoz, Principal Applications Chemist at Beckman Instruments Inc. and Scientific Research Collaborator of the C.S.I.C., Spain

**6 × 9″, xii + 493 pages, 23 tables, 156 illus., 950 lit. refs., 1968, Dfl. 80.00, £9.15.0.**

Contents: *Part I: Fundamentals*. 1. Origins of the method and nomenclature. 2. General principles and characteristics. 3. Absorption and emission. 4. The literature of atomic-absorption spectroscopy. 5. Theory. *Part II: Instrumental Systems*. 6. Instrumental systems. 7. Emission systems. 8. Absorption system. 9. Selection system. 10. Photometric system. 11. Instruments. *Part III: Range and Limitations of Atomic Absorption Methods*. 12. Determinable elements. Choice of lines. 13. Sensitivity. 14. Limitations in atomic absorption. *Part IV: Experimental Methods*. 15. Experimental process. 16. Standard solutions. 17. Preparation of the sample. 18. Experimental measurements and calibration. *Part V: Applications*. 19. Applications. Appendix. Bibliography.

Elsevier
Publishing
Company
Amsterdam London New York

230 E

## THE COULOMETRIC GENERATION OF LOWER OXIDATION STATES OF VANADIUM

The controlled-current coulometric generation of vanadium(III) and (II) has been studied as a function of cathode material, pH, and composition of the precursor electrolyte. Some formal potentials of the vanadium(IV)/(III) couple have been measured. The current efficiency of vanadium(III) generation was greatest at higher current densities at a mercury cathode in the presence of phosphoric acid.

G. A. Brydon and G. F. Atkinson,
*Anal. Chim. Acta*, 51 (1970) 425–430

---

## THE TITRIMETRIC DETERMINATION OF MERCURY(II) WITH THIOACETAMIDE

A rapid method is described for the direct titration of mercury(II) in the presence of halide ions, which cause interference in classical titrations. The mercury(II), in an alkaline solution as the (ethylenedinitrilo)tetraacetic acid (EDTA) complex, is titrated potentiometrically with thioacetamide and a silver sulfide–calomel electrode pair. Organomercury compounds which are not soluble in alkaline EDTA may be titrated after Schöniger combustion. The relative error of the method is 1%.

B. Coulter and D. G. Bush,
*Anal. Chim. Acta*, 51 (1970) 431–436

---

## DETERMINATION OF CARBON BY NON-AQUEOUS TITRATION AFTER COMBUSTION IN A HIGH-FREQUENCY INDUCTION FURNACE

### APPLICATION TO ROCKS, STONY METEORITES AND METALLURGICAL SAMPLES

Suitable non-aqueous titration methods have been developed for the determination of total carbon in silicate and carbonate rocks, stony meteorites and metallurgical samples by a high-frequency induction furnace. The method has been extended to the determination of carbon dioxide in rocks, clay and limestones by the acid evolution method. A conventional receiver with a buret for continuous titration was unsuitable in the induction heating procedure; and was replaced by two connected borosilicate glass receivers in a closed system. Acetone either alone (for 0–10 mg C) or in 1:1 mixture with methanol (for 10–30 mg C) containing 0.6% (v/v) monoethanolamine and an excess of standard sodium methylate was found to be a better absorbent for carbon dioxide than pyridine. After reaction, the excess sodium methylate was back-titrated by a standard methanolic solution of benzoic acid with phenolphthalein as indicator. The method gives reliable results up to 47% total carbon dioxide.

J. G. Sen Gupta,
*Anal. Chim. Acta*, 51 (1970) 437–447

---

## A SIMPLE AND SENSITIVE COLORIMETRIC ASSAY OF BENZYLHYDRAZINE

A new and simple procedure for the colorimetric determination of benzylhydrazine is described. It is based on the color development by *p*-dimethylaminobenzaldehyde in the presences of metaphosphoric acid and glacial acetic acid. The assay of microgram quantities of benzylhydrazine in plasma and tissues of rat treated with isocarboxazid is reported.

T. Satoh and K. Moroi,
*Anal. Chim. Acta*, 51 (1970) 449–454

# Pigments

## An Introduction to their Physical Chemistry

**edited by David Patterson**

*Senior Lecturer, Department of Colour Chemistry, University of Leeds, Great Britai*

**$5\frac{1}{2} \times 8\frac{1}{2}''$, ix + 210 pages, 93 illus., 1967, Dfl. 32.50, 65s.**

In this book the principles of physical chemistry are applied to the problems of making and using the insoluble organic and inorganic pigments manufactured for use in paints, printing inks, plastics and synthetic fibres. Development over many years has resulted in a high degre of technical quality in many of these pigments, achieved by purely empirical methods, but th use of such methods means that each case must be judged on its merits. On the other hand, the application of physico-chemical theories can bring unifying concepts to a wide range o phenomena, and provide a deeper understanding of the processes involved.

It is quite insufficient to treat the making of pigments as the synthesis of certain compounds and to emphasize this the purely preparative chemistry of pigments has been left outside th scope of this book. Instead, pigments are regarded as substances produced to exert particula optical effects on certain media by colouring and opacifying them. The ways in which pigments can be prepared to carry out these functions, together with the appropriate technique for appraising their performance of them are consequently the main content of the book. Al the problems cannot be solved at present, but this book by showing what can be achieve and attempting to provide signposts to some of the unexplored areas, will undoubtedly stimulate and encourage further work in a field that is of considerable industrial importance.

**Contents**

Elsevier
Publishing
Company

Amsterdam London New York

## THE DETERMINATION OF RHENIUM IN SEA WATER

A neutron activation procedure has been developed for the determination of rhenium in sea water. Anion exchange with Deacidite FF is used as a preconcentration stage. Rhenium is eluted with 4 *M* nitric acid and submitted to irradiation with thermal neutrons. Rhenium-186 is separated from other induced activities by solvent extraction and by an almost specific ion-exchange process employing mixed aqueous–organic solvent. Finally, rhenium is precipitated as tetraphenylarsonium perrhenate for determination of chemical yield and counting. Water from intermediate depths in the Atlantic was found to contain 6–8 ng Re $l^{-1}$.

A. D. MATTHEWS AND J. P. RILEY,
*Anal. Chim. Acta*, 51 (1970) 455–462

---

## POLAROGRAPHY OF SOME SULPHUR-CONTAINING COMPOUNDS

### PART XV. POLAROGRAPHIC AND SPECTRAL INVESTIGATION OF ACID–BASE EQUILIBRIA IN AQUEOUS SOLUTIONS OF SUBSTITUTED 2-THIOBARBITURATES

Changes of u.v. absorption spectra and polarographic reduction waves with pH indicate in solutions of 5,5′-dialkyl-2-thiobarbiturates the presence of four different species: diprotonated ($AH_2$), monoprotonated (AH), zwitterion (BH) and anionic (B). Dissociation constants p$K_2$ were determined and values of p$K_1$ and p$K_3$ estimated. In attempts to elucidate the electroactive forms, some tautomers were excluded in the 4-electron reduction of $H_2A$ and 2-electron reductions of HA and BH, the electrolyses of which gave varying yields of hydrogen sulphide. The anion B gives no reduction waves. 1,5,5′-Trialkyl-2-thiobarbiturates show u.v. spectra and polarographic waves corresponding to forms HA and BH. 1,3-Dimethyl-5,5′-dipropyl-2-thiobarbiturate is reduced in the monoprotonated and possibly diprotonated form. Predominant forms in the bulk of the solution at various pH values and the most probable electroactive forms are discussed. Reduction waves of 5,5′-dialkyl- and 1,5,5′-trialkyl-2-thiobarbiturates in 0.05 *M* borax are suitable for analytical purposes.

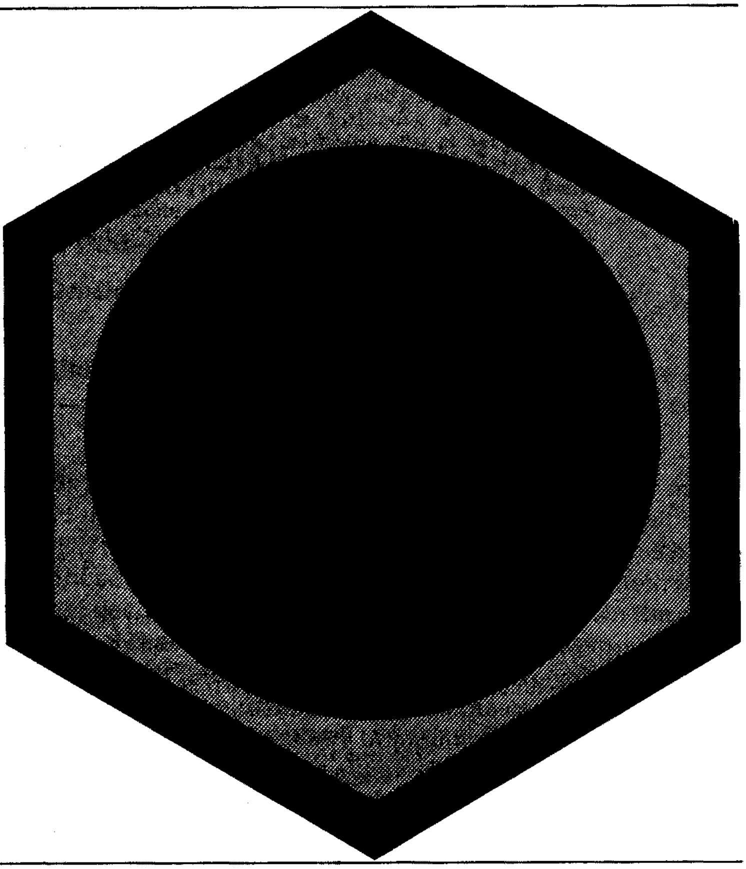
W. F. SMYTH, G. SVEHLA AND P. ZUMAN,
*Anal. Chim. Acta*, 51 (1970) 463–482

---

## THE POLAROGRAPHY OF VANADYL SULFATE IN DIMETHYLFORMAMIDE

The polarographic technique was applied to a solution of vanadyl sulfate in dimethylformamide with 0.1 *M* tetraethylammonium perchlorate as the supporting electrolyte. The three resulting polarographic waves were examined and a mechanism is proposed to explain the waves. The mechanism involves an intermediate vanadium(III) dimer that is the product of a vanadium(IV)–vanadium(II) reaction. This intermediate then breaks down to the monomeric (III) state. The mechanism was studied by optical, constant-potential coulometric, and fast-sweep polarographic techniques. The final polarographic wave was attributed to a solvent bridge connecting the electrode with the vanadium(II) produced at the electrode. This bridging structure allows the solvent to be reduced at a potential more positive than when vanadium is absent.

C. W. MANNING AND W. C. PURDY,
*Anal. Chim. Acta*, 51 (1970) 483–488



## A STUDY OF PYRIDINIUM TERNARY MOLYBDOPHOSPHATE COMPLEXES

### COLLECTION OF TRACE AMOUNTS OF TITANIUM(IV), ZIRCONIUM(IV), AND THORIUM(IV)

Trace amounts of titanium(IV), zirconium(IV), and thorium-(IV) can be quantitatively collected from pyridinium solutions at pH 1–3 with the molybdophosphate complex. The metal ions react with molybdophosphate, and are then precipitated as the pyridinium ternary heteropoly salts. These salts were investigated by infrared spectrophotometry and thermogravimetric techniques.

K. Murata and S. Ikeda,
*Anal. Chim. Acta*, 51 (1970) 489–495

## SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS IN ALUMINIUM, COPPER AND NICKEL ALLOYS, AND WHITE METALS

A method is described for the spectrophotometric determination of up to 0.08% of phosphorus in aluminium, copper and nickel alloys, white metals, tungsten, zinc, and silver babbitts based on the extraction of the phosphovanadomolybdate complex by methyl isobutyl ketone. The matrix metals are complexed by fluoride ion and do not interfere in the procedure. The molar absorptivity is 1820 and 3110 at 425 and 400 nm respectively, with a standard deviation of ±0.5%.

P. Pakalns,
*Anal. Chim. Acta*, 51 (1970) 497–501

## THE USE OF 2-NITROSO-1-NAPHTHOL AS AN EXTRACTION AND SPECTROPHOTOMETRIC REAGENT FOR COBALT IN PLANT MATERIALS

The separation and spectrophotometric determination of trace amounts of cobalt in plant materials with 2-nitroso-1-naphthol is described. The cobalt complex is formed in citrate-buffered medium in the presence of 0.5–0.75 $M$ sulphate ion which arises from the sulphuric acid used for wet oxidation of sample materials. The absorbance is measured at 367 nm ($\varepsilon = 4.4 \cdot 10^4$) which provides greater sensitivity and precision than the usual measurement at 530 nm ($\varepsilon = 1.6 \cdot 10^4$). The method is suitable for samples containing as little as 0.05–0.25 p.p.m. Co, the error being ± 5% in oxidized plant materials.

H. Ssekaalo,
*Anal. Chim. Acta*, 51 (1970) 503–508

## STUDIES ON THE CATION-EXCHANGE BEHAVIOUR OF AMMONIUM 12-MOLYBDOPHOSPHATE

### PART I. SEPARATION OF RUBIDIUM, THALLIUM AND CAESIUM

The cation-exchange behaviour of ammonium 12-molybdophosphate (AMP) for thallium(I) is discussed. Conditions are described for the separation of rubidium, thallium and caesium from one another on a column of AMP suitably mixed with asbestos. The three elements are adsorbed from 5 $M$ nitric acid. Rubidium is first eluted with 3 $M$ ammonium nitrate. Thallium is separated by oxidative elution using bromide–bromine mixture. Caesium is finally removed by 12 $M$ ammonium nitrate.

S. D. Roy and M. S. Das,
*Anal. Chim. Acta*, 51 (1970) 509–515

*A New Important Encyclopaedic Work of Reference*

# COMPREHENSIVE CHEMICAL KINETICS

edited by C.H. BAMFORD F.R.S.,
and C.F.H. TIPPER

The aim of this series is to cover in a critical way the practice and theory of kinetics and the kinetics of inorganic and organic reactions in the gas and condensed phases or at interfaces.
Each chapter is written by an expert in the field so that the series as a whole will serve as a direct source of reference and information over the whole range of kinetics.
The vast amount of material scattered through the literature has never before been gathered together and presented in this accessible form.

Elsevier

P.O. BOX 211,
AMSTERDAM - THE NETHERLANDS

Ea

Volume 1. The Practice of Kinetics

1. Experimental methods for the study of slow reactions (L. Batt)
2. Experimental methods for the study of fast reactions (D.N. Hague)
3. Experimental methods for the study of heterogeneous reactions (D. Shooter)
4. The detection and estimation of intermediates (R.P. Wayne)
5. The treatment of experimental data (D. Margerison)

**7 x 10", xiii + 450 pages, 32 tables, 161 illus., 1174 lit. refs., 1969, Dfl. 95.00, £11.5.0**
**SBN 444-40673-5**

Volume 2. The Theory of Kinetics

1. Kinetic characterization of complex reaction systems (Z.G. Szabó)
2. Chain reactions (V.N. Kondratiev)
3. Theory of the kinetics of elementary gas phase reactions (R.P. Wayne)
4. Theory of elementary reactions in solution (I.D. Clark and R.P. Wayne)
5. Theory of solid phase kinetics (L.G. Harrison)

**7 x 10", xiii + 486 pages, 13 tables, 77 illus., 794 lit. refs., 1969, Dfl. 100.00, £11.10.0**
**SBN 444-40674-3**

Volume 3. The Formation and Decay of Excited Species

1. Effect of low energy radiation (C.S. Burton and W.A. Noyes, Jr.)
2. Effect of high energy radiation (G. Hughes)
3. The chemical production of excited states (T. Carrington and D. Garvin)
4. The transfer of energy between chemical species (A.B. Callear and J.D. Lambert)

**7 x 10", xii + 300 pages, 30 tables, 53 illus., 1969, Dfl. 70.00, £8.5.0**
**SBN 444-40802-9**

The series as a whole will comprise about 25 volumes divided into a number of sections:

Section 1. The practice and theory of kinetics (3 volumes)
Section 2. Decomposition and isomerisation reactions (2 volumes)
Section 3. Inorganic reactions (2 volumes)
Section 4. Organic reactions (6 volumes)
Section 5. Polymerization reactions (2 volumes)
Section 6. Oxidation and combustion reactions (2 volumes)
Section 7. Selected elementary reactions (2 volumes)

Other sections are planned on heterogeneous reactions, solid state reactions, and kinetics and technological processes.

## THORIUM HYDROXIDE AS A COLLECTOR OF MOLYBDENUM FROM SEA WATER

*(Short Communication)*

Y. S. Kim and H. Zeitlin,
*Anal. Chim. Acta*, 51 (1970) 516–519

## LANTHANUM AS A RELEASING AGENT IN ATOMIC ABSORPTION SPECTROSCOPY IN ORGANIC SOLVENTS

*(Short Communication)*

R. A. Mostyn, B. T. N. Newland and W. E. Hearn,
*Anal. Chim. Acta*, 51 (1970) 520–522

## A NEW AUTOMATIC APPARATUS FOR THE DETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS WITH COLORIMETRIC END-POINT INDICATION

*(Short Communication; in German)*

W. Merz,
*Anal. Chim. Acta*, 51 (1970) 523–526

## THE APPLICATION OF ULTRASONICS TO THE COLLECTION OF TRACES OF ANTIMONY(V) IONS ON ALUMINA POWDER

*(Short Communication)*

K. Fukuda and A. Mizuike,
*Anal. Chim. Acta*, 51 (1970) 527–528

## RADIOCHEMICAL INVESTIGATION OF THE EXTRACTION OF COPPER(II) BY SOME SCHIFF'S BASES

*(Short Communication)*

J. Aggett and R. A. Richardson,
*Anal. Chim. Acta*, 51 (1970) 528–529

## MULTI-ELEMENT ATOMIC FLUORESCENCE SPECTROSCOPY

*(Short Communication)*

M. S. Cresser and T. S. West,
*Anal. Chim. Acta*, 51 (1970) 530–533

## SPECTROPHOTOMETRIC DETERMINATION OF BORON IN STEEL WITH METHYLENE BLUE

F. Vernon and J. M. Williams,
*Anal. Chim. Acta*, 51 (1970) 533–535

# INORGANIC ELECTRONIC SPECTROSCOPY

by A. B. P. LEVER, Associate Professor of Chemistry,
York University, Toronto, Canada

*The first monograph in the series PHYSICAL INORGANIC CHEMISTRY,*
*edited by M. F. LAPPERT*

Electronic spectroscopy has become, in recent years, a commonplace tool in inorganic research and development although few books dealing with the topic have appeared. Those books dealing with spectroscopy in general devote but a few pages to a discussion of the electronic spectra of inorganic compounds.

The aim of this book is (a) to provide the reader with a basic understanding of the methods and procedures involved in a study of the electronic spectra of inorganic compounds, (b) to discuss the information which may be derived from such study, with particular emphasis on stereochemistry and chemical bonding, and (c) to provide a reference text.

A beginning is made at a level which can be understood by an average student with a first degree, the first third of the book dealing with atomic theory, symmetry and group theory. In progressing further with the material presented, the reader can proceed from the construction of qualitative energy level diagrams and the assignment of transitions observed in the spectra of cubic molecules, to quantitative diagrams and the spectra of non-cubic molecules.

Having mastered this material the reader is shown how to derive useful information concerning stereochemistry and chemical bonding and even, qualitatively, such properties as effective nuclear charge and mean *d*-orbital radii. The spectra of the more common transition metal ions in their many oxidation states and stereochemistries are discussed in Chapter 9, which is a mine of information for the practising inorganic spectroscopist.

The book is unique in being the only reference work available which will bring the new graduate up to the level where he can read and usefully digest the original research papers in inorganic spectroscopy. Much of the material has not appeared in book form before and some of it has not appeared in print at all.

Contents: Preface. 1. Atomic structure. 2. Molecular symmetry. 3. Group theory. 4. Crystal field diagrams. 5. Term diagrams. 6. Selection rules, band intensities and dichroism. 7. Some theoretical aspects of electronic spectra. 8. Charge transfer spectra. 9. Crystal field spectra. Appendices. Indexes.

**xii + 420 pages, 78 tables, 130 illus., 465 lit. refs., 1968, Dfl. 90.00, £11 10.0.**

Elsevier
Publishing
Company
Amsterdam London New York

262 E

## DETERMINATION OF SMALL AMOUNTS OF AMINECARBOXYLIC ACID COMPLEXING AGENTS IN THE PRESENCE OF EXCESS TRIVALENT LANTHANIDES AND ACTINIDES

*(Short Communication)*

R.M. WALLACE AND J. F. HINTON,
*Anal. Chim. Acta*, 51 (1970) 536–538

## AN ANODE FILM OBTAINED DURING CONSTANT-CURRENT COULOMETRIC OXIDATION OF MANGANESE(II)

*(Short Communication)*

G. A. BRYDON AND G. F. ATKINSON,
*Anal. Chim. Acta*, 51 (1970) 539–540

## INEXPENSIVE NEAR-INFRARED AND INFRARED CELL HOLDERS FOR DISPOSABLE LIQUID INFRARED CELLS

*(Short Communication)*

H. J. HINITZ,
*Anal. Chim. Acta*, 51 (1970) 540–543

## THE PURITY OF COMMERCIAL DIPHENYLCARBAZIDE

*(Short Communication)*

G. J. WILLEMS, R. A. LONTIE AND W. A. SETH-PAUL,
*Anal. Chim. Acta*, 51 (1970) 544–548

## PREPARATION AND USE OF ELECTRODELESS DISCHARGE TUBES FOR THE ATOMIC ABSORPTION SPECTROPHOTOMETRY OF SOME ALKALI METALS

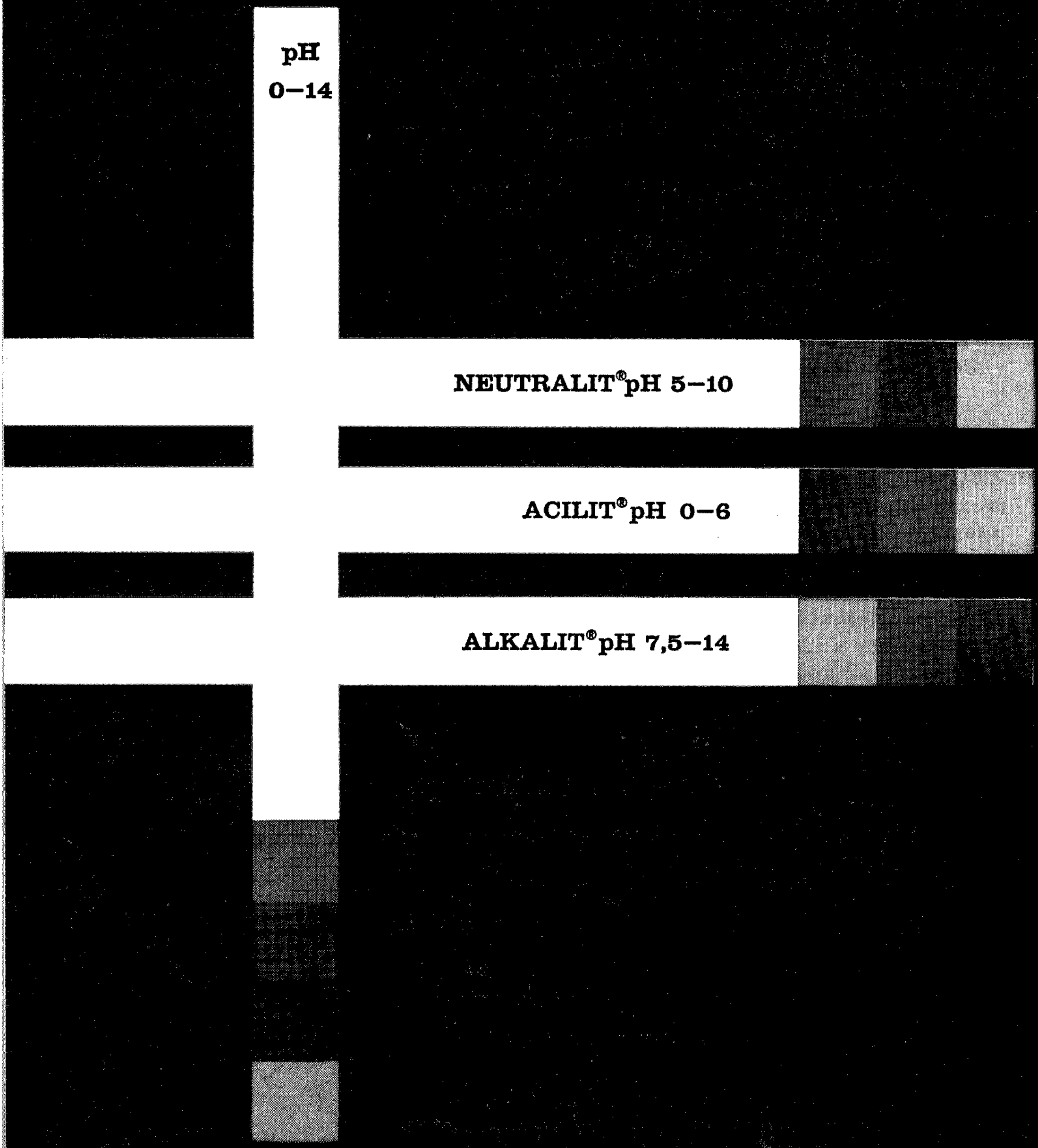
*(Short Communication)*

C. WOODWARD,
*Anal. Chim. Acta*, 51 (1970) 548–553

## TITRIMETRIC DETERMINATION OF VANADIUM(IV) WITH POTASSIUM PERMANGANATE OR CERIUM(IV) SULPHATE AT ROOM TEMPERATURE

*(Short Communication)*

N. VENKATESWARA RAO AND V. V. S. ESWARA DUTT,
*Anal. Chim. Acta*, 51 (1970) 553–556


pH
0–14
NEUTRALIT®pH 5–10
ACILIT®pH 0–6
ALKALIT®pH 7,5–14

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

# AN X-RAY FLUORESCENCE SPECTROSCOPIC METHOD FOR THE DETERMINATION OF TOTAL MANGANESE IN ROCKS AND MARINE SEDIMENTS*

L. A. WOLFE AND H. ZEITLIN
*Department of Chemistry and Hawaii Institute of Geophysics, University of Hawaii, Honolulu, Hawaii 96822 (U.S.A.)*

(Received March 31d, 1970)

X-Ray fluorescence provides a rapid, precise means for the analysis of geological samples. This method of analysis has previously been used for the determination of manganese in rocks by CHODOS AND ENGEL[1] and VOLBORTH[2]. GRUNWALD[3] attempted to use X-ray fluorescence in analysis for manganese in marine sediments. In the study by GRUNWALD, the correlation between the manganese concentration and the fluorescent X-ray intensity was considerably more inaccurate than that reported by CHODOS AND ENGEL. Since the accuracy values reported by CHODOS AND ENGEL are significantly higher than precision values expected in this kind of study, it appeared desirable to re-evaluate the accuracy problem of the determination of manganese in rocks.

Under ideal conditions the fluorescent X-ray intensity can be expressed as a simple function of the concentration of the element of interest. However, because of the complexity of the matrices that are involved, these ideal conditions are almost never present in geological samples. The problem basically is one of correcting the observed X-ray intensity so that it can be correlated to the concentration of the element of interest.

GOLDBERG[4] has shown that the concentration of most of the major elements in igneous rocks is about the same as the concentration of these elements in marine sediments. As reported by GOLDBERG AND ARRHENIUS[5], the manganese concentration in marine sediments is about 3–30 times higher than in igneous rocks. Since there is a similarity in the elemental composition of the marine sediments and igneous rocks, one would expect the interelement effects of the matrices on the X-ray intensities also to be similar.

In the present study, two methods of analyzing the X-ray intensity data from the standard rock samples were compared. The method using the scattered X-rays as an internal standard gave a more accurate correlation between the manganese concentration in the standard rocks and the fluorescent X-ray intensity, than did the net-intensity method.

---

* Chemistry Department and Hawaii Institute of Geophysics Contribution No. 344.

## EXPERIMENTAL

### *Sample preparation*

The standard rock samples used were quartz, the U.S.G.S. rock standards G-1 and W-1 (STEVENS AND NILES[6]) and the HIGS rock standards (*Analyst*, George RIDDLE, U. S. Geological Survey). Since the manganese concentration in marine sediments is higher than in igneous rocks, a standard had to be prepared with a high manganese dioxide concentration. This was done by adding a known amount of manganese dioxide to one of the HIGS standards and is referred to as HIGS-4*. All standards and samples were prepared by mixing 1.0 g of the powdered rock standard or marine sediment sample with 0.25 g of methylcellulose which was used as a binder. The sample–methylcellulose mixtures were then pressed into briquettes for analysis.

### *Instrumental*

A Norelco Vacuum X-ray Spectrograph with a tungsten target tube was employed; this was operated at 45 kV and 45 mA. A lithium fluoride analyzing crystal was used in connection with a gas flow proportional counter that was operated at 1760 V. The gas used in the counter was P-10 and the flow rate was one standard cubic foot of air per h. The pulse height analyzer base-line was set at 2.5 V; the window setting was not used.

### *Analytical methods*

The Mn K$\alpha$ peak and a scattered radiation position at $+1°$ $2\theta$ from the Mn K$\alpha$ peak were the positions that were counted. Since the intensity of the scattered radiation was about 10% of the Mn K$\alpha$ radiation in most cases, the background had to be accounted for in the analysis of the X-ray data.

The two calibration curves were prepared by using a least-squares fit of the intensity values obtained with the quartz, G-1, and W-1 standards. The intensity and chemical concentration values for the HIGS standards were then placed around this calibration curve.

The net-intensity method (n.i.m.), shown in Fig. 1, is probably the most commonly used means for evaluating X-ray data. This method consists of subtracting

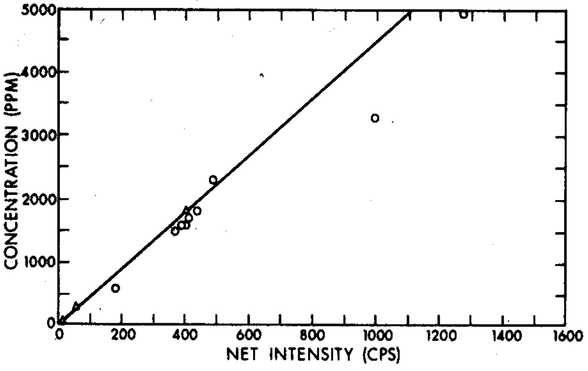


Fig. 1. Calibration curves for net-intensity method. (△) Quartz, G-1, W-1; (○) HIGS standards.

the intensity obtained at the scattered radiation position from the intensity obtained at the peak position. This procedure, however, neglects any interelement effects of the matrix of the intensities.

ANDERMANN AND KEMP[7] reported using scattered X-rays as an internal standard by means of a ratio of the peak intensity and the intensity of a scattered radiation position. They showed that this ratio reduces the effect of instrumental and physical variables on the analysis and also compensates for some of the matrix variables encountered in the analysis. In the present study, this intensity ratio method (i.r.m.) (shown in Fig. 2) was used by taking a ratio of the Mn K$\alpha$ peak and the scattered radiation intensity at $+1°$ $2\theta$ from the Mn K$\alpha$ peak. At that position the scattered radiation contained two second-order lines, W $L_{\gamma2}$ and W $L_{\gamma3}$, from the characteristic spectrum of the target.

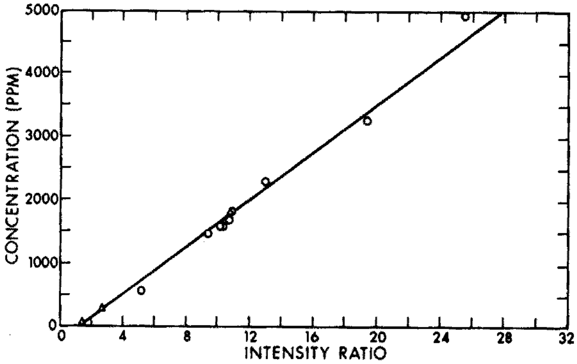


Fig. 2. Calibration curve for intensity-ratio method. (△) Quartz, G-1, W-1; (○) HIGS standards.

RESULTS

The X-ray data from twelve rock samples with manganese concentrations from 0–5000 p.p.m. were analyzed by two different X-ray methods. The results are presented in Table I, together with the chemical values for the sample. The concentration values for the different methods of X-ray analysis were calculated from the slope and intercept of the calibration curves. Table II compares the accuracies that were obtained by using the two different methods of analyzing the X-ray data.

Different instrumental methods have previously been used for the determination of manganese in rocks. A comparison of the precisions of some of these different instrumental methods and the i.r.m. for the U.S.G.S. standards G-1 and W-1 is presented in Table III.

Eight different marine sediment cores obtained from the vicinity of the Hawaiian Islands chain were analyzed in this study. Two were analyzed in about 10-cm increments to a depth of about 100 cm, and showed a fluctuation of the manganese concentration with depth, similar to that reported by BENDER *et al.*[8]. The manganese concentrations at different depths and sediment type for each of the eight cores are presented in Table IV.

TABLE I

COMPARISON OF MnO ACCURACIES OBTAINED BY TWO METHODS OF X-RAY ANALYSIS AND THE REPORTED CHEMICAL VALUES

| | *Chemical values (p.p.m.)* | *N.i.m. values (p.p.m.)* | *N.i.m. deviation (%)* | *I.r.m. values (p.p.m.)* | *I.r.m. deviation (%)* |
|---|---|---|---|---|---|
| Quartz | 0 | 83 | — | 28 | — |
| G-1 | 270 | 225 | 16.66 | 255 | 5.55 |
| W-1 | 1800 | 1802 | 0.11 | 1801 | 0.05 |
| HIGS-1 | 1800 | 1893 | 5.16 | 1821 | 1.16 |
| HIGS-2 | 1700 | 1797 | 5.70 | 1781 | 4.76 |
| HIGS-3 | 3300 | 4373 | 32.52 | 3413 | 3.42 |
| HIGS-4 | 1500 | 1635 | 9.00 | 1551 | 3.40 |
| HIGS-5 | 2300 | 2218 | 3.56 | 2161 | 6.04 |
| HIGS-6 | 1600 | 1706 | 6.62 | 1697 | 6.06 |
| HIGS-7 | 600 | 796 | 32.67 | 780 | 30.00 |
| HIGS-8 | 1600 | 1722 | 7.62 | 1735 | 8.43 |
| HIGS-4* | 4963 | 5512 | 11.06 | 4580 | 7.71 |

TABLE II

COMPARISON OF ACCURACIES OBTAINED BY X-RAY FLUORESCENCE METHODS

| *Method* | *Average deviation (p.p.m.)* | *Average deviation (%)* | *Average deviation without HIGS-7 (p.p.m.)* | *Average deviation without HIGS-7 (%)* |
|---|---|---|---|---|
| N.i.m. | 224 | 12.07 | 227 | 9.52 |
| I.r.m. | 110 | 7.08 | 103 | 4.59 |

TABLE III

COMPARISON OF ANALYTICAL PRECISION FOR ROCK STANDARDS G-1 AND W-1

| *Method* | *G-1 (%)* | *W-1 (%)* |
|---|---|---|
| "Best values"[a] | 0.0270 | 0.1800 |
| I.r.m. | 0.0255 ± 0.0004 | 0.1800 ± 0.0012 |
| Colorimetric[a] | 0.03 ± 0.01 | 0.17 ± 0.05 |
| Spectrographic[a] | 0.0260 ± 0.0086 | 0.18 ± 0.02 |
| Direct reading spectrographic[a] | 0.0240 ± 0.0016 | 0.170 ± 0.008 |
| Atomic absorption[b] | 0.0212 ± 0.0047 | 0.1360 ± 0.0014 |

[a] STEVENS AND NILES[6].
[b] BELT[9].

## DISCUSSION

From Table I, it can be seen that, in most cases, the i.r.m. gives a better correlation with the chemical concentration values than does the n.i.m. The precision of the X-ray data for these analyses was much better than the accuracy; an example of this can be seen in Tables I and III for the U.S.G.S. standards, G-1 and W-1. For

TABLE IV

CONCENTRATION AND SEDIMENT TYPE FOR EIGHT CORES

| *Core* | *Depth in core (cm)* | *Concentration (p.p.m.)* | *Sediment type* |
|---|---|---|---|
| HIG 650125-8G | 0–2 | 3309 | Deep-sea brown clay |
| HIG 650125-8G | 50–52 | 3503 | Deep-sea brown clay |
| HIG 650125-8G | 71–73 | 3602 | Deep-sea brown clay |
| HILO 7G | 2–7 | 4658 | Deep-sea brown clay |
| MOHOLE Recon-2G | 32 | 3949 | Deep-sea brown clay |
| HIG 650606-2G | 0–2 | 2960 | Diatomaceous ooze |
| HIG 650606-2G | 50–52 | 2301 | Diatomaceous ooze |
| HIG 650125-3G | Top | 1930 | Shallow-water detrital mud |
| HIG 650125-3G | 22–24 | 2729 | Shallow-water detrital mud |
| HIG 650125-3G | 91–93 | 2782 | Shallow-water detrital mud |
| HIG 650606-3G | 0–3 | 2510 | Shallow-water detrital mud |
| HIG 650623-1S | Top | 1225 | Shallow-water detrital mud |
| JAPANYON V-1G | 0–10 | 1958 | Volcanic silt |

the HIGS standards, the poor correlation may be due in part to the concentrations being reported only to the nearest 100 p.p.m. In addition, the interelement effects are probably not fully compensated for in the i.r.m.

In comparing this study with previous X-ray studies, it can be seen that the accuracy for the i.r.m. is better than the accuracy reported by CHODOS AND ENGEL on their samples, provided that the standard HIGS-7 is ignored. Note also the improvement in accuracy as compared with that reported by VOLBORTH on his samples. CHODOS AND ENGEL used a net-intensity method in their analyses. Their samples had an MnO concentration range of 0.14–0.35%. Mean and maximum deviations of 7.6 and 16.7%, respectively, were reported. When the HIGS-7 standard was not included, the i.r.m. study had a mean deviation of 4.59% and a maximum deviation of 8.43%. VOLBORTH in his analyses had deviations of 40% for 0.06% MnO, 19% for 0.11% MnO, and 10% for 0.18% MnO. The i.r.m. had deviations of 30% for 0.06% MnO, 3.40% for 0.15% MnO, and 1.16% for 0.18% MnO.

Comparison of the X-ray precision with several other instrumental methods is shown in Table III. Even though there were only two samples for each of the X-ray analyses the precision of the i.r.m. for the analyses of G-1 and W-1 seems to be better than that obtained by any of the other methods that were considered.

The authors are indebted to Dr. GEORGE ANDERMANN for his helpful comments and criticisms.

## SUMMARY

A method for the determination of manganese by X-ray fluorescence is described. By using scattered X-rays as an internal standard, a linear calibration plot is obtained for standard rocks that agrees with the chemical data. The scattered X-ray method, compared with a widely used net-intensity method, shows improvement in accuracy especially at higher concentrations.

## RÉSUMÉ

On décrit une méthode de dosage du manganèse par fluorescence avec rayons-X. En utilisant un rayonnement dispersée comme étalon interne, on obtient un calibrage linéaire pour des roches standards, correspondant avec les valeurs chimiques. La méthode aux rayons-X dispersés présente une meilleure exactitude, spécialement aux concentrations plus élevées.

## ZUSAMMENFASSUNG

Es wird eine Methode für die Bestimmung von Mangan durch Röntgenfluoreszenzanalyse beschrieben. Durch Verwendung der gestreuten Röntgenstrahlen als innerer Standard wird für Standardgesteine eine lineare Eichkurve erhalten, die mit den chemischen Werten übereinstimmt. Die Methode ergibt eine gute Genauigkeit insbesondere bei höheren Konzentrationen.

## REFERENCES

1 A. A. Chodos and C. G. Engel, *Am. Mineralogist*, 4 (1960) 120.
2 A. Volborth, *Nevada Bur. Mines Rept.*, 6 (1963) 85.
3 R. Grunwald, personal communication, 1967.
4 E. D. Goldberg, in L. H. Ahrens, F. Press, K. Rankama and S. K. Runcorn, *Physics and Chemistry of the Earth*, Vol. 4, Pergamon, Oxford, 1961, p. 281.
5 E. D. Goldberg and G. O. S. Arrhenius, *Geochim. Cosmochim. Acta*, 13 (1958) 153.
6 R. E. Stevens and W. W. Niles, *U. S. Geol. Surv. Bull.*, 1113 (1960) 1.
7 G. Andermann and J. W. Kemp, *Anal. Chem.*, 30 (1958) 1306.
8 M. L. Bender, T. Ku and W. S. Broecker, *Science*, 151 (1966) 325.
9 C. B. Belt, Jr., *Anal. Chem.*, 39 (1967) 676.

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

# ATOMIC ABSORPTION AND FLUORESCENCE SPECTROSCOPY WITH A CARBON-FILAMENT ATOM RESERVOIR

## PART II. USE OF THE ATOM RESERVOIR IN ATOMIC FLUORESCENCE SPECTROSCOPY

R. G. ANDERSON, I. S. MAINES AND T. S. WEST
*Chemistry Department, Imperial College, London, S.W.7 (England)*

(Received April 22nd, 1970)

In Part I of this series[1] a new and simple technique for the production of atomic vapours for atomic absorption and fluorescence spectroscopy was described. The apparatus consists basically of a 2-mm diameter carbon (graphite) filament under an atmosphere of argon in an enclosed glass cell. A measured drop of the solution to be analysed is placed on the filament which may be heated up to about 2500° in a very short space of time by the passage of a high current at low voltage. A transient cloud of atoms is produced, on which spectroscopic measurements of atomic absorption or fluorescence may be made.

Further progress with this technique in atomic fluorescence spectroscopy, namely, in the design of a new cell and an improved technique for its operation, are reported in the present paper and results for the determination of a number of metals in pure solution are discussed.

## EXPERIMENTAL

### *Instrumentation*

*Spectrometer and recording system.* A Techtron AA-4 spectrometer, with the burner–nebuliser unit removed, was used. The signal was taken from the galvanometer output socket and was fed directly into a 1706 "Visicorder" u.v. recording oscillograph (Honeywell Controls Ltd.) fitted with a galvanometer, type BB-160A (Honeywell Controls Ltd.). This has a frequency response up to 100 Hz and a sensitivity of 0.08 mV mm$^{-1}$.

*Primary sources.* These were either high-intensity hollow-cathode lamps of the Sullivan and Walsh type (Atomic Spectral Lamps Pty. Ltd.), or were of the electrodeless discharge lamp type. The latter were operated in a three-quarter wave cavity (Electro Medical Supplies Ltd.) and were powered by a "Microtron 200" microwave power generator operating at 2450±25 MHz (Electro Medical Supplies Ltd.). Both types of source were electronically modulated at 285 Hz, as required by the a.c.-amplification system of the Techtron AA-4.

*Optical system.* With the hollow-cathode lamps, only one lens was used. This focussed the fluorescence signal from the atomic vapour within the atom reservoir onto the slit of the monochromator. The lamp was situated as close to the filament as possible. With the electrodeless discharge lamps on the other hand, it was found advantageous to incorporate a second lens to focus the primary radiation from the electrodeless discharge lamp onto the space immediately above the filament within the atom reservoir.

*Instrument settings*. The following instrumental settings were found suitable for the atomic fluorescence work: slit, 300 $\mu$m; damping, D; oscillograph chart speed, 12 mm sec$^{-1}$; scale expansion 5 ×.

The wavelength, filament voltage, argon flow rate, and primary and secondary currents for hollow-cathode lamps, or power and depth of modulation for electrodeless discharge lamps, were optimised for each element.

Other settings, photomultiplier EHT, amplifier gain, backoff current, etc. depended on experimental conditions. Also, the alignment of the lamp and cell with respect to the lenses and monochromator slit had to be continuously checked in order to obtain maximum sensitivity.

### *The carbon-filament cell*

The cell used in this work is illustrated in Fig. 1, and differs from that described previously[1] as follows.

1. The base of the cell is made of brass and is mounted on a cylindrical stem directly into a saddle on the optical bar of the AA-4. The cell top is fixed into position with a metal collar fitting over a flange on the base of the cell top. The collar is screwed directly onto the metal base, and a rubber washer completes the seal. One of the electrodes is isolated from the base by means of a mica collar. This arrangement results in considerable saving of space and gives a much more rigid structure. The height of the filament and its orientation with respect to the primary source and slit are readily adjustable.

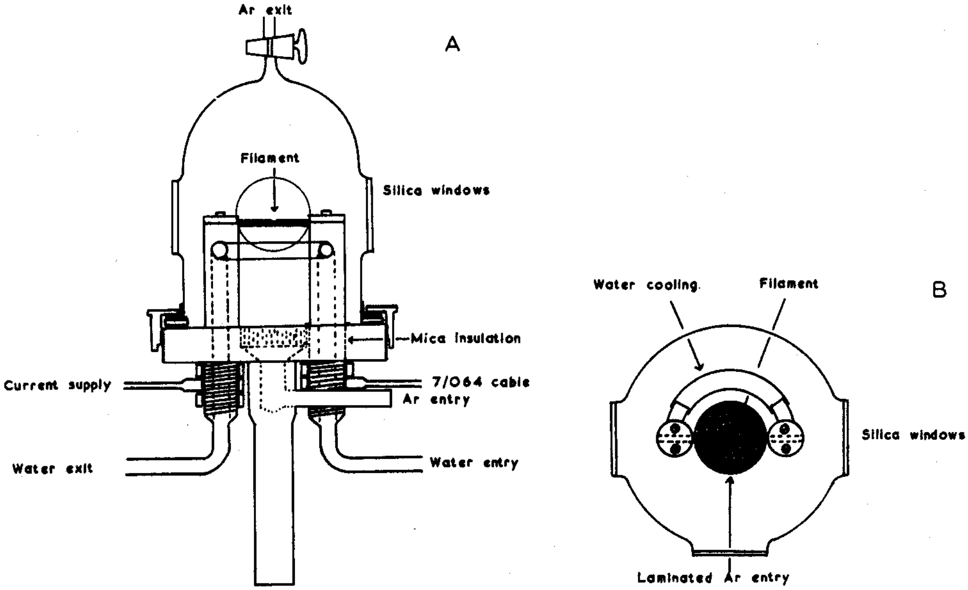


Fig. 1. Carbon-filament atom reservoir. (A) Front view, (B) plan view.

2. An effective means is provided whereby the filament supports may be water-cooled. This obviates the need for allowing long periods between readings until the filament has cooled and provides for more reproducible electrical contact with the filament.

3. The argon flow is led in from the bottom of the cell through a wide laminated opening and is passed out of the top of the cell. The cell windows are mounted directly into the side of the cell and not onto side arms as previously. The one cell top has three silica windows and so serves equally well for absorption or fluorescence measurements.

4. All glass parts of the cell and the sides of the hollow-cathode lamps are blacked out to reduce the amount of stray light reaching the spectrometer slit. Consequently, at all times, the spectrometer photomultiplier can be operated at its maximum EHT.

5. The filament is held in place by two tightly fitting caps which in turn are held in place on top of the electrode supports by four screws. This gives a better and more reproducible electrical contact than the previous clamping method.

6. A small notch is carved into the centre of the rod in order to enable the operator to place the sample in exactly the same position on the rod every time. The filament itself is cut from 2-mm diameter carbon (graphite) rod ("Morganite" electrodes, type WWS from Morgan Crucible Group) and one rod may be used for about 300 determinations.

### *Argon flow system*

This was as previously described[1].

### *Power supply to filament*

Current was supplied to the filament from the mains *via* a 1.2-kW stepdown transformer and Variac control, which permits the voltage across the filament to be continuously varied from 0 to 12 V; the maximum load current has been estimated at 70 A. The maximum temperature attained by the filament was measured with an optical pyrometer and was found to be greater than 2600° at about 10 V. The relationship between applied voltage and filament temperature for a typical graphite filament, is shown in Fig. 2.

### *Preparation of the filament*

When a new filament was mounted in the cell, it was necessary to heat it to 2500° for a few seconds, let it cool and repeat the process several times until no recorder deflection was obtained when the filament was heated without a sample on it.

### *Sampling system*

The Agla syringe used previously[1] was found to be unsatisfactory because of adsorption and desorption of ions on the ground glass parts of the syringe. Therefore, calibrated capillary glass pipettes of 1–5-$\mu$l volume (Drummond Scientific Co., U.S.A.) were used; these were treated with silicone "Repelcote" water repellant (Hopkin and Williams) in order to decrease adsorption and desorption problems further, and to enable the pipette to be emptied more reproducibly. The volume delivered by a 1-$\mu$l pipette has a coefficient of variation of 2%.

*Preparation of solutions*

All solutions were prepared from analytical-grade materials. Water was distilled from a glass still and then further purified by passing through a cation-exchange column in the H+ form. All glassware, after being scrupulously cleaned, was treated with silicone "Repelcote" to minimise adsorption. Stock solutions of 100 p.p.m. were prepared and only diluted immediately before use. The water used to prepare the solutions was continually checked for contamination by the ion under study.

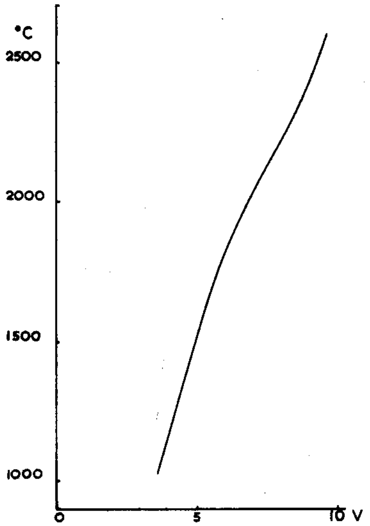


Fig. 2. Filament temperature *vs.* applied voltage.

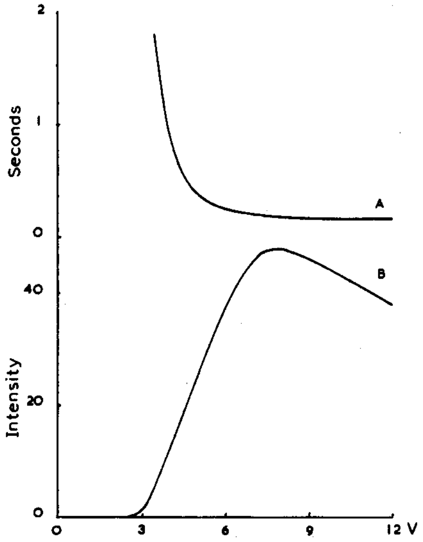


Fig. 3. Fluorescence intensity. (A) Peak width at half height *vs.* filament voltage, (B) fluorescence intensity (arbitrary units) *vs.* filament voltage for 10 ng of lead.

*Procedure*

Check all the instrument settings. Turn on the water supply, argon flow, lamp, EHT, etc. Allow time for the electronics and gas flow to stabilise.

Turn on the filament current and oscillograph chart drive for 3 sec. No deflection in the recorder trace should be observed. Exactly 15 sec after turning on the current, remove the top of the cell and place the 1–5 $\mu$l sample in the hollow in the filament. Replace the top of the cell immediately. After 30 sec turn the filament current on and off as quickly as possible. This will heat the filament to 150–250° and all solvent will be driven from the filament and the cell. Exactly 90 sec after first turning on the current, turn it on again for a definite length of time, typically 2–3 sec, doing likewise with the oscillograph chart drive, and note the deflection on the recorder.

Exactly 105 sec after the filament was first turned on, remove the top of the cell and place the next sample on the filament.

This procedure results in 40 determinations per h. The strict timing schedule was found to be necessary in order to obtain the best reproducibility. If the argon is allowed to flow for less time, both sensitivity and reproducibility are diminished.

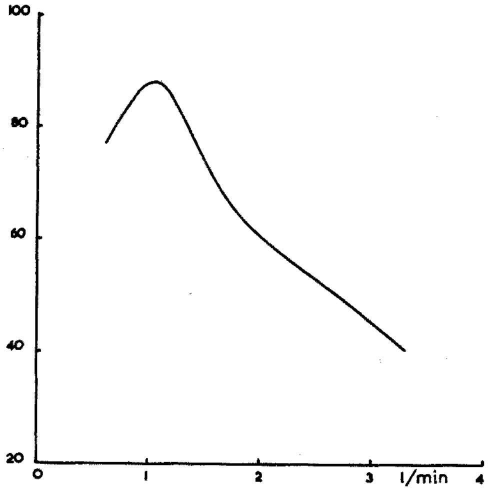
In all the systems studied, it has been found that if, after the sample has been vaporised, the filament current is turned on again, no deflection on the recorder is observed, *i.e.* the filament is self-purging and there are no memory effects. Also, for optimal reproducibility it is best to take the cell through the above routine a few times without applying a sample until the filament and cell acquire an equilibrium ambient temperature under the above timing schedule. If this is not done, the first few readings will tend to be low.

## RESULTS

### *Optimal conditions*

*Primary source.* With the high-intensity hollow-cathode lamps the primary current was always the maximum recommended by the manufacturers. In certain cases, no significant increase in sensitivity was obtained by increasing the secondary current beyond 100 mA. With the electrodeless discharge lamps the power and depth of modulation required to give maximum fluorescence intensity consistent with source stability had to be established separately for each lamp.

*Filament voltage.* A typical plot of fluorescence intensity against filament voltage is shown in Fig. 3, which also shows the relationship between peak width at half height and filament voltage. It should be borne in mind that the temperatures quoted in Fig. 2 are the stable temperatures reached by the filament after about 5 sec whereas in most instances the sample is vapourised after only 1–2 sec, *i.e.* well before the filament has reached its maximum temperature.



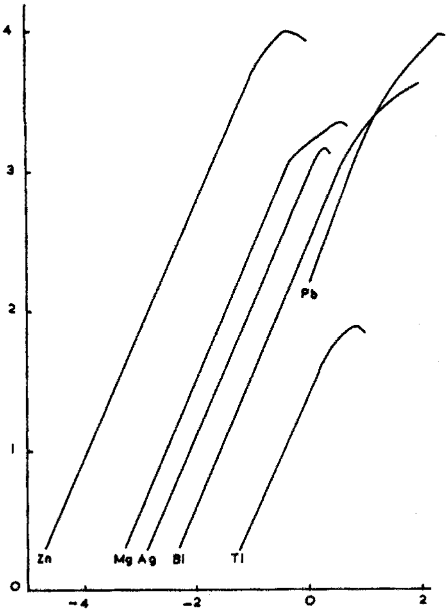


Fig. 4. Fluorescence intensity of 10 ng of lead *vs.* argon flow rate.

Fig. 5. Plot of log fluorescence intensity *vs.* log sample size in ng.

*Argon flow rate.* Figure 4 shows the relationship between fluorescence intensity and argon flow rate. The argon is required to maintain a non-oxidising atmosphere and to sweep the atoms reproducibly through the light path. At high argon flow rates, turbulence sets in, adversely affecting the reproducibility. It is also possible that a high argon flow rate may have an adverse cooling effect on the atomic vapour.

*Wavelength.* Optimal wavelengths for the fluorescence of the metals studied here have all been determined previously for flames. In all cases, the wavelengths were confirmed.

Table I shows the optimal conditions chosen for each element studied.

TABLE I

OPTIMAL CONDITIONS FOR THE ATOMIC FLUORESCENCE SPECTROSCOPY OF ELEMENTS IN THE CARBON FILAMENT ATOM RESERVOIR

| *Element* | *Wavelength (nm)* | *Cathode-lamp current (mA)* | | *Discharge lamp* | | *Filament voltage (V)* | *Argon flow rate (l min$^{-1}$)* |
|---|---|---|---|---|---|---|---|
| | | *Iy* | *IIy* | *Power (W)* | *Modln (%)* | | |
| Mg | 285.21 | 15 | 300 | — | — | 9.0 | 3.3 |
| Ag | 328.07 | 20 | 400 | — | — | 10.8 | 0.6 |
| Pb | 405.78 | 15 | 100 | — | — | 8.4 | 1.1 |
| Zn | 213.86 | — | — | 75 | 50 | 7.2 | 1.7 |
| Bi | 306.77 | — | — | 30 | 40 | 9.0 | 2.5 |
| Tl | 377.57 | — | — | 100 | 80 | 9.0 | 1.7 |
| Ga | 417.21 | — | — | 110 | 35 | 9.0 | 1.7 |

### *Scatter*

No scatter was observed from the filament below about 2600° or from pure water. With each element, 100 ng were placed on the filament and evaporated off whilst using a lamp of another element which had a line of similar wavelength and intensity to that of the analytical line of the element. In no cases for the elements studied were any signals observed, thus showing that these results are due to fluorescence and not scatter.

### *Reproducibility*

Aliquots (1 $\mu$l) of a 10-p.p.m. lead solution were repeatedly analysed under optimised conditions after the cell had been taken several times through the heating cycle described above. Fifteen determinations gave a mean peak height of 69.5 with a coefficient of variation of 1.7%. Since the coefficient of variation associated with delivering a 1-$\mu$l volume from the pipette was found to be 2%, this is probably the major source of error in the determination. Other sources of error, within the control of the operator, that may increase the coefficient of variation to values of 3% or higher include insufficient preheating of the cell (resulting in low, irreproducible results), poor electrical contact between the electrode supports and the filament (a common cause of irreproducibility in the previous work[1]), turbulent argon flow, insufficient time allowed for the argon to flush out the cell, or instabilities in the primary source.

### *Limits of detection and calibration curves*

Table II gives the limits of detection (the amount of the particular element required to give a signal equal to twice the r.m.s. of the noise in the background signal) and the maximum amounts of material, below which the calibration curves are linear enough for analytical purposes. Above these latter figures, the calibration curves rapidly become horizontal with respect to the sample weight or assume a negative slope because of self-absorption phenomena. Since all these figures were obtained on 1-$\mu$l samples, the equivalent concentrations corresponding to the detection limit can be calculated, and are given in column 4. In column 5 are given the reported detection limits in flame media, measured at the same wavelengths and with similar primary sources (except where otherwise stated).

Figure 5 shows calibration curves actually obtained. The limit of detection for magnesium is higher than that previously reported[1], but the present value is considered to be more reliable because of the possibility of cumulative contamination of the solution by the Agla syringe used in the previous work.

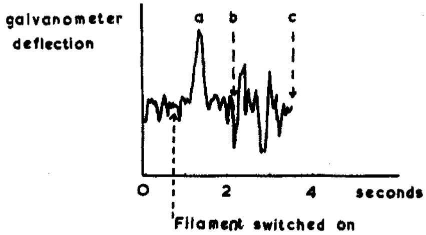


Fig. 6. Fluorescence signal from 0.1 ng of thallium.

TABLE II

LIMITS OF FLUORESCENCE DETECTION, MAXIMUM DETERMINABLE AMOUNTS AND CORRESPONDING CONCENTRATIONS

(Sample volume = 1 $\mu$l)

| *Element* | *Limit of detection (g)* | *Maximum determinable amount (g)* | *Concentration (p.p.m.)* | *Previously reported limit of detection in flames (p.p.m.)* | *Ref. to column 5* |
|---|---|---|---|---|---|
| Mg | $10^{-12}$ | $10^{-9}$ | 0.001 | 0.002 | 2 |
| Ag | $10^{-12}$ | $2 \cdot 10^{-9}$ | 0.001 | 0.002 | 3 |
| Pb | $10^{-11}$ | $1.5 \cdot 10^{-7}$ | 0.01 | 0.5[a] | 4 |
| Zn | $2 \cdot 10^{-14}$ | $4 \cdot 10^{-10}$ | 0.00002 | 0.00004 | 4 |
| Bi | $10^{-11}$ | $10^{-8}$ | 0.01 | 0.7 | 4 |
| Tl | $5 \cdot 10^{-11}$ | $2 \cdot 10^{-9}$ | 0.05 | 0.008 | 4 |
| Ga | $5 \cdot 10^{-11}$ | $10^{-8}$ | 0.05 | 0.1 | 4 |

[a] With electrodeless discharge lamp.

From Table II, it can be seen that with a 1-$\mu$l sample (the smallest volume conveniently handled) slightly lower concentrations of many elements can be determined with the filament atom reservoir. The high detection limit of thallium is probably due to the use of an inefficient discharge lamp. Previous work showed a detection limit of only 0.12 p.p.m. for thallium[5] in a flame with another discharge lamp.

The low detection limit of bismuth demonstrates the inherent advantage of the filament over a flame with regard to the lack of flame emission background. This is particularly strong at 306.8 nm because of the presence of an OH emission band at this wavelength[6].

Since these detection limits were obtained with the smallest sample volume, more dilute solutions can be analysed by increasing the sample volume. The largest volume that can be conveniently placed on the filament is 5 $\mu$l. Furthermore, it is possible to decrease the concentration detection limit by multiple sample application, evaporating the solvent between additions by brief passage of current. For example, by applying five 5-$\mu$l samples, equivalent to a sample volume of 25 $\mu$l, lead was detected in solutions down to a concentration of 0.0004 p.p.m. Accordingly, this technique should prove to be useful for measuring extremely low levels of concentration of elements in, say, water, biological or medical samples. Furthermore, these detection limits may be obtained without serious sacrifice of the advantages of small sample volume discussed previously[1]. Thus, use of the carbon filament enables one not only to work with very small sample volumes (1–25 $\mu$l), but also to obtain concentration detection limits which are often superior to those obtained in atomic fluorescence spectroscopy in flames.

Figure 6 shows a typical fluorescence signal obtained near the detection limit of the particular element. The signal obtained consists of a peak (a) lasting for about 0.3 sec. The noise immediately after the peak is of the same level as that before it, but from b to c the noise increases markedly as the level of unmodulated emission from the rapidly heating filament becomes significant.

The signal duration of 0.3–0.4 sec is typical of all the elements when the filament is operated under optimal conditions as shown in Fig. 3 and Table I. If the filament voltage is lowered, then the peak becomes broader and shallower as more time is required to evaporate the sample. However, increasing the filament voltage beyond the optimal value does not result in sharper peaks. Instead, it retains the same width and merely loses height. The rise time of the AA-4 amplifier under the conditions used was found to be 0.2–0.25 sec, hence at very high filament voltages the sample is probably evaporated too quickly for the amplifier used to follow the fluorescence signal properly.

The carbon filament atom reservoir provides the basis for very sensitive determinations of a number of metals by atomic fluorescence spectroscopy. The effect of various matrices on these determinations will be reported shortly.

Thanks are due to Mr. D. Alger for his assistance with the design and construction of part of the apparatus. We are grateful to Laporte Titanium Ltd. for assistance and support for this programme, and to the S.R.C. for the provision of a CAPS award for I.S.M.

## SUMMARY

The design and operation of an improved carbon-filament atom reservoir is described. The improvements incorporated are: a rigid metal base, a system of water cooling the electrode supports, introduction of a laminar gas flow through the cell, improved electrical contact between the filament and its supports and the use of calibrated micropipettes to apply the sample. Optimum conditions for determination

by atomic fluorescence of a number of metals are described and limits of detection are reported. The latter generally appear to be somewhat better than those obtained by flame methods, but it is the absolute size of the amount determined which is most significant. The coefficient of variation for a single determination with the improved cell is less than 3%.

## REFERENCES

1 T. S. West and X. K. Williams, *Anal. Chim. Acta*, 45 (1969) 27.
2 T. S. West and X. K. Williams, *Anal. Chim. Acta*, 42 (1968) 29.
3 T. S. West and X. K. Williams, *Anal. Chem.*, 40 (1968) 335.
4 K. E. Zacha, M. P. Bratzel, Jr., J. D. Winefordner and J. M. Mansfield, Jr., *Anal. Chem.*, 40 (1968) 1733.
5 R. F. Browner, R. M. Dagnall and T. S. West, *Talanta*, 16 (1969) 75.
6 R. M. Dagnall, K. C. Thompson and T. S. West, *Talanta*, 14 (1967) 1467.

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

# ATOMIC ABSORPTION AND FLUORESCENCE SPECTROSCOPY WITH A CARBON-FILAMENT ATOM RESERVOIR

## PART III. A STUDY OF THE DETERMINATION OF CADMIUM BY ATOMIC FLUORESCENCE SPECTROSCOPY WITH AN UNENCLOSED ATOM RESERVOIR

J. F. ALDER AND T. S. WEST
*Chemistry Department, Imperial College, London, S.W. 7 (England)*

(Received May 6th, 1970)

The first paper in this series[1] described the determination of silver and magnesium by atomic absorption and atomic fluorescence spectroscopy with a carbon(graphite)-filament atom reservoir, whilst the second described considerable improvements to the basic design of the cell and gave fluorescence detection limits for a number of other elements[2]. In this paper, a further modification of the cell which allows it to be used without surrounding glassware, etc. is described and a detailed study of the atomic fluorescence characteristics of cadmium in this cell, with a microwave excited electrodeless discharge lamp as the source of excitation, is reported.

## EXPERIMENTAL

### *Apparatus*

A Unicam SP 900A thermal emission–atomic absorption flame spectrophotometer, which has a quartz prism monochromator of high light gathering power (f 7) and a resolution of 0.4 nm for a 0.1 mm slit at 250 nm, was used. The photodetector was an eleven stage EMI 9601B u.v.-sensitive photomultiplier with a Corning glass window. The output was connected to a Sargent (Type SR) fast response stripchart pen recorder (*ca.* 0.8 sec full scale deflection) used on the 0–10 mV range.

An EMS "Microtron 200" microwave generator attached to a $\frac{3}{4}$-wave cavity (EMS Type 210L cavity) was used to power the cadmium electrodeless discharge lamp which was run at 50 W incident power without cooling. The modified filament atom reservoir cell is shown in Fig. 1. The sheathing gas was led up the central stem through a box packed with layers of plain and corrugated metal strips to produce a laminar flow, and passed around the filament which was thus protected from atmospheric oxidation at high temperatures. The cell was located on a small optical bench attached to the rear of the spectrophotometer frame. A small steel tube, 25 mm long of 4 mm i.d., acting as a light guide, was positioned between the slit of the spectrophotometer and the carbon filament, so as to prevent light from the glowing filament entering the monochromator system. Although this cut down the "field of view" of the monochromator, it also minimised background noise. Attempts to modulate the system at 100 Hz with an electronic modulating system

(EMS Modulator Unit MkII), and hence cut out the background were fruitless, mainly because the glow from the carbon filament had a mains frequency ripple superimposed on it. The power supply to the cell was from the mains via a "Variac" transformer to a transformer capable of delivering up to 100 A at 5–8 V. The filament working temperature was controlled by using the Variac transformer to alter the voltage across the input coils of the second transformer.

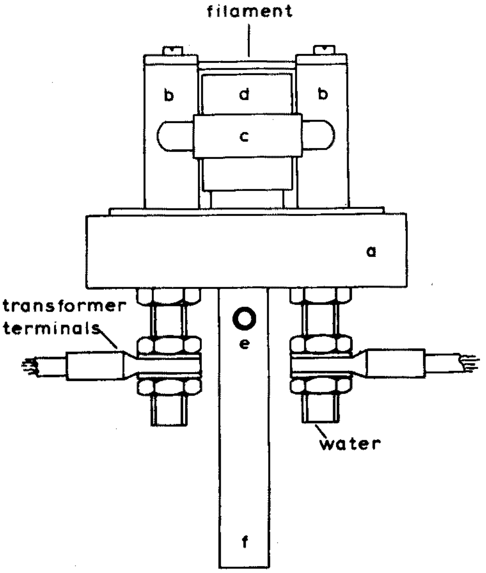


Fig. 1. Filament atom reservoir modified for use in open atmosphere. (a) Base, (b) water-cooled electrodes, (c) water link between electrodes, (d) laminar flow box, (e) inlet for shield gas, (f) support stem for reservoir.

The instrument settings were adjusted to suit the working conditions. The entrance slit-width of the monochromator was usually between 0.05 and 0.2 mm. Readings were always taken with minimum damping and minimum possible amplifier gain usually 2.0 or 3.0. The atom reservoir cell was positioned as close to the monochromator entrance slit as possible and the light from the discharge lamp was focussed on the centre of the filament.

### *Reagents*

All reagents were of analytical-reagent grade and the water was glass-distilled and then deionised. All gases used were of high purity.

The 1-$\mu$l samples were transferred to the filament with a 1-$\mu$l pipette; this and all glassware were treated with "Repelcote" as described previously.

### *Procedure*

The instrumental set-up is shown in Fig. 2. Set the monochromator at the required wavelength, adjust the sheathing gas flow to the required value, switch on the cooling water to the electrodes and then heat the filament to its normal working temperature for about 10 sec to remove any unwanted contamination on its surface.

After the filament has cooled, pipette a 1-µl sample of the test solution on to a small notch in the carbon in the centre of the light spot from the focussed discharge lamp. Heat the filament for about 0.25 sec to drive off the solvent from the sample.

After a few seconds heat the filament for 3 sec to about 1400° (this was previously established by means of a hot-wire optical pyrometer), during which time the metal salt on the filament is atomised and the analytical signal is recorded. The total cycle involving pretreatment, sample addition, etc., takes about 1 min.

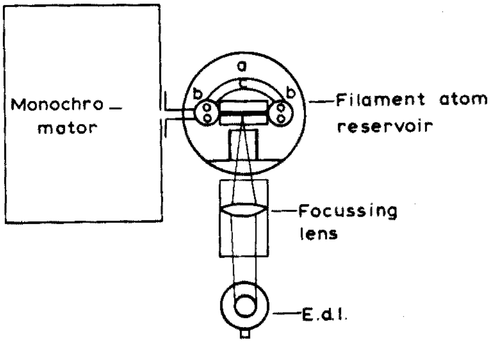


Fig. 2. Atom reservoir and discharge lamp in position for fluorescence measurements. Key as for Fig. 1.

## RESULTS AND DISCUSSION

A comparison was made of the limits of detection for cadmium at the two main resonance lines, 228.8 and 326.1 nm, with nitrogen or argon as the sheathing gas (Table I).

TABLE I

DETECTION LIMIT[a] FOR CADMIUM IN NITROGEN OR ARGON

| | *228.8 nm* | *326.1 nm* |
|---|---|---|
| Nitrogen | Concentration 0.0003 p.p.m.<br>Absolute limit $3 \cdot 10^{-13}$ g | 0.0003 p.p.m.<br>$3 \cdot 10^{-13}$ g |
| Argon | Concentration 0.00015 p.p.m.<br>Absolute limit $1.5 \cdot 10^{-13}$ g | 0.005 p.p.m.<br>$5 \cdot 10^{-12}$ g |

[a] Limit of detection defined as signal to noise ratio = 2.

### *Comparison of sheathing gases*

The intensities of luminescence obtained from 1.0 µl of a 0.01-p.p.m. cadmium solution at 228.8 nm and 326.1 nm, with various sheathing gases are shown in Table II.

In the absorption mode at 228.8 nm the atomic absorption signals were found to be unchanged when different sheathing gases were used. This shows that the effects of the various gases listed in Table II are due to selective quenching of the $5p\ ^1P_1{}^0$ excited state of cadmium(I) and that the surrounding atmosphere has no effect on the rate of production of $5s^2\ ^1S_0$ ground state atoms by the filament itself.

The increase in the emission intensity observed for cadmium at 326.1 nm with nitrogen as sheathing gas can be explained as follows: the diatomic nitrogen is more capable of deactivating the upper energy levels of an excited cadmium atom than a monatomic gas such as argon. If the $5p\ ^1P_1^0$ level (Fig. 3) is deactivated not to the singlet ground state, $5s^2\ ^1S_0$, but to the triplet $5p\ ^3P_1^0$ level, one might expect greater luminescence intensity at 326.1 nm when nitrogen is used as sheathing gas than when argon is used, despite deactivation of this level also by nitrogen[3]. When carbon dioxide was used, the analytical signals both at 228.8 and 326.1 nm were almost completely quenched. Nitrous oxide and hydrogen had similar marked quenching actions at 228.8 nm and they also seemed to quench cadmium(I) directly to the singlet ground state. The fact that the degree of atomic absorption of the 228.8-nm line is un-

TABLE II

EFFECT OF SHEATHING GAS ON FLUORESCENCE INTENSITY

| | *228.8 nm*[b] | *326.1 nm*[b] |
|---|---|---|
| Argon | 100 | 100 |
| Nitrogen | 20 | 1500 |
| $N_2O$ | 11 | 0 |
| $CO_2$ | 9 | 0 |
| $H_2$[a] | 2.5 | — |

[a] With a protective dome in place[2].

[b] The values for the fluorescence signal intensities at the two different wavelengths are not comparable. In both cases the signal obtained with argon as sheathing gas was given an arbitrary value of 100.

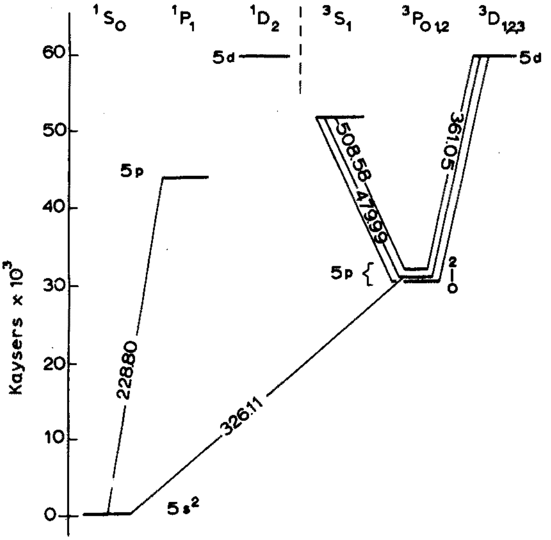


Fig. 3. Partial term diagram for cadmium(I). The nitrogen or, to a much lesser extent argon, causes collisional quenching between the 5*p* singlet and triplet states, so that absorption (excitation) occurs at 228.80 nm and (phosphorescence) emission subsequently at 326.11 nm from the collisionally enriched 5*p* triplet state.

changed supports this theory. The specific nature of the partial quenching of nitrogen gas is of considerable interest.

Absorption at 326.1 nm was not observed because the transition probability to the triplet state is so low (gA for the $5s^2\ {}^1S_0$–$5p\ {}^3P_1^0$, 326.1-nm transition is 0.0090 ($10^8$ sec$^{-1}$) compared to 12 ($10^8$ sec$^{-1}$) for the $5s^2\ {}^1S_0$–$5p\ {}^1P_1^0$, 228.8-nm transition[4]). The lack of absorption at 326.1 nm indicates that the intense luminescence signal obtained in nitrogen at this wavelength must come by stepwise deactivation from the $5p\ {}^1P_1^0$ to the $5p\ {}^3P_1^0$ state followed by radiative transfer back to the $5s^2\ {}^1S_0$ state. To verify this postulate further, an arsenic electrodeless discharge lamp was used to excite the cadmium 228.802-nm line. This lamp has an intense line at 228.812 nm owing to the $4p^3\ {}^2D_{2\frac{1}{2}}^0$–$5s\ {}^2P_{1\frac{1}{2}}$ transition[3], but does not emit at 326.1 nm. The 228.812-nm line has enough spectral overlap with the Cd 228.802-nm line to excite fluorescence of the latter line. With the arsenic lamp as excitation source, luminescence at both 228.8 and 326.1 nm was observed with nitrogen as sheathing gas, but none at 326.1 nm when argon was used. The signal at 326.1 nm was of course much weaker than when a cadmium source was used which may explain why no 326.1-nm emission was observed with argon as sheathing gas. Fluorescence was observed at 228.8 nm with argon as sheathing gas with a relative enhancement similar to that obtained when the Cd 228.80-nm line was used as excitation source. This evidence strongly supports the postulate of "stepwise fluorescence" involving the Cd 228.8-nm and 326.1-nm lines. It does appear in this particular instance that the 326.1-nm emission might more appropriately be called atomic phosphorescence because a triplet/singlet transition is involved following singlet/singlet excitation. We were unable to form an estimate of the life time of the excited state.

### *Calibration curves*

Calibration curves were obtained for cadmium at both 228.8 and 326.1 nm. These are shown in Fig. 4. Although the calibration curves are non-linear over a wide range, they are linear over short ranges at low concentrations, *e.g.* $1 \cdot 10^{-12}$–$1 \cdot 10^{-11}$ g of cadmium. The shape of the fluorescence curves at 228.8 nm is not altered when argon is used instead of nitrogen.

### *Optimum sheathing gas flow rates*

Curves showing the variation of the analytical fluorescence signal from $1 \cdot 10^{-11}$ g of cadmium with sheathing gas flow rate are given in Fig. 5. The curve maxima at 228.8 nm are both at about 2 l min$^{-1}$ for argon and nitrogen, whereas at 326.1 nm they are at about 3.8 l min$^{-1}$. An important point is the rather more extreme effect of the nitrogen flow rate on the luminescence at 326.1 nm. This would be expected, considering the important role that the nitrogen plays in populating the $5p\ {}^3P_1^0$ level. Indeed, this relationship is further evidence to support the theory of stepwise energy transfer.

### *Interference studies*

Interference studies were carried out with a 1000-fold amount of the test element on 0.01 p.p.m. Cd at 228.8 nm with nitrogen as the sheathing gas (Table III).

The interferences were not quantitatively reproducible from day to day, although the reproducibility of the signal obtained from any single solution was within ±7% of the mean at a 95% confidence level. On ten replicate runs of a pure

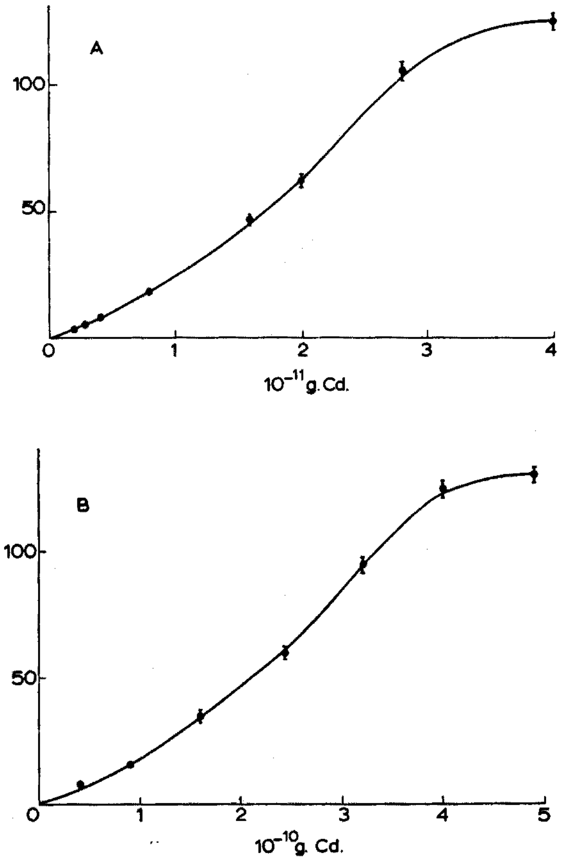


Fig. 4. Analytical calibration curves. (a) Resonance fluorescence at 228.8 nm, (b) stepwise fluorescence (phosphorescence) at 326.1 nm.

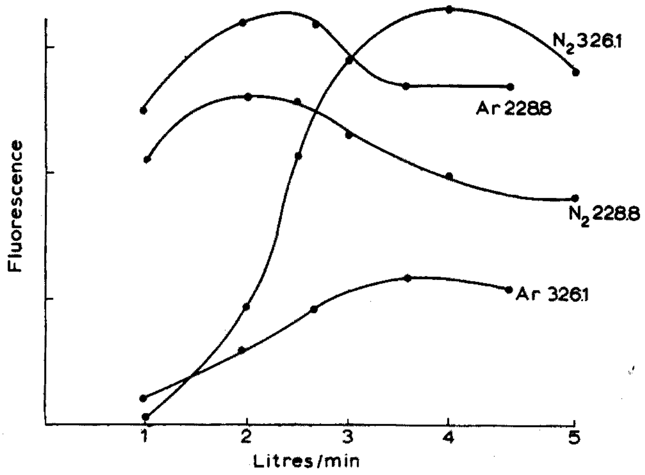


Fig. 5. Effect of flow rate and nature of shield gas on fluorescence response.

TABLE III

INTERFERENCES IN THE DETERMINATION OF CADMIUM AT 228.8 nm WITH A SLOW RESPONSE AMPLIFICATION SYSTEM

| *Element* | *% Change of fluorescence signal* | *Element* | *% Change of fluorescence signal* |
|---|---|---|---|
| Al | −10 | K | +30 |
| Au | −50 | Mg | +30 |
| As | −40 | Na | −10 |
| Bi | −40 | Ni | 0 |
| Ca | 0 | Pb | −10 |
| Cr | 0 | Sb | 0 |
| Cu | 0 | Sn | −30 |
| Ga | −30 | Tl | 0 |
| Hg | −30 | V | 0 |
| In | −50 | Zn | −30 |

cadmium solution the adjusted standard error[5] was within ±2.5% of the mean at a 95% confidence level.

The nature of these interferences and their non-reproducibility is of considerable interest. It will be observed that elements such as aluminium and vanadium which would be expected to produce quite prominent matrix effects in flame media have relatively little effect in the filament atom reservoir, but that others, *e.g.* sodium and potassium, have quite pronounced effects. This can almost certainly be ascribed, together with non-reproducibility of interference, to: (*a*) the cold atmosphere above the filament which will lead to rapid condensation of free atoms, *cf.* flame media; (*b*) the transient nature of the signal; and (*c*) the slow response of the amplifier/recorder used in this study. The presence of a cloud of rapidly condensing atoms of another (indifferent) species in the neighbourhood of the filament would tend to lead to more rapid than normal condensation of the cadmium atoms. Since the response of the amplifier/recorder is slow, it is not surprising that interference should be prominent and that it should be more so with those elements that evaporate most rapidly from the surface of the filament than from those which do not evaporate so quickly. This suggests that interferences should be less prominent with the use of rapid response measurements.

This study also shows how quenching effects may be studied more unequivocally in atomic fluorescence with a filament than they can in a flame where a mixture of deactivating species is always involved, making interpretation more difficult.

We are grateful to the B.P. Co. Ltd. for the award of a research grant to J.F.A., to I.C.I. Ltd., for a grant for the purchase of the SP 900 A spectrophotometer and to the Courtauld Foundation for further financial assistance. We would also like to thank Mr. D. ALGER of this Department for his help in the design of the cell.

## SUMMARY

A modified filament atom reservoir cell is described which permits atomic fluorescence measurements to be made without surrounding the electrically heated graphite element with a glass dome. The fluorescence behaviour of cadmium in this atom reservoir is described. At 228.8 nm, cadmium exhibits resonance fluorescence more strongly in argon than in nitrogen, but at 326.1 nm cadmium exhibits much stronger "stepwise fluorescence" in nitrogen than in argon. Nitrous oxide, carbon dioxide and hydrogen atmospheres show very strong quenching action at 228.8 nm and no luminescence is shown at 326.1 nm. Various interference effects and their elimination are discussed. The detection limits for cadmium are $1.5 \cdot 10^{-13}$ g (0.00015 p.p.m.) at 228.8 nm in argon and $3 \cdot 10^{-13}$ g (0.0003 p.p.m.) in nitrogen.

## RÉSUMÉ

On décrit un nouveau modèle de réservoir atomique à filament pour des mesures de fluorescence atomique. On examine le cas du cadmium; sa fluorescence de résonance à 228.8 nm est plus intense dans l'argon que dans l'azote. Cependant à 326.1 nm le cadmium présente une fluorescence plus forte dans l'azote que dans l'argon. On examine les diverses possibilités d'interférences. Les limites de détection du cadmium sont à 228.8 nm de $1.5 \cdot 10^{-13}$ g (0.00015 p.p.m.) dans l'argon et de $3 \cdot 10^{-13}$ g (0.0003 p.p.m.) dans l'azote.

## ZUSAMMENFASSUNG

Es wird eine modifizierte Glühfadenkammer als Atomreservoir beschrieben, die Atomfluoreszenzmessungen ohne Glaskuppel ermöglicht, die sonst den elektrisch geheizten Graphit umgibt. Das Fluoreszenzverhalten von Cadmium in dieser Atomisierungskammer wird beschrieben. Bei 228.8 nm ergibt Cadmium eine stärkere Resonanzfluoreszenz in Argon als in Stickstoff; jedoch ist die "stufenweise Fluoreszenz" des Cadmiums bei 326.1 nm viel stärker in Stickstoff als in Argon. Distickstoffoxid-, Kohlendioxid- und Wasserstoff-Atmosphären zeigen eine sehr starke Löschwirkung bei 228.8 nm; bei 326.1 nm tritt keine Lumineszenz auf. Verschiedene Störeffekte und deren Eliminierung werden diskutiert. Die Nachweisgrenzen für Cadmium sind $1.5 \cdot 10^{-13}$ g (0.00015 p.p.m.) bei 228.8 nm in Argon und $3 \cdot 10^{-13}$ g (0.0003 p.p.m.) in Stickstoff.

## REFERENCES

1 T. S. West and X. K. Williams, *Anal. Chim. Acta*, 45 (1969) 27.
2 R. G. Anderson, I. S. Maines and T. S. West, *Anal. Chim. Acta*, in press.
3 R. Mavrodineanu and H. Boiteux, *Flame Spectroscopy*, John Wiley, New York, 1965.
4 *Experimental Transition Probabilities*, N.B.S. Monograph 53, Washington, D.C., 1962, p. 19.
5 N. C. Barford, *Experimental Measurements, Precision, Error and Truth*, Addison-Wesley, London, 1967.

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

# MULTI-ELEMENT ATOMIC FLUORESCENCE SPECTROSCOPY

## PART II. A DUAL-ELEMENT ARSENIC-ANTIMONY ELECTRODELESS DISCHARGE TUBE SPECTRAL LINE SOURCE FOR ATOMIC FLUORESCENCE AND ATOMIC ABSORPTION SPECTROSCOPY

A. FULTON, K. C. THOMPSON AND T. S. WEST
*Chemistry Department, Imperial College of Science and Technology, London, S.W. 7 (England)*

(Received March 1st, 1970)

The feasibility of using dual-element microwave-excited electrodeless discharge tubes as excitation sources in atomic fluorescence spectroscopy has been established by MARSHALL AND WEST[1], who concluded that the source resonance line intensities in the multi-element tubes examined, *viz.* Se–Te–Hg, Cd–Zn and In–Ga, were of the same order of magnitude as those in the single-element sources. In this paper, the preparation and operation of dual-element arsenic and antimony sources are described and their use is reported for both atomic absorption and atomic fluorescence spectroscopy. The sensitivities and detection limits are compared with those obtained with single-element sources, and potential interferences are also examined.

## EXPERIMENTAL

### *Instruments*

An A1740 Southern Analytical Grating Flame Photometer coupled to a Honeywell-Brown Recorder was used. A Techtron AA4 Atomic Absorption Spectrophotometer was employed for some experiments. Unless otherwise stated, an air–acetylene flame was used and was adjusted to give maximum sensitivity for each element. The electrodeless discharge tubes were operated with a "Microtron 200" microwave generator (2450±25 MHz) and a three-quarter wave resonant cavity (Electro-Medical Supplies, Wantage, U.K., Model 210L). The discharge was initiated with a high-frequency "Tesla" vacuum tester.

### *Preparation of electrodeless discharge tubes*

The single-element arsenic and antimony sources were prepared as described previously[2,3]; the silica tubes (45–50 mm in length) contained a mixture of *ca.* 4 mg of arsenic and 15 mg of iodine or *ca.* 4 mg of antimony and 12 mg of iodine respectively. Argon was used as filler gas at a pressure of *ca.* 3 Torr.

The dual-element sources were prepared by the following method. A silica tube (45–50 mm in length) was degassed under vacuum at red heat for about 5 min during which time argon was periodically flushed through the system to remove impurities. The bulb was cooled under vacuum to room temperature and removed from the vacuum line, and *ca.* 4 mg of antimony were introduced. The bulb was reconnected to the vacuum line, evacuated and flushed with argon. A length of moist asbestos cord was secured around the middle of the bulb to keep this portion of the tube cold, and the antimony in the bottom of the bulb was gently heated with a microburner until it sublimed 10–20 mm up the walls of the bulb; this procedure removed occluded gases or moisture in the antimony. The bulb was then cooled to room temperature under vacuum and removed from the vacuum system, and *ca.* 4 mg of arsenic were introduced. The above procedure was repeated and then *ca.* 27 mg of iodine were added. The bulb was again connected to the vacuum system, evacuated, flushed with argon and pumped down to a pressure of *ca.* 0.1 Torr. After 5 min, to allow moisture present in the iodine to volatilise, argon was introduced at a pressure of *ca.* 3 Torr and the bube was finally sealed. The tube was then heated strongly in a Bunsen flame to cause iodide formation, and then, after cooling, it was conditioned in the microwave cavity at a fairly high power for *ca.* 1 h.

## RESULTS AND DISCUSSION

### *Source stability*

In general, an electrodeless discharge tube prepared in the laboratory has more

TABLE I

STABILITY OF ELECTRODELESS DISCHARGE TUBES[a]

(The drift was measured over 60 min unless otherwise mentioned)

| *Source* | *Microwave power (W)* | *Drift (%)* | | *Source* | *Microwave power (W)* | *Drift (%)* | |
|---|---|---|---|---|---|---|---|
| | | *Short term*[b] | *Long term*[c] | | | *Short term*[b] | *Long term*[c] |
| *Wavelength of measurement: 193.7 nm* | | | | *Wavelength of measurement: 217.6 nm* | | | |
| As (1) | 45 | 1.9 | 7.5 | Sb (1) | 35 | 1.2 | 1.1 |
| | 45 | 2.4 | 0.0 | | 35 | 2.4 | 1.8 |
| | 45 | 3.8 | 4.4 | Sb (2) | 40 | 3.5 | 2.8 |
| | 45 | 3.1 | 2.5 | | 40 | 2.5 | 8.1 |
| | 45 | 2.5 | 0.0[d] | As + Sb (1) | 40 | 2.5 | 1.3 |
| | 35 | 1.9 | 0.0 | | 40 | 2.7 | 19.3 |
| | 35 | 3.1 | 1.3 | | 40 | 2.5 | 0.0 |
| | 35 | 1.7 | 6.1 | | 35 | 4.3 | 3.7 |
| | 35 | 3.1 | 3.1 | | 35 | 2.5 | 10.6 |
| As (2) | 45 | 2.5 | 0.0 | | 35 | 2.7 | 0.0 |
| | 45 | 3.0 | 0.6[e] | As + Sb (2) | 45 | 2.5 | 0.0 |
| | 35 | 2.2 | 3.7 | | 45 | 2.5 | 0.0 |
| | 35 | 2.2 | 3.6 | | 34 | 2.6 | 8.7 |
| | 35 | 2.7 | 10.0 | | 35 | 2.5 | 5.6 |
| | 35 | 3.8 | 0.6 | | | | |
| As + Sb (1) | 55 | 2.5 | 8.8[f] | | | | |
| | 55 | 3.7 | 4.4 | | | | |
| | 35 | 2.5 | 1.2 | | | | |
| | 35 | 4.1 | 0.0[f] | | | | |
| As + Sb (2) | 45 | 1.9 | 11.2 | | | | |
| | 45 | 2.1 | 7.6[g] | | | | |
| | 34 | 2.9 | 1.2 | | | | |
| | 35 | 2.7 | 2.0 | | | | |

[a] With an A1740 Southern Analytical Flame Photometer; all sources give emission signals of similar magnitude at a given gain setting. The numbers in column 1 refer to different tubes.
[b] Maximum percentage variation in intensity per minute of operation.
[c] Percentage change in intensity over the total time of measurement.
[d] 48 min. [e] 36 min. [f] 58 min. [g] 32 min.

operating parameters (operating power, source position in cavity, rate of cooling, etc.) than a commercial hollow-cathode lamp and so its stability is more difficult to reproduce. The method of preparation is a further variable factor which must also be considered.

Several sources were prepared containing arsenic, or antimony or a combination of both, and all were operated for *ca.* 1 h at various microwave powers with sufficient air-cooling to give maximum stability. The emission at the major resonance lines was recorded and monochromator drift was corrected by optimising the wavelength setting to maximum signal at the end of the stability run. Table I summarises the results obtained for the various sources examined. It is worth noting that stability does not seem to depend on the power applied, and that the dual-element sources appear to be as stable as the single-element sources.

### *Determination of arsenic and antimony*

A Techtron AA4 Absorption Spectrophotometer was used for both atomic

TABLE II

COMPARISON OF ATOMIC ABSORPTION SENSITIVITIES FOR ARSENIC AND ANTIMONY WITH SINGLE-ELEMENT TUBES AND THE DUAL As–Sb SOURCE[a]

| *Source* | *Element* | *Wavelength of measurement (nm)* | *Microwave power (W)* | *A.a.s. sensitivity (p.p.m. for 0.0044 absorbance)* |
|---|---|---|---|---|
| As | As | 193.7 | 30 | 4.5 |
| As + Sb | As | 193.7 | 30 | 4.5 |
| Sb | Sb | 217.6 | 40 | 1.0 |
| As + Sb | Sb | 217.6 | 40 | 1.2 |

[a] Measurements made on AA4 Spectrophotometer.

TABLE III

ATOMIC FLUORESCENCE LIMITS OF DETECTION FOR ARSENIC AND ANTIMONY WITH SINGLE-ELEMENT TUBES AND THE DUAL As–Sb SOURCE[a]

| *Source*[b] | *Microwave power (W)* | *Limit of detection*[c] *(p.p.m.)* |
|---|---|---|
| *Determination of arsenic at 235.0 nm* | | |
| As | 32 | 25 |
| As | 32 | 30 |
| As + Sb | 45 | 25 |
| As + Sb | 45 | 30 |
| *Determination of antimony at 217.6 nm* | | |
| Sb | 35 | 0.4 |
| Sb | 35 | 0.4 |
| Sb | 35 | 0.2 |
| Sb | 35 | 0.2 |
| As + Sb | 40 | 0.9 |
| As + Sb | 40 | 1.0 |
| Sb | 35 | 0.5 |
| Sb | 35 | 1.3[d] |
| As + Sb | 40 | 1.0[d] |
| As + Sb | 40 | 1.2[d] |

[a] Measurements made on AA4 Spectrophotometer with ×5 scale expansion.
[b] Each entry in this column is for a different preparation of source tube.
[c] Signal-to-noise ratio = 1.
[d] No scale expansion was used in these measurements.

absorption and fluorescence measurements[4]. A mechanical chopper was interposed between the flame and source for the atomic absorption studies, but electronically modulated sources[5] were used for the atomic fluorescence measurements because it is most beneficial for the source, flame and monochromator entrance slit to be in close proximity.

Table II shows the atomic absorption sensitivities for arsenic and antimony which are similar for both the single-element and dual-element sources. Figures 1 and 2 show the atomic absorption and fluorescence analytical working curves for antimony. Table III shows the atomic fluorescence limits of detection with both types

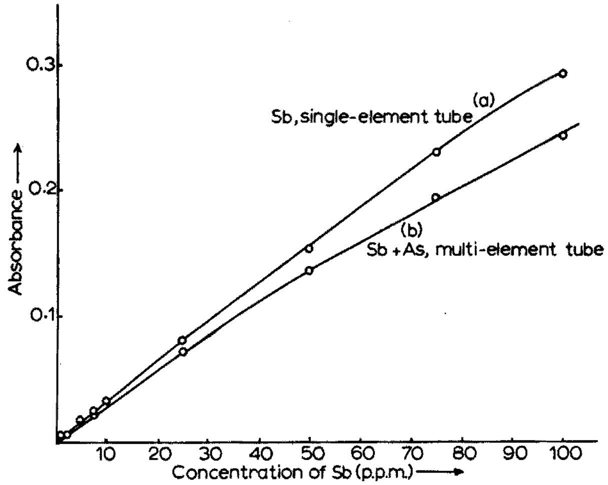


Fig. 1. Atomic absorption concentration curves for antimony at 217.6 nm. (a) Antimony (iodide) microwave-excited electrodeless discharge tube; (b) antimony/arsenic (iodide) dual-element microwave-excited electrodeless discharge tube.

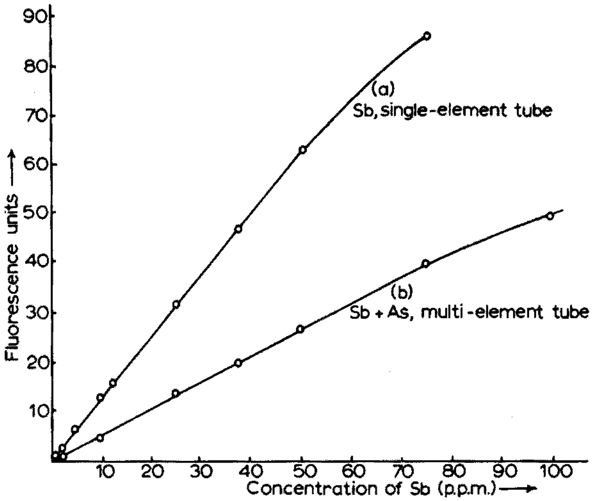


Fig. 2. Atomic fluorescence concentration curves for antimony at 217.6 nm. (a) Antimony (iodide) microwave-excited electrodeless discharge tube; (b) antimony/arsenic (iodide) dual-element microwave-excited electrodeless discharge tube.

of source. A lower limit of detection was obtained with the single-element sources, presumably because the power applied is shared in the dual-element sources. The poor limit of detection obtained for arsenic may be explained by the difficulty of achieving close proximity of source, flame and monochromator entrance slit because of the bulky nature of the AA4 nebuliser unit. In this instance the exciting radiation at 193.7 nm is subject to considerable absorption by the atmosphere; the use of lenses is equally undesirable in the far ultraviolet region. The A1740 Southern Analytical instrument could not be used because the grating was blazed at 500 nm.

### *Determination of other elements by atomic fluorescence and atomic absorption with the As–Sb source*

The As–Sb electrodeless discharge tube thus prepared emits atomic lines for

TABLE IV

ATOMIC FLUORESCENCE LIMITS OF DETECTION FOR BISMUTH AND CADMIUM WITH THE As–Sb AND INDIVIDUAL-ELEMENT SOURCES

| *Source*[a] | *Microwave power (W)* | *Limit of detection*[b] *(p.p.m.)* |
|---|---|---|
| *Determination of bismuth at 302.5 nm with AA4 Spectrophotometer* | | |
| As + Sb | 40 | 6 |
| As + Sb | 40 | 2.5 |
| As + Sb | 40 | 2.5 |
| Bi | 30 | 9 |
| Bi | 35 | 1.6[c] |
| *Determination of cadmium at 228.8 nm with A1740 Spectrophotometer* | | |
| As + Sb | 45 | 10.0[d] |
| Cd | 150 | 0.0017[d] |

[a] Each entry in this column is for a different preparation of source tube.
[b] Signal-to-noise ratio = 1.
[c] Measured at 306.8 nm.
[d] Detection limit taken as twice standard deviation because of use of integration (20 sec).

TABLE V

ATOMIC ABSORPTION SENSITIVITIES FOR BISMUTH AND CADMIUM WITH THE As–Sb AND INDIVIDUAL-ELEMENT SOURCES

| *Source* | *Wavelength of measurement (nm)* | *Microwave power (W)* | *A.a.s. sensitivity (p.p.m. for 0.0044 absorbance)* |
|---|---|---|---|
| *Determination of bismuth* | | | |
| As + Sb | 206.2[a] | 35 | 50 |
| Bi | 206.2[a] | 35 | 40 |
| Bi | 223.1[a] | 35 | 4.0 |
| Bi | 223.1[b] | 35 | 1.0 |
| *Determination of cadmium* | | | |
| As + Sb | 228.8[a] | 30 | 45 |
| Cd | 228.8[a] | 150 | 0.3 |

[a] A1740 Spectrophotometer set on profile without use of integration.
[b] AA4 Spectrophotometer.

the iodine used in preparing the volatile halide in the tube. The spectral overlap of the iodine non-resonance line at 206.163 nm and the bismuth line at 206.170 has already been used to excite direct-line atomic fluorescence of bismuth at 302.5 nm[6]; MARSHALL AND WEST[1] in describing the operation of the Se–Te–Hg tube also applied it to the determination of bismuth. The same phenomenon was found with the arsenic–antimony tube in this study.

Another interesting possibility arose from the near coincidence of the arsenic line at 228.812 nm and the cadmium line at 228.802 nm. It was, therefore, decided also to examine the possibilities of measuring the atomic absorption of cadmium.

The limits of detection obtained by atomic fluorescence spectroscopy (Table IV) and by atomic absorption spectroscopy (Table V) were established for both a single bismuth or cadmium discharge tube and the dual-element As–Sb source. These results show that the sensitivity obtainable by spectral overlap excitation for iodine–bismuth and arsenic–cadmium with the As–Sb source is quite good in fluorescence work where the necessity for spectral overlap within the half intensity width of the line is not so critical as in absorption measurements. Not unexpectedly, the sensitivities are not so good for absorption. Thus the use of spectral overlap absorption spectroscopy is of academic rather than of practical value when conventional equipment is used, though for fluorescence of bismuth, at least, atomic fluorescence with the iodine–bismuth spectral overlap excitation is a practical proposition.

### *Interferences*

No interference (*i.e.*, less than ±5% deviation in signal) in the atomic fluorescence determination of antimony (25 p.p.m.) at 217.6 nm was observed for *ca.* 100-fold molar excesses of $Co^{2+}$, $Cu^{2+}$, $Fe^{3+}$, $Pb^{2+}$, $As^{3+}$, $Cd^{2+}$, $Bi^{3+}$, and $Se^{3+}$. These elements were selected principally because of the proximity of their resonance line to those of the elements being determined. A similar study was made for arsenic (1000 p.p.m.) at 235.0 nm although in this instance only an equimolar excess of the extraneous ions was investigated because of the poor limit of detection obtained for arsenic; again no interference was observed. Solutions were also prepared containing mixtures of extraneous ions, *viz.* $As^{3+}$ and $Cd^{2+}$, $As^{3+}$ and $Bi^{3+}$, and $Cd^{2+}$ and $Bi^{3+}$ for the determination of antimony, and $Bi^{3+}$ and $Sb^{3+}$, $Bi^{3+}$ and $Cd^{2+}$ and $Sb^{3+}$ and $Cd^{2+}$ for the determination of arsenic. As before, no interference was observed.

The fact that no spectral interference was observed when the dual-element tube was used to excite fluorescence of arsenic or antimony indicates that such multi-element electrodeless discharge tubes have very considerable potentialities for atomic fluorescence spectroscopy both from economic and practical viewpoints. Such multi-element sources appear to offer some of the flexibility of determination, which is characteristic of flame photometry, to the newer techniques of atomic absorption and atomic fluorescence spectroscopy, whilst still providing the inherent near-specificity of these latter two methods of analysis.

We thank the Royal Commission for the Exhibition of 1851 for the award of a scholarship and the South African Council for Scientific and Industrial Research for the award of a supplementary grant to one of us (A.F.) and Southern Instruments Ltd. for the loan of the spectrophotometer used in this study. Thanks are also due to Dr. R. M. DAGNALL for useful discussion during the progress of this work.

## SUMMARY

The preparation and operation of a dual-element arsenic–antimony microwave-excited electrodeless discharge tube is described; it can be applied to atomic fluorescence and atomic absorption spectroscopy. The dual source is as stable as the corresponding single-element sources, and the sensitivities in atomic absorption and detection limits in fluorescence are similar to those obtained for individual electrodeless discharge tubes. Interference studies with a selected number of other ions show that there is no extra interference introduced by use of the multi-element source. In addition, bismuth can be determined by direct-line fluorescence at 302.5 nm by spectral-overlap excitation from the 206.163-nm iodine line which is emitted by the As–Sb–I source. Arsenic–cadmium spectral-overlap excitation also permits the fluorimetric or absorptiometric determination of cadmium at 228.802 nm by means of the 228.81-nm arsenic line from the dual-element source; in this case the sensitivities obtained by both techniques are much inferior to those obtained with a cadmium electrodeless discharge tube.

## RÉSUMÉ

On examine les possibilités de la préparation et d'utilisation de tube à décharge, sans électrode, arsenic–antimoine, pour la fluorescence atomique et la spectroscopie par absorption atomique. La stabilité et les sensibilités, de même que les limites de détection en fluorescence, sont les mèmes que pour les tubes à un élément. Le bismuth peut être dosé par fluorescence à 302.5 nm, en utilisant la raie de l'iode 206.163 nm émise par la source As–Sb–I. L'excitation spectrale arsenic–cadmium permet également le dosage du cadmium à 228.802 nm, au moyen de la raie de l'arsenic à 228.81 nm, à partir de la source à deux éléments; dans ce cas les sensibilités des deux techniques sont considérablement inférieures à celles obtenues avec un tube à cadmium.

## ZUSAMMENFASSUNG

Es werden Herstellung und Anwendung einer mikrowellenerregten elektrodenlosen Zweielement-Entladungsröhre für Arsen und Antimon beschrieben. Sie kann für Atomfluoreszenz und Atomabsorption verwendet werden. Die Zweielementlampe ist ebenso stabil wie die entsprechenden Einzelelementlampen. Die Empfindlichkeiten bei Atomabsorption und Nachweisgrenzen bei Atomfluoreszenz sind ähnlich wie bei den individuellen elektrodenlosen Entladungsröhren. Versuche mit einer ausgewählten Anzahl anderer Ionen zeigen, dass durch die Verwendung der Multielementlampe keine zusätzliche Störung hervorgerufen wird. Ausserdem kann Wismut durch Fluoreszenz bei 302.5 nm auf Grund einer Anregung durch spektrale Überlappung der Jodlinie 206.163 nm bestimmt werden, die von der As–Sb–J-Lampe emittiert wird. Die spektrale Überlappung bei Arsen–Cadmium erlaubt auch die fluorimetrische oder absorptiometrische Bestimmung von Cadmium bei 228.802 nm mit Hilfe der Arsenlinie 228.81 nm aus der Zweielementlampe; in diesem Fall sind die mit beiden Verfahren erhaltenen Empfindlichkeiten schlechter als die bei einer elektrodenlosen Cadmiumentladungsröhre erhaltenen Empfindlichkeiten.

## REFERENCES

1 G. B. Marshall and T. S. West, *Anal. Chim. Acta*, in press.
2 R. M. Dagnall, K. C. Thompson and T. S. West, *Talanta*, 15 (1968) 667.
3 R. M. Dagnall, K. C. Thompson and T. S. West, *Talanta*, 14 (1967) 1151.
4 T. S. West and X. K. Williams, *Anal. Chem.*, 40 (1967) 335.
5 R. F. Browner, R. M. Dagnall and T. S. West, *Anal. Chim. Acta*, 45 (1969) 163.
6 R. M. Dagnall, K. C. Thompson and T. S. West, *Talanta*, 14 (1967) 1467.

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

# INTERFERENCES OF ACIDS IN ATOMIC ABSORPTION SPECTROPHOTOMETRY

TOSHIHISA MARUTA, MASAMI SUZUKI AND TSUGIO TAKEUCHI
*Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya (Japan)*

(Received March 3rd, 1970)

Many papers have described the interferences of acids in atomic absorption spectrophotometry. RAMAKRISHNA *et al.*[1] reported the depressing effect of hydrochloric, sulfuric and perchloric acids on copper in oxy–hydrogen flames. ŠTUPAR[2] described the serious effect of nitric acid on copper and of nitric and perchloric acids on iron by a long absorption-cell technique, and concluded that the effect of oxidizing acids on copper and iron resulted from a greatly increased rate of oxide formation. IIDA AND FUWA[3] pointed out the enhancing effect of perchloric acid on chromium. However, the mechanism of acid interferences has not been fully elucidated. In this work the interferences of various acids were compared in an attempt to elucidate the mechanism of acid interferences for copper, iron and chromium.

## EXPERIMENTAL

### *Apparatus*

A Nippon Jarrell-Ash AA-1E atomic absorption spectrophotometer was used with Hitachi burner–atomizer systems. The light sources were hollow-cathode lamps from Westinghouse Electric Corp. for copper, Hitachi Ltd. for iron, and Hamamatsu TV Co., Ltd., for chromium.

The light beam through the air–acetylene flame was controlled by an aperture for measuring absorbance in a small region of the flame. Nitrous oxide–acetylene flames were also used for comparison.

### *Reagents*

*Copper solution, 1000 μg ml$^{-1}$.* Dissolve 0.250 g of copper metal in hydrochloric and nitric acids, boil to remove all oxides of nitrogen, add enough hydrochloric acid to make the final acidity about 0.1 *M*, and dilute to 250 ml. Prepare weaker solutions by dilution with water just before use.

*Iron solution, 1000 μg ml$^{-1}$.* Dissolve 0.250 g of electrolytic iron in hydrochloric and nitric acids, boil to remove all oxides of nitrogen, add enough hydrochloric acid to make the final acidity about 0.1 *M* and dilute to 250 ml. Prepare weaker solutions just before use.

*Chromium solution, 1000 μg ml$^{-1}$.* Dissolve 0.707 g of potassium dichromate in water and dilute to 250 ml. Prepare weaker solutions by heating a suitable aliquot of stock solution with hydrochloric acid to reduce chromium, followed by dilution.

All acids were of analytical grade.

*Procedure*

The solution (10 $\mu$g ml$^{-1}$) of copper, iron or chromium containing hydrochloric, perchloric, nitric or phosphoric acid was prepared to give an acidity of 0.1 *M*. Each solution was also 0.01 *M* in hydrochloric acid. These solutions were sprayed into the flame and the absorbances of the metals were measured in various flame conditions and in various regions of the flame.

## RESULTS AND DISCUSSION

*Hydrochloric acid*

The interferences of hydrochloric acid on copper, iron and chromium absorbances are shown in Fig. 1. This acid had a depressing effect on copper absorbance irrespective of flame conditions and beam heights. The depressing effect may be attributed to the incomplete dissociation of CuCl molecules in the flame. The appearance of CuCl bands at 4281, 4333 and 4354 Å confirmed this mechanism of interference. Sodium chloride solution (0.1 *M*) had little effect on copper absorbance, hence it is assumed that the free acid is responsible for the depressing effect. Moreover, little effect was observed when a copper solution 0.1 *M* in hydrochloric acid was made ammoniacal before spraying. No interference from chloride was observed in the nitrous oxide–acetylene flame although the size of the copper absorbance was small.

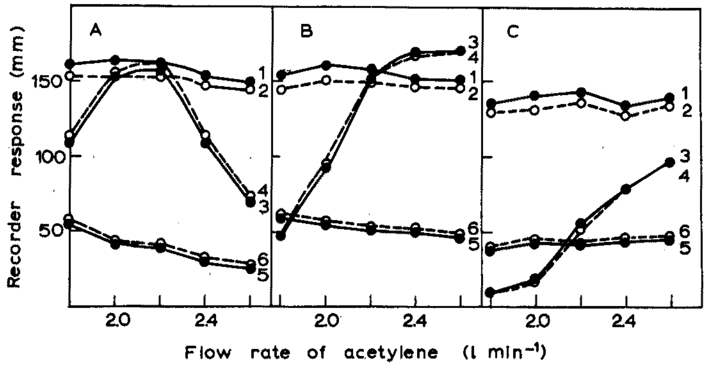


Fig. 1. Interferences of hydrochloric acid on copper, iron and chromium absorbances: (A) 6 mm above burner tip, (B) 10 mm above burner tip, (C) 18 mm above burner tip; (1) 10 $\mu$g Cu ml$^{-1}$, 0.01 *M* HCl; (2) 10 $\mu$g Cu ml$^{-1}$, 0.11 *M* HCl; (3) 10 $\mu$g Cr ml$^{-1}$, 0.01 *M* HCl; (4) 10 $\mu$g Ci ml$^{-1}$, 0.11 *M* HCl; (5) 10 $\mu$g Fe ml$^{-1}$, 0.01 *M* HCl; (6) 10 $\mu$g Fe ml$^{-1}$, 0.11 *M* HCl; flow rate of air: 6.2 l min$^{-1}$.

A small enhancing effect on iron was found in the whole region of the flame, but an enhancing effect on chromium was observed only in the lower region of the flame. This effect may be derived from the chlorinating action of hydrochloric acid on iron and chromium; the chlorides of these elements have relatively low melting and boiling points, which are some indication of the rate of vaporization. For chromium, the high stability of chromium oxide seems to provide a reasonable explanation for the slight enhancing effect in the higher region of the flame. More concentrated acid (1 *M*) gave essentially the same effect as 0.1 *M* for iron and chromium.

*Perchloric acid*

Figure 2 shows the interferences of perchloric acid on copper, iron and chromium. Perchloric acid gave an enhancing effect for chromium, but a depressing effect for iron. The enhancing effect on chromium absorbance decreased with increasing height in the flame. GIBSON *et al.*[4] have explained the enhancing effect of perchloric acid on calcium emission, on the basis that calcium perchlorate dissociates to a greater extent than calcium chloride. IIDA AND FUWA[5] demonstrated that the enhancing effect on chromium absorbance could result from the oxidation of chromium with perchloric acid. The production of volatile compounds such as oxychloride may also contribute to the enhancement of chromium.

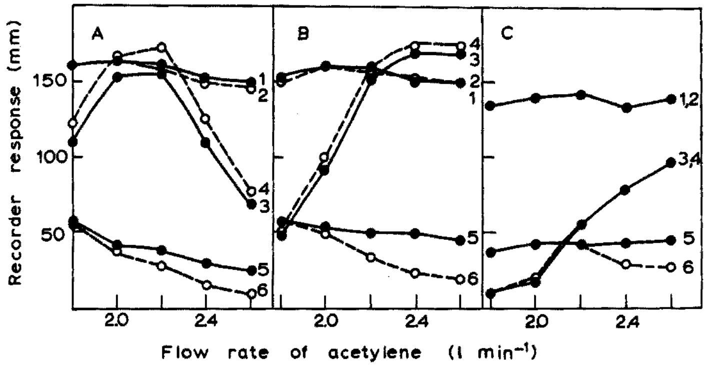


Fig. 2. Interferences of perchloric acid on copper, iron and chromium absorbances: (A) 6 mm above burner tip, (B) 10 mm above burner tip, (C) 18 mm above burner tip; (1) 10 $\mu$g Cu ml$^{-1}$, 0.01 $M$ HCl; (2) 10 $\mu$g Cu ml$^{-1}$, 0.01 $M$ HCl + 0.10 $M$ $HClO_4$; (3) 10 $\mu$g Cr ml$^{-1}$, 0.01 $M$ HCl; (4) 10 $\mu$g Cr ml$^{-1}$, 0.01 $M$ HCl + 0.10 $M$ $HClO_4$; (5) 10 $\mu$g Fe ml$^{-1}$, 0.01 $M$ HCl; (6) 10 $\mu$g Fe ml$^{-1}$, 0.01 $M$ HCl + 0.10 $M$ $HClO_4$; flow rate of air: 6.2 l min$^{-1}$.

The depressing effect on the iron absorbance might be explained by a greatly increased rate of oxide formation in the presence of perchloric acid. ŠTUPAR[2] also reported the marked depression on iron absorbance.

RAMAKRISHNA *et al.*[1] noted the depressing effect on copper. In the present work, a larger depressing effect at a higher concentration (1 $M$) of perchloric acid was observed for copper, but not for iron. No interferences were shown in the nitrous oxide–acetylene flame; the high temperature of the flame may be effective in the dissociation of oxides.

*Nitric acid*

Nitric acid caused a depressing effect on both copper and chromium in the lower region of the flame, but little effect was observed with increasing height in the flame (Fig. 3). RAMAKRISHNA *et al.*[1] reported no interference on copper from nitric acid in an oxy–hydrogen flame, while ŠTUPAR[2] found a depressing effect in the air–hydrogen flame. From these facts it seems reasonable to consider that the temperature of the flame is an important factor for interference of nitric acid on copper. This was confirmed by the fact that no interference of nitric acid was found in nitrous oxide–acetylene flames. However, the interference on chromium was not reduced even in nitrous oxide–acetylene flames; chromium differed from the other elements in this respect.

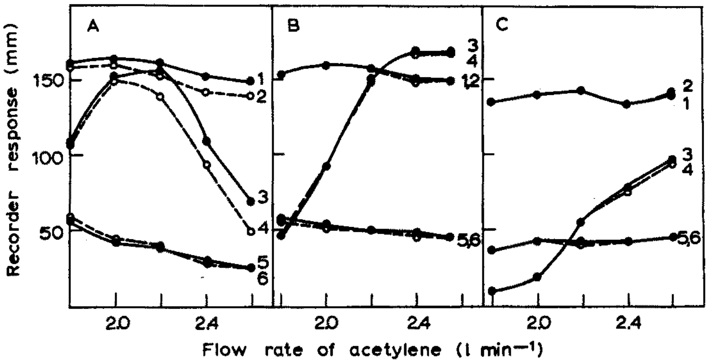


Fig. 3. Interferences of nitric acid on copper, iron and chromium absorbances: (A) 6 mm above burner tip, (B) 10 mm above burner tip, (C) 18 mm above burner tip; (1) 10 μg Cu ml⁻¹, 0.01 *M* HCl; (2) 10 μg Cu ml⁻¹, 0.01 *M* HCl + 0.10 *M* $HNO_3$; (3) 10 μg Cr ml⁻¹, 0.01 *M* HCl; (4) 10 μg Cr ml⁻¹, 0.01 *M* HCl + 0.10 *M* $HNO_3$; (5) 10 μg Fe ml⁻¹, 0.01 *M* HCl; (6) 10 μg Fe ml⁻¹, 0.01 *M* HCl + 0.10 *M* $HNO_3$; flow rate of air: 6.2 l min⁻¹.

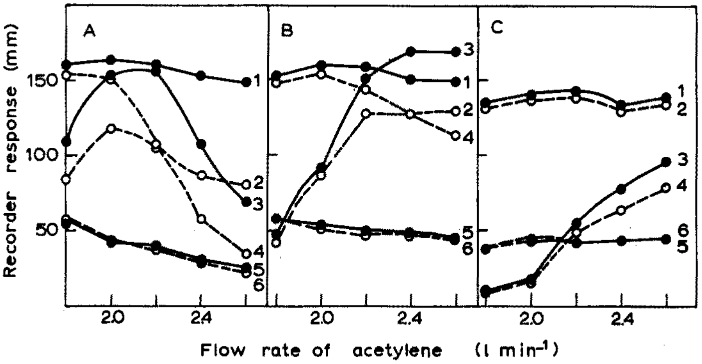


Fig. 4. Interferences of phosphoric acid on copper, iron and chromium absorbances: (A) 6 mm above burner tip, (B) 10 mm above burner tip, (C) 18 mm above burner tip; (1) 10 μg Cu ml⁻¹, 0.01 *M* HCl; (2) 10 μg Cu ml⁻¹, 0.01 *M* HCl + 0.10 *M* $H_3PO_4$; (3) 10 μg Cr ml⁻¹, 0.01 *M* HCl; (4) 10 μg Cr ml⁻¹, 0.01 *M* HCl + 0.10 *M* $H_3PO_4$; (5) 10 μg Fe ml⁻¹, 0.01 *M* HCl; (6) 10 μg Fe ml⁻¹, 0.01 *M* HCl + 0.10 *M* $H_3PO_4$; flow rate of air: 6.2 l min⁻¹.

### *Phosphoric acid*

The effect of phosphoric acid on copper, iron and chromium is shown in Fig. 4. Phosphoric acid caused a marked depressing effect on copper and chromium, especially in the lower region of the flame. This may be due to the formation of compounds which are stable in the cooler flame. The size of the effect depends on the flame temperature, and no interference was found in nitrous oxide–acetylene flames. CURTIS[5] noted that the effect of phosphoric acid on iron was most serious when the flame became luminous and that the interference was quite small with the light beam passing above the unburnt cone of gases under normal oxidizing conditions. In the present work, the depressing effect of phosphoric acid on iron was found to be not serious, irrespective of flame conditions and flame heights.

The acid effects are complex in nature and depend on various factors, and the choice of acid is important in minimizing their effect in atomic absorption spectrometry.

The authors would like to thank Mr. M. YANAGISAWA for assistance throughout this work.

## SUMMARY

Hydrochloric, perchloric, nitric and phosphoric acids were examined to elucidate the mechanism of their interferences on the atomic absorption spectrophotometry of copper, iron and chromium. The interferences were complex in nature and varied for different elements and for different acids. The mechanism of the interferences is discussed.

## RÉSUMÉ

On examine l'influence des acides chlorhydrique, perchlorique, nitrique et phosphorique sur la spectrophotométrie par absorption atomique, du cuivre, du fer et du chrome. Ces interférences sont complexes et varient suivant les éléments et les acides. Une discussion est présentée sur le méchanisme de ces interférences.

## ZUSAMMENFASSUNG

Salz-, Perchlor-, Salpeter- und Phosphorsäure wurden zur Deutung der Ursachen der Störungen dieser Säuren bei der Atomabsorptionsflammenphotometrie von Kupfer, Eisen und Chrom untersucht. Die Störungen waren komplexer Natur und variierten bei verschiedenen Elementen und Säuren. Der Mechanismus der Störungen wird diskutiert.

## REFERENCES

1 T. V. RAMAKRISHNA, J. W. ROBINSON AND P. W. WEST, *Anal. Chim. Acta*, 37 (1967) 20.
2 J. ŠTUPAR, *Mikrochim. Acta*, (1966) 722.
3 C. IIDA AND K. FUWA, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 87 (1966) 303.
4 J. H. GIBSON, W. E. L. GROSSMAN AND W. D. COOKE, *Anal. Chem.*, 35 (1963) 266.
5 K. E. CURTIS, *Analyst*, 94 (1969) 1068.

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

# A NEW METHOD FOR THE NEBULIZATION OF SOLID SAMPLES FOR ATOMIC ABSORPTION SPECTROSCOPY

MASAYUKI KASHIKI AND SHOZO OSHIMA
*Maruzen Oil Co., Ltd., Research & Development Center, P.O. Box 1, Satte, Saitama 340-01 (Japan)*

(Received April 2nd, 1970)

GATEHOUSE AND WALSH[1] have discussed the possibilities of obtaining atomic vapour directly from metallic samples by a cathodic sputtering method. VENGHIATTIS[2] has described a method in which solid samples are mixed with a solid fuel and burned in the light path from a hollow-cathode lamp, whereas COUDERT AND VERGNARD[3] have proposed a direct injection method for powders in premix burners. In the present paper, a new method is proposed for the atomic absorption analysis of powders and other materials without the requirement of prior dissolution. The powder sample is mixed in the proper proportion with a solvent and burned in the path of the light beam from a hollow-cathode lamp. The technique developed is useful for the analysis of both solution and powder samples, on a more routine basis than has hitherto been reported.

A sample chamber has been developed for the nebulization of powder samples; powder injection into flames has been reported before[3], but not for successful spectroscopic analysis. In the present method, the powder is agitated with a solvent by vibration of a dispersion blade and a low oxidant (air) flow rate is adequate to carry the material to the flame. The advantage of the arrangement is that by control of the rate of vibration and of the oxidant flow, a given quantity of powder can be transferred to the flame over a reasonably long exposure period, ensuring efficient heat transfer from the flame to the sample particles. Powders of widely different density have been introduced smoothly and reproducibly into the flame by this method, without disturbing the stability of the flame and without contamination.

By eliminating the preliminary dissolution or ashing step, improvements in convenience and accuracy can be achieved. Examples of the application of the technique are given for the determination of cobalt and molybdenum in alumina catalysts.

## EXPERIMENTAL

### *Instrumentation*

A Perkin-Elmer Model 303 instrument was employed, with a Perkin-Elmer premix-type burner with an air–acetylene burner head. Automatic null recording was used with scale expansion and noise suppression. Hollow-cathode lamps for cobalt and molybdenum were obtained from Perkin-Elmer Ltd.

*Powder dispersion assembly.* Samples were introduced by the arrangement shown in Fig. 1. The polyethylene tubing between the stainless steel tubing and the nebulization unit provided sufficient flexibility for vibration. The dispersion blade was made from 1.5-mm thick Teflon sheet with a diameter of 30 mm. The holes in the blade (see Fig. 1) had an upper diameter of 5 mm and a lower diameter of 2 mm.

*Atomic absorption measurements*

All the measurements were made with the operating conditions listed in Table I, unless otherwise specified.

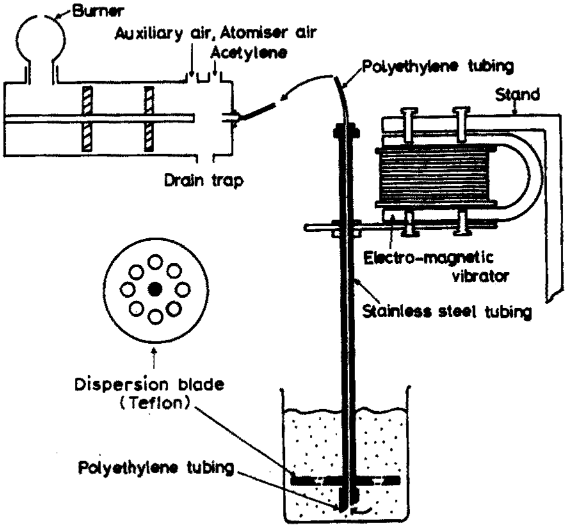


Fig. 1. Powder dispersion assembly.

TABLE I

OPERATING CONDITIONS

| | *Co* | *Mo* |
|---|---|---|
| Wavelength (nm) | 240.7 | 313.3 |
| Slit (mm) | 0.3 | 0.3 |
| Lamp current (mA) | 30 | 30 |
| Acetylene flow (l min$^{-1}$) | 3.5 | 4.1 |
| Air flow (l min$^{-1}$) | 24.8 | 21.0 |
| Burner height (mm) | 14.0 | 8.0 |

*Determination of cobalt and molybdenum*

The powder dispersion unit was used to determine cobalt and molybdenum in alumina catalyst. Solid samples were crushed to a fine powder in an agate mortar, and the resultant powder was sieved through a No. 200 sieve. A sample weighing 10–50 mg was transferred to a glass beaker and dispersed in 100 g of methanol for measurement.

*Standard curves*

To prepare standard curves, 5 aliquots of standard cobalt and molybdenum catalyst powders, to encompass the range 6–30 p.p.m. of cobalt and 12.8–63.8 p.p.m. of molybdenum, were transferred to 200-ml glass beakers and mixed with methanol. The cobalt and molybdenum stock solutions used in the preparation of the powders were standardized gravimetrically.

## RESULTS AND DISCUSSION

### *Burner height*

Six different burner settings were used, corresponding to heights of the center of the light beam above the burner top of 8, 14, 20, 26, 32 and 38 mm. Moving the burner so that the center of the light beam was below 8 mm resulted in blockage of the light beam. Plots of absorbance *vs.* concentration for these six positions are shown in Figs. 2 and 3. Variations in the gas flow rates were also examined. As shown in Figs. 2 and 3, the optimal conditions were found with an acetylene flow of 3.5 l $\text{min}^{-1}$ with an air flow of 24.8 l $\text{min}^{-1}$ for cobalt, and with an acetylene flow of 4.1 l $\text{min}^{-1}$ and an air flow of 21.0 l $\text{min}^{-1}$ for molybdenum, at burner heights of 14 mm and 8 mm, respectively. Under these conditions absorbance measurements were stable.

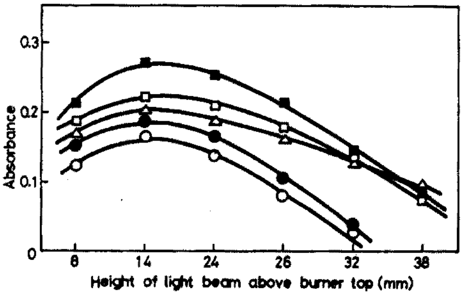


Fig. 2. Effect of variation of acetylene–air mixture and height of path in the flame on the sensitivity for cobalt. The acetylene and air flows were varied. Co concentration 30 p.p.m. Solvent: methanol. Flows (l $\text{min}^{-1}$): (○) acetylene 1.7, air 11.4; (●) acetylene 2.1, air 14.5; (□) acetylene 2.7, air 19.5; (■) acetylene 3.5, air 24.8; (△) acetylene 4.1, air 29.1.

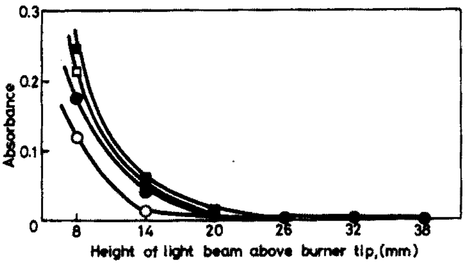


Fig. 3. Effect of variation of acetylene–air mixture and height of path in the flame on the sensitivity for molybdenum. The acetylene and air flows were varied. Mo concentration 63.8 p.p.m. Solvent: methanol. Flows (l $\text{min}^{-1}$): (○) acetylene 2.1, air 11.4; (●) acetylene 2.7, air 14.5; (□) acetylene 3.5, air 19.5; (■) acetylene 4.1, air 21.0.

### *Influence of solvents*

The presence of certain solvents influences the sensitivity for many elements. Experiments with water, methanol, isopropanol, methyl isobutyl ketone, methyl ethyl ketone, *n*-butyl ether, toluene and xylene, were conducted in order to determine the extent of the enhancement of the absorbances for cobalt and molydenum. Table II shows that methanol gave the highest absorbance readings. In the case of cobalt, methyl ethyl ketone and toluene gave the lowest readings whereas in the case of molybdenum, toluene and xylene gave the lowest readings.

### *Influence of grain size*

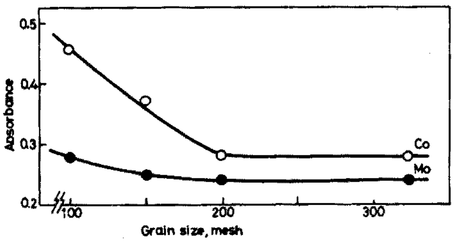
A high burning rate is desirable because it leads to a more sensitive analysis by rapidly populating the flame with ground-state atoms. However, the absorbance is generally influenced by the size and shape of the grains of sample powder. As shown in Fig. 4, grain sizes below No. 200 mesh yielded stable and constant absorbances.

TABLE II

INFLUENCE OF SOLVENTS ON Co AND Mo ABSORBANCE[a]

| *Solvent* | *Co* | *Mo* |
|---|---|---|
| $H_2O$ | 0.3188 | 0.0506 |
| Methanol | 0.4559 | 0.0706 |
| Isopropanol | 0.2218 | 0.0177 |
| Methyl isobutyl ketone | 0.2366 | 0.0132 |
| Methyl ethyl ketone | 0.0362 | 0.0132 |
| *n*-Butyl ether | 0.0706 | 0.0315 |
| Toluene | 0.0362 | 0.0044 |
| Xylene | 0.0706 | 0.0044 |

[a] All solutions contained 50.0 p.p.m. Co and 13.0 p.p.m. Mo.



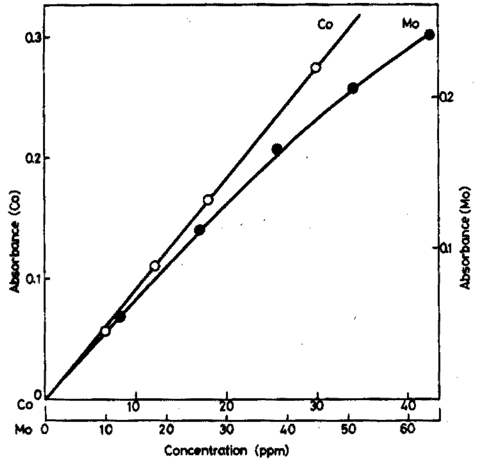


Fig. 4. Effect of sample grain size on absorbance. Concentration: Co, 30.0 p.p.m.; Mo, 63.8 p.p.m. Solvent: methanol.

Fig. 5. Calibration curves.

### *Calibration curve*

The calibration curves shown in Fig. 5 were obtained as described under EXPERIMENTAL. As can be seen, reasonably good linear relationships were obtained.

This work has generally confirmed the expectations of other authors. The powder dispersion assembly is very efficient in the sense that a much greater proportion of the solid or colloidal sample can be utilised in the flame and hence the same sensitivity as that given by the standard method of introducing samples can be achieved on a smaller amount of sample. The system described here enables several readings to be obtained on as little as 10 ml of sample and this could undoubtedly be improved by a more advanced design.

Table III summarizes the results obtained by the proposed method, compared to the values given by a conventional assay; for the latter, the samples were decomposed with the generally used nitric and hydrochloric acids before atomic absorption spectrophotometry. The differences between the results are well within the usual analytical error.

TABLE III

COMPARISON OF RESULTS OF DETERMINATION OF COBALT AND MOLYBDENUM IN CATALYST BY THE DISPERSION METHOD AND BY ASSAY

| *Sample no.* | *Concentration found (%)* | | | |
|---|---|---|---|---|
| | *Assay method* | | *Dispersion method* | |
| | *Co* | *Mo* | *Co* | *Mo* |
| 1 | 2.70 | 10.8 | 2.66 | 10.7 |
| 2 | — | 10.2 | — | 10.1 |

TABLE IV

DETERMINATION OF COBALT AND MOLYBDENUM IN CATALYST

(Five determinations were done in each case)

| *Sample concentration (p.p.m.)* | *Average concentration found (p.p.m.)* | *Relative error (%)* | *Sample concentration (p.p.m.)* | *Average concentration found (p.p.m.)* | *Relative error (%)* |
|---|---|---|---|---|---|
| *Cobalt* | | | *Molybdenum* | | |
| 6.0 | $6.0_8$ | 1.3 | 12.8 | $11.8_8$ | 7.2 |
| 12.0 | $12.1_4$ | 1.2 | 25.6 | $26.2_0$ | 2.3 |
| 18.0 | $18.7_8$ | 4.6 | 38.4 | $40.6_4$ | 5.8 |
| 24.0 | $23.4_6$ | 2.3 | 51.1 | $50.1_4$ | 1.9 |
| 30.0 | $31.8_6$ | 6.2 | 63.8 | $68.3_4$ | 7.1 |

The reproducibility of the proposed method is shown in Table IV. Five replicate samples were weighed and the relative error was calculated on the separate atomic absorption readings taken. The results are well within the limits of reproducibility necessary for studies of catalytic metal chemistry.

The method described has been in routine use for several months for the analysis of catalysts containing cobalt and molybdenum in the 2–10% range and also for samples containing up to 40% cobalt and molybdenum.

The authors wish to express their thanks to Mr. T. KOZUMA and Dr. T. AMEMIYA, Directors of Maruzen Oil Co., Ltd., for their encouragement throughout the work, and to Dr. H. HASEGAWA, General Manager of the Research & Development Center, for his kind guidance.

## SUMMARY

A dispersion system for the nebulization of solid samples for atomic absorption spectrophotometry is described. Compared to the conventional method of nebulization, the proposed method has the advantages of avoiding any preliminary dissolution step, and of requiring less sample. Absorbance measurements show good sensitivity and stability. Powdered samples (< 200 mesh) are dispersed in methanol with a special vibrating stirrer and the suspension is sucked directly into the flame. The method is applied to the determination of cobalt and molybdenum in alumina catalysts. Application to other samples should be possible.

## REFERENCES

1 B. M. GATEHOUSE AND A. WALSH, *Spectrochim. Acta*, 16 (1960) 602.
2 A. A. VENGHIATTIS, *Spectrochim. Acta*, 22B (1967) 67.
3 M. COUDERT AND J.-M. VERGNARD, *Compt. Rend.*, C628 (1969) 1255.

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

# CATHODE-RAY-EXCITED EMISSION SPECTROSCOPIC ANALYSIS OF TRACE RARE EARTHS

## PART IV. DETERMINATION OF THULIUM IN ZINC SULFIDE

SIMON LARACH*, ROSS E. SHRADER AND RICHARD A. KAUFFUNGER
*RCA Laboratories, Princeton, N. J. (U.S.A.)*

(Received March 18th, 1970)

Cathode-ray-excited emission spectroscopy of rare earths is a rapid, non-destructive analytical procedure, which can be utilized for qualitative or quantitative analyses for trace amounts in certain matrices. Previous papers in this series have established the qualitative aspect of this technique[1], and determinations of europium[2] and of terbium[3] have also been reported. This paper describes the determination of trace amounts of thulium in zinc sulfide, the *f–f* emission line at 478 nm being used for the analysis.

Zinc sulfide phosphors doped with rare earths have been known for many years; the luminescence emission from such materials usually consists of broad bands, upon which are superimposed lines. In 1963 GOLDSMITH *et al.*[4] found that luminescence excited from many rare earths in zinc sulfide by an a.c. field need not be accompanied by broad-band emission, and in 1965 YOCOM AND LARACH[5] reported the effect of alkali metal charge compensation in minimizing the broad-band emission from rare earths in zinc sulfide. The effect of such compensators has been discussed by LARACH[6] for rare earths in Group II–VI compounds, and in the case of thulium, it was found that lithium served to enhance the emission, particularly in the visible region of the spectrum. For this reason, lithium was used as a charge-compensating ion in the present materials.

## EXPERIMENTAL

### *Sample preparation*

The matrix material used in the preparation of all samples was "luminescent grade" zinc sulfide, designated as RCA 33-Z-19. Slurries were made with distilled water, and the doping ions were added as aqueous sulfate solutions. Crystallization firings were carried out in Vitreosil fused quartz vessels, which were prefired with pure zinc sulfide. The firing atmosphere was hydrogen sulfide. To improve sample uniformity, firings were carried out in the apparatus shown in Fig. 1A. The firing tube was preflushed by passing the hydrogen sulfide through the inlet tube. During the firing, the gas flow was shunted through the cap of the firing tube, thus maintaining a positive pressure of hydrogen sulfide in the tube, while flow around the sample was avoided. The samples were fired at 800° for 15 min, and at 1100° for 45 min.

---

* At the Department of Physics and Department of Inorganic and Analytical Chemistry, the Hebrew University of Jerusalem, Israel, 1969–1970.

Thulium in zinc sulfide showed detectable luminescence emission at or above firing temperatures of 800° and Table I shows the cathode-ray-excited intensity as a function of firing temperature, for one composition.

With the low rare-earth content investigated in this work, it was found that sequential firings introduced expected variations from run to run. For this reason, a multiple sample holder was designed, shown in Fig. 1B, which allowed six samples to be fired simultaneously in the same ambience.

Sample mixes in each firing were repeated in subsequent firings, thereby providing a method of normalizing the various firings.

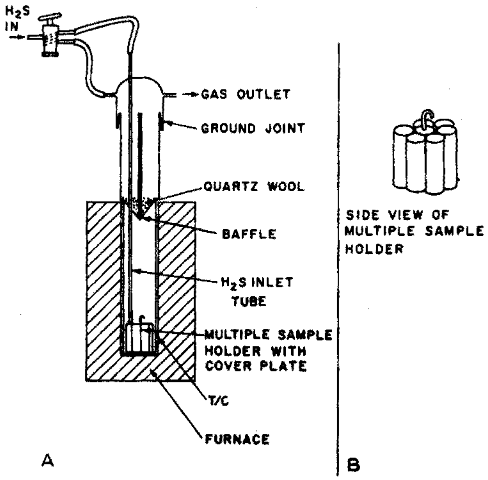


Fig. 1. Apparatus for firing samples for analysis. (A) View of apparatus, (B) side view of multiple sample holder.

TABLE I

EMISSION INTENSITY OF THULIUM *vs.* FIRING TEMPERATURE

| *Firing temperature (°)* | *Relative intensity* |
|---|---|
| 800 | 3.8 |
| 900 | 9.0 |
| 1000 | 14 |
| 1100 | 51 |

### *Measurements*

As in the previous work, a "demountable" cathode-ray tube was used. Demountable refers to the tube's capability of being repeatedly opened to the atmosphere for the purpose of changing test-samples, electron-gun structures and window-material (quartz, sapphire, etc.). Of special importance is the capability of accommodating, at one pumping, all samples of one or more series to minimize the error from carrying over a standard from one pumping to another. The unit used here can handle 29 samples. The voltage applied to the beam is not particularly critical if one avoids low or high voltages (*i.e.*, 3 kV < V < 20 kV). The proper region of voltage also depends on the secondary emission characteristics of the material under test. For zinc sulfide, voltages in the range 8–12 kV are satisfactory. Electron beam currents also are not critical if one avoids high current densities (*i.e.*, a defocused beam is used) and keeps the wattage-loading below some safe value (*e.g.* 10 mW $cm^{-2}$). In these tests, a 1-$\mu$A beam, focused to a 1-mm diameter spot, was scanned over a test area, 10 × 20 $mm^2$.

The radiant flux to be studied can be introduced into any type of monochromator for measuring with a detector suitable for the wavelength and intensity involved. A Spex grating monochromator (Model 1700) fitted with a #7265 multiplier phototube was used in this instance. It was found desirable to scan the monochromator over a small range including the rare-earth line (*i.e.* 470–485 nm) while recording the photocurrent (or detector output) to determine the amount of background luminescence. Obviously the resolution (or band-pass) should be adequate to distinguish the line emission from the background. Since the spectral character of the rare-earth emission is quite insensitive to concentration below 100–500 p.p.m., one needs to read only a peak-height above background for each sample. Availability of zero-offset for the background before amplification is helpful in providing accuracy when a weak line is superimposed on a strong background.

## RESULTS AND DISCUSSION

The visible emission from thulium in zinc sulfide consists of two spectral complexes (manifolds)[6], the major being about 470–485 nm, and the minor about 630–665 nm. The spectral distribution curves are shown in Fig. 2.

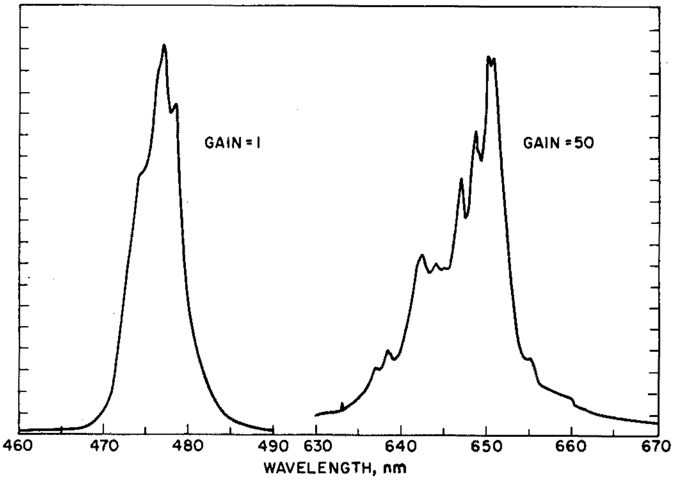


Fig. 2. Cathodoluminescence spectral distribution curves of blue and red emission bands from thulium in zinc sulfide. (Note the gain change.)

The cathodoluminescence emission intensity of the 470–485-nm emission from thulium as a function of concentration (between one and 300 p.p.b.) in zinc sulfide is shown in Fig. 3. A detection limit of 0.01 p.p.b. is indicated for this type of analysis.

"Added–found" data are shown in Table II, for thulium prepared in a zinc sulfide matrix. For *Tm found*, two columns are given, one for cathode-ray-excited emission analysis (CREE) and the other for solid-state mass spectrometry (SSMS). The mass spectrometer was an AEI MS-7, equipped with an r.f. spark source and photographic detection. The spark source was operated at 25 kV between the sample electrodes, at a repetition frequency of 300 Hz and a pulse duration of 200 μsec. Positive ions from the spark were accelerated to 20 kV, passed through both an electrostatic and a magnetic analyzer, and collected on an Ilford Q-2 ion-sensitive emulsion. The samples were mixed 1:1 by weight with high-purity silver powder, and were briquetted in a polyethylene-slug die to form solid, conducting electrodes.

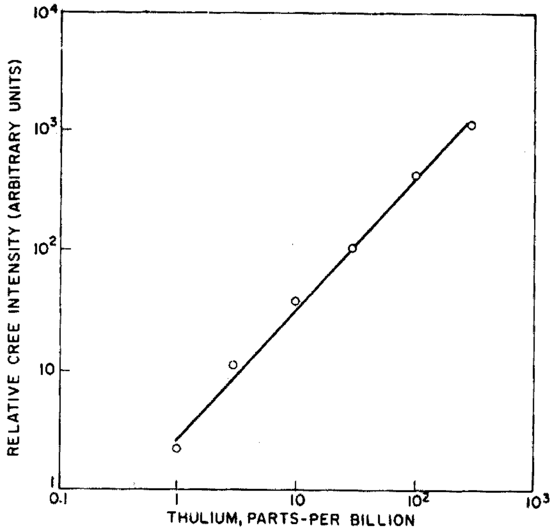


Fig. 3. Relative intensity as a function of thulium concentration.

TABLE II

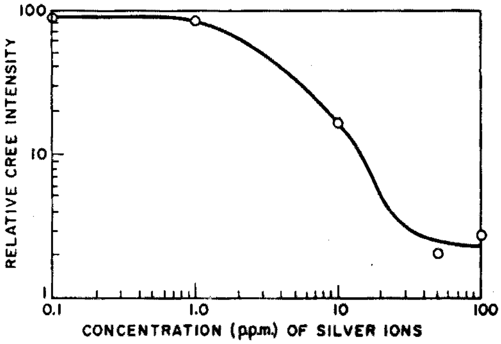
DETERMINATION OF THULIUM IN ZINC SULFIDE MATRIX WITH CHARGE COMPENSATION

| *Tm added (p.p.b.)* | *Tm found (p.p.b.)* | |
|---|---|---|
| | *CREE* | *SSMS* |
| 6 | 6.2 | 6.8 |
| 20 | 24 | 23 |
| 20 | 19.5 | |
| 60 | 54 | 64 |
| 60 | 54 | |
| 200 | 220 | 222 |
| 200 | 205 | |

The response of the ion-sensitive plate was calibrated with a series of platinum exposures by relating blackening on the plate to the total ion beam monitor, and fitting these data to an equation developed by HULL[7]. Thulium concentrations were calculated by comparing the blackening for the $^{169}Tm^+$ ion to the total ion beam passing through the instrument. The agreement between the two sets of results is consistent within the accuracy of the measurements.

### *Interferences*

Interference effects caused by the presence of silver ion which itself promotes a blue cathodoluminescence emission[8], were investigated. Various concentrations of silver were incorporated into zinc sulfide containing 5 p.p.m. of thulium. This large thulium concentration was used to increase the accuracy of measurement for the case of large interference. Any effect of interference observable at this concentration would be enhanced for lower concentrations. The results are shown in Fig. 4. It is seen that silver ions begin to decrease the emission intensity from thulium at concentrations somewhat greater than one p.p.m. At 10 p.p.m., the silver ion has decreased the thulium emission by a factor of about five, and a levelling-off is indicated at about 50 p.p.m., where the residual thulium emission is only about 2% of the original.



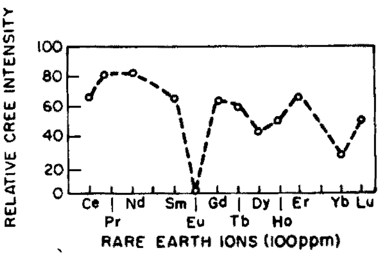


Fig. 4. Relative intensity as a function of concentration of silver in zinc sulfide containing 5 p.p.m. of thulium and lithium.

Fig. 5. Relative intensity of thulium (5 p.p.m.) in zinc sulfide as a function of rare earth interferences.

The interference effects of twelve rare earths were also studied. The results of using 100-p.p.m. amounts as interfering ions in the analysis of 5 p.p.m. of thulium in zinc sulfide (lithium) are shown in Fig. 5. The slight general trend, with the exception of europium, would appear to be decreasing emission intensity from thulium with increasing atomic number of the interfering rare earth. The relationship indicated previously[3] (for terbium in an yttrium oxide matrix) between emission intensity and the magnetic moment of the rare-earth interfering ion was not found for thulium in a zinc sulfide matrix. Whether or not this is due to the difference in matrix will be investigated in future work. The fact that with europium present as the interfering ion, *no* cathode-ray-excited emission was detected from thulium, may be connected with the fact that the europium in zinc sulfide is *divalent*, as shown by e.p.r. investigations[9]. Further work is planned to investigate this effect.

The determination of thulium by X-ray-excited fluorescence has been reported by WALTERS *et al.*[10], with a detection limit of 10 p.p.m. in yttrium oxide, while OZAWA AND TORYU[11] reported a detection limit in the region $10^{-9}$–$10^{-8}$ *mole*, for each of several rare earths, including thulium, in yttrium oxide, utilizing photoluminescence techniques.

The authors wish to acknowledge, with thanks, the aid of Dr. W. L. HARRINGTON, who obtained the mass spectrographic data.

## SUMMARY

The method of analysis for trace amounts of rare earths in a matrix by cathode-ray-excited emission spectroscopy has been extended to the determination of thulium in a zinc sulfide matrix, with lithium added as a charge-compensating ion. If the 478-nm emission from thulium is used as the detection wavelength, one p.p.b. can be readily determined, with an estimated detection limit of the order of 0.01 p.p.b. Thulium determinations by this means are compared with those from solid-state mass spectrometry. Effects of sample firing parameters and interferences are discussed.

## RÉSUMÉ

La méthode d'analyse de traces de terres rares dans une matrice, par spectroscopie d'émission à rayon cathodique, a été étendu au dosage du thulium dans une matrice de sulfure de zinc avec addition de lithium. En utilisant l'émission 478 nm du thulium comme longueur d'onde de détection, il est possible de doser facilement 1 p.p.b., avec une limite de détection de l'ordre de 0.01 p.p.b. Les résultats de thulium ainsi obtenus sont comparés à ceux de la spectrométrie de masse à l'état solide. On examine divers paramètres et interférences possibles.

## ZUSAMMENFASSUNG

Die Methode der Analyse von Seltenerd-Spuren in einer Matrix durch Emissionsspektroskopie mit Kathodenstrahlanregung ist auf die Bestimmung von Thulium in einer Zinksulfid-Matrix erweitert worden, wobei Lithium als ladungskompensierendes Ion zugegeben wird. Als Nachweiswellenlänge wird die Emission des Thuliums bei 478 nm benutzt. Ein p.p.b. kann leicht bestimmt werden, die geschätzte Nachweisgrenze liegt in der Grössenordnung 0.01 p.p.b. Thuliumbestimmungen nach dieser Methode werden mit den durch Festkörper-Massenspektrometrie durchgeführten Bestimmungen verglichen. Die Einflüsse der Probenvorbehandlung und Störungen werden diskutiert.

## REFERENCES

1 S. Larach, *Anal. Chim. Acta*, 41 (1968) 189.
2 S. Larach, *Anal. Chim. Acta*, 42 (1968) 407.
3 S. Larach and R. E. Shrader, *Anal. Chim. Acta*, 45 (1969) 227.
4 G. J. Goldsmith, S. Larach, R. E. Shrader and P. N. Yocom, *Solid State Comm.*, 1 (1963) 25.
5 P. N. Yocom and S. Larach, *Extended Abstracts, Electrochem. Soc., San Francisco Meeting*, 1965, p. 16.
6 S. Larach, in G. Szigetti, *Proc. Int. Conf. Luminescence 1966*, Budapest, 1968, pp. 1549–1569.
7 C. W. Hull, *E-14 Conference, New Orleans, La., 1962*, paper No. 72.
8 H. W. Leverenz, *Introduction to Luminescence of Solids*, Wiley, New York, 1950.
9 S. Larach, unpublished data.
10 R. M. Walters, J. F. Cosgrove and D. J. Bracco, *Symp. on Trace Charac., Gaithersburg, Md., October 1966*, pp. 174–180.
11 L. Ozawa and T. Toryu, *Anal. Chem.*, 40 (1) (1968) 187.

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

# THE DETERMINATION OF SCANDIUM AND GOLD IN METEORITES, TEKTITES AND STANDARD ROCKS BY NEUTRON ACTIVATION ANALYSIS WITH AN INTERNAL-REFERENCE METHOD

K. NOMURA, A. MIKAMI*, T. KATO AND Y. OKA
*Department of Chemistry, Faculty of Science, Tohoku University, Sendai (Japan)*

(Received March 15th, 1970)

Scandium and gold are the important elements from a geochemical point of view, and several papers have been concerned with the determination of the contents of both elements in samples of geochemical origin. A method with very high sensitivity is required, and hence neutron activation techniques have preferably been applied.

The purpose of the present work was to establish an accurate method for the determination of scandium and gold in trace levels by activation analysis, by applying the internal-reference method proposed previously[1,2]. The method was verified to be accurate for both elements even at p.p.b. levels, and was utilized for the determination of both elements in several geochemical samples: Bruderheim and Canyon Diablo meteorites, Indochinite tektite, and G-1, W-1 and JG-1 standard rocks.

## *Method of determination*

In cases of thermal neutron activation, where the atomic number of the element to be analyzed is higher by one unit than that of the element chosen as reference and where the former element and the secondary $\beta^-$-decay product from the latter are favorable for subsequent $\gamma$-ray spectrometric measurements, it is possible to determine the content of the element in question on the basis of the activity ratios of the two radioactive species. Trace amounts of scandium and gold can be determined by $\gamma$-ray spectrometry through the induced 83.9-d $^{46}$Sc and 2.7-d $^{198}$Au, respectively, in a sample irradiated with thermal neutrons. Calcium and platinum can be used, respectively, as the reference elements in these cases. Of the nuclides formed by the (n,$\gamma$) reactions on both reference elements, those of present importance are formed through the following reaction schemes:

$$^{46}\text{Ca}(\text{n},\gamma)^{47}\text{Ca} \xrightarrow[4.7\text{ d}]{\beta^-} {}^{47}\text{Sc} \xrightarrow[3.4\text{ d}]{\beta^-} {}^{47}\text{Ti (stable)}$$

$$\begin{tikzcd}
{}^{198}\text{Pt}(\text{n},\gamma)^{199\text{m}}\text{Pt} \arrow[d, "\text{IT 14 sec}"] & & \\
{}^{199}\text{Pt} \arrow[r, "\beta^-", "30\text{ min}"'] & {}^{199}\text{Au} \arrow[r, "\beta^-", "3.15\text{ d}"'] & {}^{199}\text{Hg (stable)}
\end{tikzcd}$$

When the scandium or gold activity is isolated from an irradiated mixture of scandium and calcium or gold and platinum, respectively, therefore, a composite $\gamma$-ray spectrum which corresponds to a mixture of $^{46}$Sc and $^{47}$Sc or of $^{198}$Au and $^{199}$Au

---

* Present address: The Ishizuka Research Institute Ltd., Hiratsuka-shi, Kanagawa-ken, Japan.

is measured. The activity ratio of $^{46}$Sc to $^{47}$Sc, or of $^{198}$Au to $^{199}$Au, is determined in terms of $\gamma$-ray photopeak areas.

In the determination of scandium, each of the 0.887-MeV and the 1.119-MeV $\gamma$-ray photopeak areas of $^{46}$Sc was compared with that of the 0.160-MeV $\gamma$-ray of $^{47}$Sc. In the determination of gold, the 0.412-MeV $\gamma$-ray photopeak area of $^{198}$Au was compared with that of the 0.158-MeV $\gamma$-ray of $^{199}$Au. The accuracy of the area determinations depended on the high resolving power of a lithium-drifted germanium detector. The following linear relationship should then hold between the ratio of the photopeak activity determined at identical times after each irradiation ($R_{A_t}$) and the ratio of the concentrations ($R_W$):

$$R_W = K\, R_{A_t} \tag{1}$$

The constant, $K$, can be determined by irradiating synthetic mixtures of scandium and calcium or of gold and platinum with known compositions. For the general application of this method, a proper amount of calcium or platinum is mixed with a sample to be analyzed, and, after irradiation together with the synthetic mixtures, the mixed scandium or gold activities are chemically separated, and then the $R_{A_t}$ values are compared with those of the synthetic mixtures. The content of scandium or gold can be easily determined by means of the above relationship.

Since the results can be calculated on the basis of the activity ratios, errors which arise from neutron flux irregularities and self-shielding effects can be avoided, and no corrections for chemical yield are necessary. Hence, an accurate result can be expected by this method.

## EXPERIMENTAL

### *Materials*

A series of synthetic scandium–calcium mixtures was prepared as follows. To each of a series of silica tubes (i.d. 6 mm) were added 20 mg of calcium in the form of calcium carbonate, and varying amounts of an aqueous solution of scandium chloride; the contents were evaporated to dryness and the tubes were sealed. The calcium carbonate used was guaranteed grade reagent and was further purified by repeated reprecipitations. The aqueous scandium chloride solution was prepared by dissolving scandium oxide of 99.9% purity in dilute hydrochloric acid. Proper dilution was made from this just before use.

The synthetic samples of known gold-to-platinum ratios were prepared by mixing aliquots of an *aqua regia* solution of platinum containing $1.5 \cdot 10^{-2}$ mg of platinum with varying amounts of gold also in *aqua regia* solution. Each of these mixtures was placed into a silica tube (i.d. 6 mm) and evaporated to dryness, and the tubes were sealed. Platinum was processed from potassium chloroplatinate of guaranteed grade; after repeated recrystallizations, the reagent was dissolved in aqueous ammonia solution. Platinum was reduced to the metal from this solution by addition of aqueous hydrazine solution, repeatedly washed with water and dried in a vacuum. The *aqua regia* solution of gold was made by dissolving gold wire of 99.9% purity. The hydrochloric acid, nitric acid and water were all redistilled.

Samples of three kinds of standard rocks (G-1, W-1 and JG-1), Canyon Diablo (iron meteorite), Bruderheim (stone meteorite) and Indochinite tektite were analyzed for their scandium and gold contents. These samples were powdered before use. A part of each sample weighing 10–500 mg was subjected to analysis for scandium after mixing with 50 mg of calcium carbonate, and another part was used for analysis for gold after the addition of $1.5 \cdot 10^{-2}$ mg of platinum. Duplicate or triplicate analyses were carried out for each sample. Those samples were also sealed individually in silica tubes of the same size, and set together with a series of the synthetic mixtures in an aluminium capsule for pile irradiation. Titanium metal powder weighing 100 mg was also irradiated in order to check the effects of fast neutrons.

### *Irradiation*

The JRR-2 and the JRR-3 reactors of the Japan Atomic Energy Research Institute were the irradiation facilities. Both reactors were operated at 10 MW, providing thermal neutron fluxes of $4.0 \cdot 10^{13}$ n cm$^{-2}$ sec$^{-1}$ with the former and $2.0 \cdot 10^{12}$ n cm$^{-2}$ sec$^{-1}$ with the latter at the irradiation site.

The irradiations were performed for 200 h in the JRR-3 reactor for determination of scandium, and for 231 h in the JRR-2 reactor for determination of gold.

After irradiation, the contents of capsules were cooled for a time and then subjected to the radiochemical procedures for the isolation of the scandium or gold activity.

### *Chemical separation*

The radiochemical procedure for the isolation of the scandium activities is outlined in Fig. 1. Separations were performed at identical times after irradiation

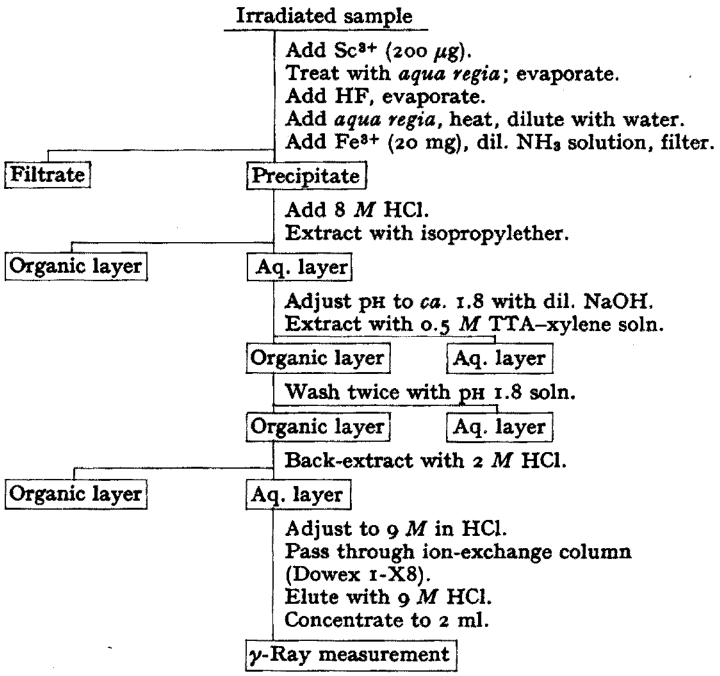


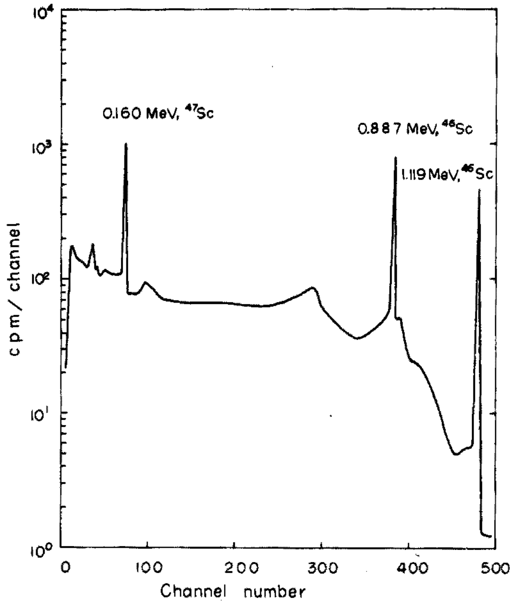
Fig. 1. Separation scheme for radioscandium from the irradiated sample.

(11.8 days). The final aqueous layer was drained into a polyethylene tube for γ-ray measurements.

Radiogold was extracted from a hydrochloric acid solution of an irradiated sample with ethylether. The sample was treated with *aqua regia* along with the addition of 20 mg of gold carrier and then with hydrofluoric acid. After evaporation to dryness, the residue was dissolved with a small amount of *aqua regia*, and diluted to a volume of 25 ml with 2.5 *M* hydrochloric acid. To this, 25 ml of ethylether was added and the radiogold was extracted. The organic layer was further purified by successive back-washings with 25-ml portions of 2.5 *M* hydrochloric acid, 3 *M* hydrobromic acid, 10 *M* nitric acid, and finally twice with 2.5 *M* hydrochloric acid. After evaporation to dryness, the residue of the organic layer was dissolved with 2 ml of *aqua regia*, and transferred to a polyethylene tube for γ-ray measurements.

*γ-Ray measurement*

For measurements of γ-ray spectra, a lithium-drifted germanium detector with a sensitive volume of 36 cm$^3$ (Ortec model 8101-30P) coupled to a TMC 1024-channel pulse-height analyzer was used. The resolution of this system was 3.9 keV for the 661.6-keV γ-line of $^{137}$Cs. The sample was measured at a fixed position, 1 cm from the active surface of the detector.



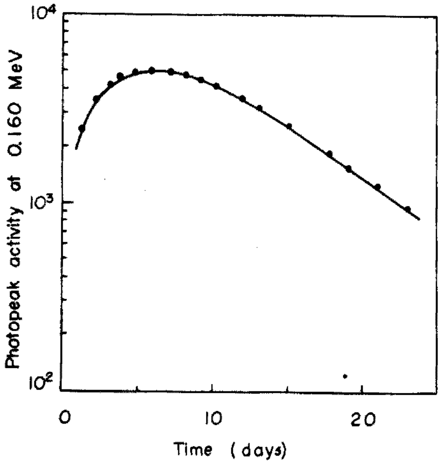


Fig. 2. γ-Ray spectrum of radioscandium separated from irradiated calcium–scandium mixture (Ca $19.8_9$ mg + Sc 0.202 μg), 71.7 h after separation.

Fig. 3. Transient equilibrium curve of

$${}^{47}\mathrm{Ca} \xrightarrow[T_{\frac{1}{2}}=4.7\ \mathrm{d}]{\beta^-} {}^{47}\mathrm{Sc} \xrightarrow[T_{\frac{1}{2}}=3.4\ \mathrm{d}]{\beta^-} {}^{47}\mathrm{Ti}.$$

## RESULTS AND DISCUSSION

### *$R_W$ vs. $R_{A_t}$ for scandium–calcium mixtures*

A typical $\gamma$-ray spectrum of the mixed scandium activities is shown in Fig. 2. Decontamination from other nuclides was successful. The 3.4-d ${}^{47}$Sc is the $\beta^-$-decay product of the 4.7-d ${}^{47}$Ca. Figure 3 gives the ${}^{47}$Sc activity as a function of the elapsed time after irradiation.

The ${}^{47}$Sc activity was separated after 11.8 days from an irradiated mixture, *i.e.* after radiochemical equilibrium had been attained between ${}^{47}$Ca and ${}^{47}$Sc. From the composite spectra obtained from the scandium and calcium mixtures, photopeak areas were measured for the 0.160-MeV $\gamma$-ray of ${}^{47}$Sc and the 0.887-MeV and the 1.119-MeV $\gamma$-rays of ${}^{46}$Sc. The $R_{A_t}$ values in eqn. (1) were computed from the data thus obtained. Some ${}^{46}$Sc activity arising from the original calcium was observed, and this would cause a positive error in the method. Hence, a correction coefficient for this additional ${}^{46}$Sc was introduced in eqn. (1):

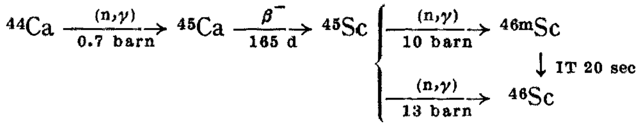
$$R_W = K\left(\frac{A_{{}^{46}\mathrm{Sc}}}{A_{{}^{47}\mathrm{Sc}}} - \alpha\right)_{t=11.8\ \mathrm{d}} \tag{2}$$

where

$$\alpha = \left(\frac{A_{{}^{46}\mathrm{Sc}}}{A_{{}^{47}\mathrm{Sc}}}\right)_{\mathrm{orig.}} \tag{3}$$

and where $A$'s represent the photopeak activities. The $\alpha$ values obtained under the present conditions were $9.15 \cdot 10^{-4}$ for the 0.887-MeV $\gamma$-ray photopeak and $7.08 \cdot 10^{-4}$ for the 1.119-MeV $\gamma$-ray photopeak. This corresponds to an amount of $4.36 \cdot 10^{-4}$ $\mu$g of scandium in 50 mg of the original calcium carbonate.

The need for these corrections may arise from two reasons. One of them is due to the amount of scandium contained in the calcium carbonate reference as an impurity, and the other may arise from the systematic second-order reactions:



$$ {}^{44}\mathrm{Ca} \xrightarrow[0.7\ \mathrm{barn}]{(n,\gamma)} {}^{45}\mathrm{Ca} \xrightarrow[165\ \mathrm{d}]{\beta^-} {}^{45}\mathrm{Sc} \begin{cases} \xrightarrow[10\ \mathrm{barn}]{(n,\gamma)} {}^{46m}\mathrm{Sc} \\ \qquad\qquad \downarrow \mathrm{IT}\ 20\ \mathrm{sec} \\ \xrightarrow[13\ \mathrm{barn}]{(n,\gamma)} {}^{46}\mathrm{Sc} \end{cases} $$

The production rate of ${}^{46}$Sc formed through the above reaction scheme was computed by the use of the BATEMAN equation[3]. In the irradiation of 20 mg of calcium for 231 h at a flux of $2.0 \cdot 10^{12}$ n cm$^{-2}$ sec$^{-1}$, an apparent scandium amount produced was computed to be $3.34 \cdot 10^{-4}$ $\mu$g. This turned out to be 77% of the total amount of scandium.

Table I shows the $R_W$ values *versus* the $R_{A_t}$ values for the mixtures; it can be seen that a good proportionality is obtained between them. A relative standard deviation of less than 1% was obtained in each case. The present results show that an accurate determination can be expected by means of these relationships.

### *$R_W$ vs. $R_{A_0}$ for gold–platinum mixtures*

A typical $\gamma$-ray spectrum of the mixed gold activities separated from a gold–

TABLE I

$R_W$ *vs.* $R_{A_t}$ FOR CALCIUM–SCANDIUM MIXTURES

| $R_W$ | $R_{A_t}$[a] | | $R_W/R_{A_t}$ | |
|---|---|---|---|---|
| | *0.887 MeV* | *1.119 MeV* | *0.887 MeV* | *1.119 MeV* |
| $1.01_9 \cdot 10^{-5}$ | $4.85_8 \cdot 10^{-1}$ | $3.83_7 \cdot 10^{-1}$ | $2.10 \cdot 10^{-5}$ | $2.66 \cdot 10^{-5}$ |
| $4.76_9 \cdot 10^{-6}$ | $2.32_9 \cdot 10^{-1}$ | $1.79_7 \cdot 10^{-1}$ | $2.05 \cdot 10^{-5}$ | $2.65 \cdot 10^{-5}$ |
| $4.26_5 \cdot 10^{-6}$ | $2.07_3 \cdot 10^{-1}$ | $1.61_3 \cdot 10^{-1}$ | $2.06 \cdot 10^{-5}$ | $2.64 \cdot 10^{-5}$ |
| $3.00_4 \cdot 10^{-6}$ | $1.44_1 \cdot 10^{-1}$ | $1.10_9 \cdot 10^{-1}$ | $2.08 \cdot 10^{-5}$ | $2.71 \cdot 10^{-5}$ |
| $9.89_3 \cdot 10^{-7}$ | $4.79_1 \cdot 10^{-2}$ | $3.70_7 \cdot 10^{-2}$ | $2.07 \cdot 10^{-5}$ | $2.67 \cdot 10^{-5}$ |
| | | Mean | $2.07 \cdot 10^{-5}$ | $2.67 \cdot 10^{-5}$ |
| | | Std. dev. | $0.02 \cdot 10^{-5}$<br>(± 0.9%) | $0.02 \cdot 10^{-5}$<br>(± 0.8%) |

[a] 11.8 days after the end of irradiation.

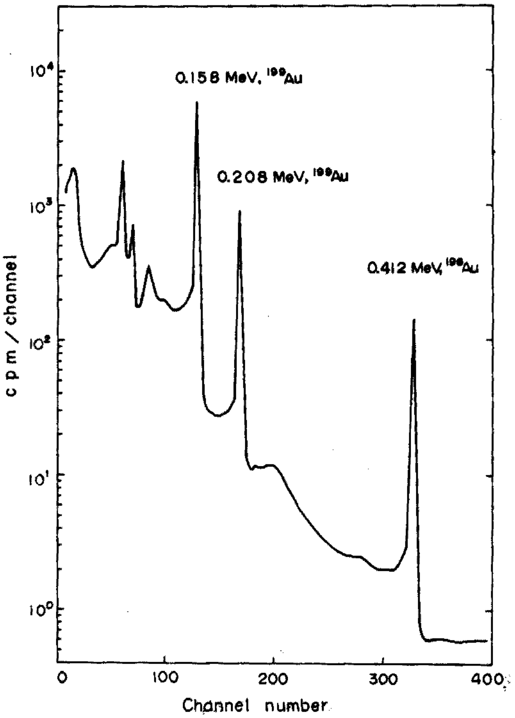
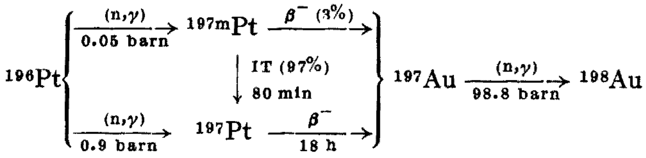


Fig. 4. $\gamma$-Ray spectrum of radiogold separated from irradiated platinum–gold mixture (Pt $1.42_8 \cdot 10^{-2}$ mg + Au $1.58_3 \cdot 10^{-3}$ $\mu$g), 182.1 h after the end of irradiation.

platinum mixture is shown in Fig. 4. From these spectra, photopeak areas were obtained for the 0.412-MeV $\gamma$-ray from $^{198}$Au and for the 0.158-MeV $\gamma$-ray from $^{199}$Au. The ratios of the areas were computed and corrected for decay at the end of the irradiation. Those ratios were related to the concentration ratios of gold to platinum: $R_W = K' R_{A_0}$, where $R_{A_0}$ denotes the activity ratio and $R_W$ is the weight ratio of gold to platinum.

In this case, the correction coefficient for $^{198}$Au arising from the original platinum was estimated as $\alpha = (A^{198}\mathrm{Au}/A^{199}\mathrm{Au})_{\mathrm{orig.}} = 1.02 \cdot 10^{-3}$. This corresponds to a gold amount of $5.3 \cdot 10^{-5}$ μg in an original platinum weight of $1.5 \cdot 10^{-2}$ mg.

The second-order reaction scheme is given by the following sequence:



The amount of $^{198}$Au formed through the above scheme, in the irradiation for 200 h at a flux of $4.0 \cdot 10^{13}$ n cm$^{-2}$ sec$^{-1}$, corresponded to an apparent gold amount of $5.3 \cdot 10^{-5}$ μg in an original platinum weight of $1.5 \cdot 10^{-2}$ mg. In this case, therefore, all $^{198}$Au activity in the correction coefficient came from the original platinum through the second-order reactions. The relation between the $R_W$ and the $R_{A_0}$ is given in Table II. A good proportionality was again obtained between them. A relative standard deviation of ±2.7% was obtained for amounts of gold ranging from $4.43 \cdot 10^{-3}$ μg to $4.35 \cdot 10^{-4}$ μg.

TABLE II

$R_W$ *vs.* $R_{A_0}$ FOR PLATINUM–GOLD MIXTURES

| $R_W$ | $R_{A_0}$ | $R_W/R_{A_0}$ |
|---|---|---|
| $2.89_1 \cdot 10^{-4}$ | $8.44_6 \cdot 10^{-2}$ | $3.47 \cdot 10^{-3}$ |
| $1.10_8 \cdot 10^{-4}$ | $3.32_2 \cdot 10^{-2}$ | $3.44 \cdot 10^{-3}$ |
| $4.86_1 \cdot 10^{-5}$ | $1.54_2 \cdot 10^{-2}$ | $3.38 \cdot 10^{-3}$ |
| $2.90_1 \cdot 10^{-5}$ | $9.01_5 \cdot 10^{-3}$ | $3.63 \cdot 10^{-3}$ |
|  | Mean | $3.48 \cdot 10^{-3}$ |
|  | Std. dev. | $0.09 \cdot 10^{-3}$<br>(± 2.7%) |

*Interference*

There were no additional problems with the reference elements other than the second-order interferences described above. Interferences which would arise from the samples are examined here. When a sample to be analyzed contains a considerable amount of calcium or platinum, corrections for activity from this origin would be required in the present calculations.

In addition, the reactions $^{46}$Ti(n,p)$^{46}$Sc and $^{47}$Ti(n,p)$^{47}$Sc would cause interferences. The literature data for the contents of calcium, platinum and titanium are listed in Table III[4–11]. The amounts of calcium and platinum, except in case of

TABLE III

CALCIUM, PLATINUM AND TITANIUM CONTENTS IN SAMPLES

|  | *G-1* | *W-1* | *JG-1* | *Canyon Diablo* | *Bruderheim* | *Indochinite* |
|---|---|---|---|---|---|---|
| Ca (%) | 1.0 [4] | 7.8 [4] |  |  | 1.27 [8,9] | 1.8 [10] |
| Pt (p.p.m.) | 0.0082 [5] | 0.0092 [5] |  | 5.7 [6], 9.95 [7] | 0.9 [6] | 50[a] [11] |
| Ti (p.p.m.) | 0.156 [4] | 0.64 [4] |  |  | 0.072 [8] | 0.56 [10] |

[a] Value of Australite.

TABLE IV

SCANDIUM CONTENT DETERMINED BY THIS METHOD

| *Sample* | *Sample taken (mg)* | *CaCO$_3$ added (mg as Ca)* | *Scandium content (p.p.m.)* | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | *This work* | | | | *Previous work* | |
| | | | *0.887 MeV* | *1.119 MeV* | *Average* | | | |
| | $16.9_8$ | $20.3_7$ | $2.7_1$ | $2.7_7$ | $2.7_4$ | | 2.7[12] | 2.75[13] |
| G-1 | $14.1_9$ | $20.2_5$ | $2.7_8$ | $2.7_6$ | $2.7_7$ | $2.7_5 \pm 0.0_2$ | 2.4[14] | 2.8[15] |
| (Granite) | $14.6_4$ | $20.5_8$ | $2.7_4$ | $2.7_4$ | $2.7_4$ | | | |
| | $6.6_9$ | $19.6_4$ | 31.5 | 31.7 | 31.6 | | 33[12] | 36[13] |
| W-1 | $5.2_6$ | $20.0_4$ | 33.5 | 33.7 | 33.6 | $32.1 \pm 1.5$ | 35[14] | 34[15] |
| (Diabase) | $6.1_7$ | $20.8_9$ | 31.1 | 30.9 | 31.0 | | | |
| JG-1 | $10.3_8$ | $20.6_9$ | $5.9_5$ | $5.9_7$ | $5.9_6$ | $5.9_8 \pm 0.0_2$ | | |
| (Granodiorite) | $9.6_9$ | $20.3_0$ | $5.9_3$ | $6.0_5$ | $5.9_9$ | | | |
| Bruderheim | $5.8_1$ | $19.9_4$ | $6.1_3$ | $6.0_1$ | $6.0_7$ | | | |
| (Stone) | $7.4_6$ | $20.5_9$ | $5.9_3$ | $5.9_5$ | $5.9_4$ | $5.9_8 \pm 0.0_9$ | 8[16] | |
| | $7.5_8$ | $20.3_5$ | $5.9_4$ | $5.9_2$ | $5.9_3$ | | | |
| Canyon Diablo | $536.9_4$ | $21.6_5$ | $0.13_5$ | $0.13_9$ | $0.13_7$ | $0.13_8 \pm 0.00_1$ | | |
| (Iron) | $512.0_2$ | $20.0_6$ | $0.13_8$ | $0.13_7$ | $0.13_8$ | | | |
| Indochinite | $13.3_2$ | $20.1_5$ | 10.8 | 10.9 | 10.9 | $10.9 \pm 0.1$ | 11.3[17] | |
| (Tektite) | $11.3_4$ | $20.2_7$ | 10.6 | 11.0 | 10.8 | | 10.4[17] | |

calcium in W-1, were so small as to cause no serious problem. If the amount of calcium in W-1 were excluded in the calculation, a result of 31.3 p.p.m. for scandium would have been obtained instead of 32.1 p.p.m. (Table IV). As to interferences with titanium, the experimental result showed that 1 mg of titanium produced the photopeak activities of 0.26 counts min$^{-1}$ for the 0.160-MeV $\gamma$-ray of $^{47}$Sc, and of 0.02 counts min$^{-1}$ for the 0.887-MeV $\gamma$-ray of $^{46}$Sc through the (n,p) reactions. From these facts and the data listed in Table III, it can be concluded that the amount of titanium in samples gave no trouble.

### *Sensitivity*

In the case of scandium analysis, a photopeak activity of 50 counts min$^{-1}$ can be determined accurately, being clearly distinguished from the background caused by accompanying activities. The lower limit of determination, therefore, is 0.005 $\mu$g for scandium under the described experimental conditions.

The limiting factor for the determination of gold is the background $^{198}$Au activity which comes from platinum through second-order reactions. This was estimated as 120 counts min$^{-1}$ under the 0.412-MeV $\gamma$-ray photopeak at the end of irradiation. When an amount of gold needed to give a photopeak activity of 120 counts min$^{-1}$ is selected as a limit of determination, it can be set at 0.0005 $\mu$g.

### *Data obtained*

The results obtained for scandium and gold are given in Tables IV and V, respectively, together with those by other workers. Since this internal-reference method was verified to be accurate even at the p.p.b. levels for both elements, the

ABLE V

OLD CONTENT DETERMINED BY THIS METHOD

| *ample* | *Sample taken (mg)* | *Platinum added (mg)* | *Gold content (p.p.b.)* | | |
|---|---|---|---|---|---|
| | | | *This work* | | *Previous work* |
| | | | | *Average* | |
| | $196.0_8$ | $1.37_8 \cdot 10^{-2}$ | $2.3_9$ | | 2.0 [6] |
| -1 | $208.4_2$ | $1.75_3 \cdot 10^{-2}$ | $2.3_7$ | $2.4_3 \pm 0.1_0$ | 2.6 [4] |
| Granite) | $214.9_6$ | $1.47_9 \cdot 10^{-2}$ | $2.5_3$ | | 4.6 [18] |
| V-1 | $199.3_8$ | $1.23_8 \cdot 10^{-2}$ | $3.5_3$ | | 4.8 [6] 4.9 [6] |
| Diabase) | $199.3_4$ | $1.19_7 \cdot 10^{-2}$ | $3.7_0$ | $3.6_2 \pm 0.0_9$ | 3.5 [4] 5.0 [18] |
| G-1 | $220.6_7$ | $1.27_6 \cdot 10^{-2}$ | $0.3_3$ | $0.3_1 \pm 0.0_2$ | |
| Granodiorite) | $203.6_4$ | $1.18_9 \cdot 10^{-2}$ | $0.2_9$ | | |
| | $49.3_3$ | $1.23_1 \cdot 10^{-2}$ | 172 | | 130 [6] |
| ruderheim | $49.6_7$ | $1.25_6 \cdot 10^{-2}$ | 138 | $156 \pm 18$ | 170 [6] |
| Stone) | $51.6_6$ | $1.36_6 \cdot 10^{-2}$ | 159 | | |
| anyon Diablo | $10.5_4$ | $1.42_2 \cdot 10^{-2}$ | 1370 | | |
| Iron) | $15.9_3$ | $1.45_8 \cdot 10^{-2}$ | 1330 | $1350 \pm 20$ | 1430 [6] |
| ndochinite | $201.3_1$ | $1.70_9 \cdot 10^{-2}$ | $1.8_9$ | | 1.5 (Australite) [6] |
| Tektite) | $204.2_1$ | $1.50_2 \cdot 10^{-2}$ | $1.7_1$ | $1.8_1 \pm 0.1_0$ | 1.3 (Java tektite) [6] |
| | $202.6_6$ | $1.38_5 \cdot 10^{-2}$ | $1.8_2$ | | 11.8 (Philipinite) [6] |

present results should be reliable. As to the new Japanese standard granodiorite, JG-1, the data for a number of traces in it will be accumulated in the future. The new datum for the scandium content in Canyon Diablo meteorite has been presented as 0.14 p.p.m. by this work.

In conclusion, the authors believe that the method presented here holds considerable promise for the accurate determinations of scandium and gold in samples of various origins.

The authors wish to express their thanks to Dr. MAKOTO SHIMA of the Institute of Physical and Chemical Research for providing meteorites and standard rocks, and to Professor YOSHIO KATO of the Tohoku University for the tektite.

## SUMMARY

An internal-reference method has been established for the determination of scandium and of gold by neutron activation analysis, with calcium and platinum, respectively, as the reference elements; the method has been applied to the determination of both elements in several materials of geochemical origin. The composite $\gamma$-ray spectra of scandium and gold activities arising from scandium and gold in a sample and from the element used as reference by the (n,$\gamma$) reaction followed by $\beta^-$-decay are measured. The results can be calculated on the basis of the activity ratio of the two species in terms of the photopeak areas. The success of the method depends on chemical separations and on the high resolving power of a lithium-drifted germanium detector. Sensitivity and accuracy were assessed by analyzing synthetic mixtures of known composition. The proposed method was verified to be accurate for both elements even at p.p.b. levels. The Bruderheim and Canyon Diablo meteorites, Indochinite tektite, and standard rocks, G-1, W-1 and JG-1 were tested.

## RÉSUMÉ

Une méthode à étalon interne est proposée pour le dosage du scandium et de l'or par activation neutronique, avec calcium et platine, respectivement, comme éléments de référence. Ce procédé a été appliqué au dosage de ces deux éléments dans divers échantillons géochimiques. La sensibilité et l'exactitude ont été déterminées à l'acide de mélanges synthétiques, de composition connue. Diverses roches standards ont été ainsi analysées.

## ZUSAMMENFASSUNG

Es ist eine Methode des inneren Vergleichs für die Bestimmung von Scandium und Gold durch Neutronenaktivierungsanalyse ausgearbeitet worden, wobei Calcium bzw. Platin als Vergleichselemente verwendet worden sind. Die Methode ist auf die Bestimmung beider Elemente in verschiedenen Proben geochemischen Ursprungs angewendet worden. Es werden die zusammengesetzten $\gamma$-Spektren der Scandium- und Goldaktivitäten gemessen, die aus Scandium und Gold in einer Probe und dem als Vergleich verwendeten Element durch die (n,$\gamma$)-Reaktion mit anschliessendem $\beta^-$-Zerfall entstehen. Die Ergebnisse werden aus dem Aktivitätsverhältnis der beiden Spezies, ausgedrückt durch die Photopeak-Flächen, erhalten. Der Erfolg der Methode hängt von den chemischen Trennungen und dem hohen Auflösungsvermögen des lithiumgedrifteten Germaniumdetektors ab. Empfindlichkeit und Genauigkeit wurden mittels Analyse synthetischer Mischungen bekannter Zusammensetzung abgeschätzt. Die vorgeschlagene Methode ist für beide Elemente sogar im p.p.b.-Bereich genau. Es wurden die Bruderheim- und Canyon-Diablo-Meteorite, Indochinit-Tektit und die Standardgesteine G-1, W-1 und JG-1 untersucht.

## REFERENCES

1 Y. Oka, T. Kato, H-T. Tsai and K. Nomura, *Bull. Chem. Soc. Japan*, 41 (1968) 329.
2 Y. Oka, T. Kato and H-T. Tsai, *Bull. Chem. Soc. Japan*, 41 (1968) 2427.
3 G. Friedlander, J. W. Kennedy and J. M. Miller, *Nuclear and Radiochemistry*, 2nd Edn., John Wiley, New York, 1964, p. 76.
4 M. Fleischer, *Geochim. Cosmochim. Acta*, 33 (1969) 65.
5 M. Fleischer, *Geochim. Cosmochim. Acta*, 29 (1965) 1263.
6 P. A. Baedecker and W. D. Ehmann, *Geochim. Cosmochim. Acta*, 29 (1965) 329.
7 H. Hamaguchi, T. Nakai and Y. Kamemoto, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 82 (1961) 1489.
8 M. Duke, A. D. Maynes and H. Brown, *J. Geophys. Res.*, 66 (1961) 3557.
9 A. D. Maynes, *Anal. Chim. Acta*, 32 (1965) 288.
10 B. Mason, *Meteorites*, John Wiley, New York, 1962, pp. 204, 207.
11 S. R. Taylor and M. Sachs, *Nature*, 188 (1960) 387.
12 J. C. Cobb, *Anal. Chem.*, 39 (1967) 127.
13 H. Hamaguchi, T. Watanabe, N. Onuma, K. Tomura and R. Kuroda, *Anal. Chim. Acta*, 33 (1965) 13.
14 J. C. Norman and L. A. Haskin, *Geochim. Cosmochim. Acta*, 32 (1968) 32.
15 D. M. Kemp and A. A. Smales, *Anal. Chim. Acta*, 23 (1960) 410.
16 M. Honda and M. Shima, *Earth Planetary Sci. Let.*, 2 (1967) 344.
17 J. C. Norman and L. A. Haskin, *Geochim. Cosmochim. Acta*, 32 (1968) 93.
18 Yu. G. Shcherbakov and G. A. Perzhogin, *Geochemistry (USSR)*, 1963 (1963) 882.

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

# DIRECT DETERMINATION OF FLUORIDE IN MISCELLANEOUS FLUORIDE MATERIALS WITH THE ORION FLUORIDE ELECTRODE

R. T. OLIVER* AND A. G. CLAYTON
*Alcoa Research Laboratories, New Kensington, Pa. 15068 (U.S.A.)*

(Received March 31st, 1970)

Fluoride salts are present in the electrolyte used in the Hall process for the production of aluminum. Determination of the concentration of fluoride in these salts has always been a tedious process demanding a caustic fusion, distillation to separate fluoride from aluminum and other interferences, and a colorimetric titration. The distillation and titration require a high degree of skill and experience.

An extensive investigation has been carried out to develop direct potentiometric methods with the Orion fluoride electrode for determining fluoride in such materials as Hall electrolyte (bath), technical-grade aluminum fluoride, cryolite, fluorspar, mixtures of alumina and aluminum fluoride, and solutions containing phosphate, silicate, aluminum and/or calcium.

The lanthanum fluoride membrane electrode (along with selective ion electrodes in general) is well suited for trace analysis by direct potentiometry[1] and for use as an indicator electrode for potentiometric titrations[2]. However, it has not been widely employed for the direct determination of fluoride in samples containing fluoride as a major constituent.

DURST[3] measured the fluoride content of $Na_2La_8Si_6O_{24}F_2$ by direct potentiometry. The sample was fused with sodium carbonate, dissolved in water, and the pH adjusted to 6 before the potentiometric measurements. VAN LOON[4] used a sodium hydroxide fusion to solubilize samples of fluorite, cryolite, topaz, chiolite and matlockite before measuring the fluoride by direct potentiometry. After fusion, the samples were dissolved in water, the pH was adjusted to 7 or 8 and the solutions were then diluted to less than 50 p.p.m. F before measurement.

This paper describes means of dissolving sample materials and masking interfering ions, details of the equipment used, and precision data for the results obtained. The effects of fluoride-complexing ions and the interference of hydroxyl ions are discussed.

## EXPERIMENTAL

### *Reagents*

Sodium carbonate and sodium tetraborate were of reagent grade.

Total ionic strength adjustment buffer contained 0.5 *M* potassium chloride, 0.5 *M* potassium acetate and 1 *M* sodium citrate.

---

* Present address: The Foxboro Company, Foxboro, Mass.

### *Equipment*

The Orion fluoride electrode (Model 94-09) was used throughout this work. Various reference electrodes were used, including sleeve-type saturated calomel electrodes and Ag–AgCl electrodes with either a ceramic plug junction, remote junction, or plastic sleeve-type junction.

Potential measurements were made with an Orion Model 801 Digital pH Meter. An air-driven magnetic stirrer was used because electric stirrers tended to heat the solutions, resulting in errors of measurement. Samples were analyzed at ambient temperature, which was maintained at 25±1°. At the maximum, this temperature variation could introduce a ±1.5% relative error.

### *Procedures*

Various techniques were developed for the preliminary treatment of different types of samples. Each procedure was designed to bring the fluoride into solution if necessary and to provide a constant (or at least similar) pH and ionic background.

Samples (0.5 g) of bath, cryolite, aluminum fluoride and fluorspar were fused with 6 g of sodium carbonate, dissolved in water, and adjusted to volume (250 ml) without pH adjustment.

Liquid samples were treated merely by diluting with water and a high ionic strength buffer and adjustment of pH to 8. The buffer used was 0.5 *M* in both potassium chloride and potassium acetate and, because of the high aluminum concentrations in most of the samples concerned, 1 *M* in sodium citrate.

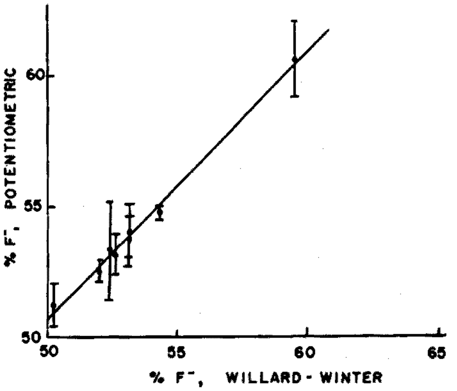
For alumina containing a small amount of aluminum fluoride, the sample (0.5 g) was first fused with 3 g of either sodium carbonate or 2:1 sodium carbonate–sodium tetraborate mixture, the melt was dissolved in water and ionic strength buffer, and the pH was adjusted to 8.

Standards of at least three concentrations bracketing the sample fluoride concentrations were prepared, containing the same amounts of fusion salts and buffer, and adjusted to the same pH as the samples. In the case of samples of alumina containing fluoride, standards were prepared from fluoride-free alumina, fused with sodium carbonate, and treated in the same manner as the samples. Known additions of sodium fluoride were made to produce the standard series. During both standardization and sample measurement, one reference standard was checked at frequent intervals and any drift was corrected with the calibration control. A calibration curve was drawn with the logarithm of fluoride concentration plotted against the cell potential.

## RESULTS AND DISCUSSION

Figure 1 shows the results of the direct determination of fluoride in Alcoa standard reference materials including one aluminum fluoride, one cryolite, and six Hall bath standards. The points on the curve are the average of five or six independent potentiometrically determined values (referred to the *y*-axis) plotted against the values obtained by the Willard–Winter method (on the *x*-axis). The bars through the points represent twice the standard deviations for the potentiometric measurements on each sample. The *x* values are assumed to be invariant, since they had previously been determined by umpire methods.

The straight line represents the best fitting line through these points as determined by the least squares method. The equation for this line is $y=1.004x-1.437$ and the coefficient of correlation is 0.949. Perfect agreement between the two methods would yield a slope of 1.00 instead of 1.04, an intercept of 0 instead of $-1.44$, and a correlation coefficient of 1.00 instead of 0.95. The intercept $-1.44$ is of minor significance because the curve is extrapolated to zero from measurements made at 50–60% fluoride. Differences in the matrix between sample and standard solutions may account for the high slope and the upward displacement (about 0.9% fluoride) of the regression curve.



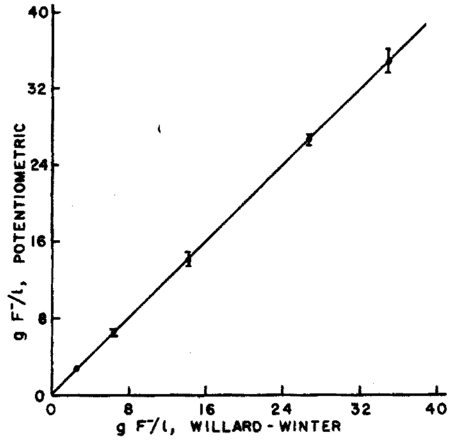


Fig. 1. Regression analysis, potentiometric *vs.* Willard–Winter determination of fluoride in Hall bath materials.

Fig. 2. Regression analysis, potentiometric *vs.* Willard–Winter determination of fluoride in solutions containing aluminum, phosphate, calcium and silicon.

Figure 2 shows a similar comparison of results for five solutions containing up to 35 g F/l, 10 g Al/l, 5 g Si/l, 2 g P/l, and 2 g Ca/l. The samples were diluted to less than 100 p.p.m. F with water and mixed with ionic strength buffer at pH 8 before measurement. The $y$ values are the average of 5 or 6 replicate fluoride determinations on each sample. The equation of the regression line is $y=0.98x+0.11$. The small positive intercept is probably a result of the difference between the matrices in the standard and sample solutions. The correlation coefficient, 0.999, and the standard deviations indicate that the method is sufficiently accurate and precise for routine analysis, although not precise enough for umpire analyses.

The data used in plotting the regression curves in Figs. 1 and 2 are tabulated in Table I. These figures show the absolute relationships of the potentiometric determinations to the Willard–Winter determinations.

The results for the determination of aluminum fluoride in $Al_2O_3$–$AlF_3$ mixtures are shown in Table II. These results are the averages of seven similar determinations. Four determinations were made after the samples had been fused with sodium carbonate; for the other three determinations the samples were fused with a mixture of sodium carbonate and sodium tetraborate. Slopes for the calibration curves were identical indicating no interference from borate at pH 8. The only difference in the results of the two methods is that the addition of borate in the fusion yields a completely soluble melt.

A sample of silica containing 18.9% fluoride (as determined by the Willard–Winter method) was analyzed by the same method used for bath samples, *i.e.*, it was fused with sodium carbonate and dissolved in water without buffering or pH adjustment. The mean of five repeated analyses was 20.05% fluoride with a standard deviation of 0.33%. At pH 12, fluorosilicates apparently are completely dissociated; consequently, silicon creates no interference in fluoride activity.

TABLE I

WILLARD–WINTER ($x$) AND POTENTIOMETRIC ($y$, ± $2S$) DATA FOR REGRESSION ANALYSES

| $x$ (% $F^-$) | $y$ (% $F^-$) | ± $2S$ |
|---|---|---|
| 59.17 | 60.54 | 1.76 |
| 54.30 | 54.84 | 0.23 |
| 53.15 | 54.25 | 0.89 |
| 53.15 | 53.85 | 0.98 |
| 52.40 | 53.35 | 1.80 |
| 52.45 | 53.30 | 0.73 |
| 51.90 | 52.55 | 0.58 |
| 50.20 | 51.35 | 1.02 |
| $x$ ($gF^-/l$) | $y$ ($gF^-/l$) | ± $2S$ |
| 35.2 | 34.55 | 1.33 |
| 26.2 | 25.50 | 0.66 |
| 14.3 | 14.18 | 0.70 |
| 6.2 | 6.22 | 0.29 |
| 2.6 | 2.57 | 0.08 |

TABLE II

PERCENTAGE OF ALUMINUM FLUORIDE IN $Al_2O_3$–$AlF_3$ MIXTURES

| *Sample no.* | *Mean* % $AlF_3$ | *Std. deviation* |
|---|---|---|
| 18 | $1.17_1$ | $0.02_1$ |
| 19 | $1.06_4$ | $0.03_1$ |
| 20 | $1.08_7$ | $0.07_7$ |
| 21 | $1.19_0$ | $0.03_1$ |
| 22 | $1.09_3$ | $0.05_8$ |
| 23 | $1.05_6$ | $0.03_6$ |

To show the effects of aluminum and hydroxyl ions on fluoride measurement, calibration curves were drawn for sodium fluoride solutions at pH 8 and pH 12, with and without aluminum at the 500-p.p.m. level. Curve 1 of Fig. 3 is the calibration curve at pH 8 for sodium fluoride standards. The shape and position of curve 3 indicates that at pH 8 the aluminum greatly lowered the fluoride activity in a non-uniform manner. At pH 12, solutions both with and without aluminum (curves 4 and 2, respectively) produced curves nearly coincident from 10 to 1,000 p.p.m. of fluoride but divergent at points below 10 p.p.m. The agreement in the upper half of the curves is consistent with the fact that at pH 12 the stability of sodium aluminate is greater than that of aluminum fluoride complexes[5]. However, below 10 p.p.m. the ratio of hydroxide activity to fluoride activity becomes high enough that the electrode becomes sensitive to hydroxyl ion[1,2] causing the change in slope in this area. Curve 5 shows that the addition of a high citrate ionic strength buffer to aluminum-containing samples at pH 8 has the same effect that hydroxide does at pH 12; that is, the aluminum citrate complex is more stable than the aluminum fluoride complex up to 100 p.p.m. F. Above 100 p.p.m., fluoride begins to compete with citrate for aluminum due to mass action. The apparent deviation from Nernstian response below 1 p.p.m. fluoride is probably due to the release of a small amount of fluoride from the lanthanum fluoride crystal by the high citrate concentration.

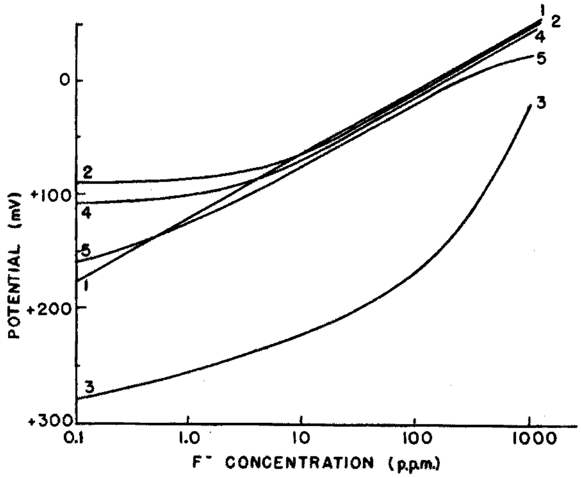


Fig. 3. Effects of aluminum (500 p.p.m.), pH, and buffer on calibration curve. (1) NaF at pH 8, (2) NaF at pH 12, (3) NaF + $Al^{3+}$ at pH 8, (4) NaF + $Al^{3+}$ at pH 12, (5) NaF + $Al^{3+}$ + buffer at pH 8.

The important point demonstrated by these curves is that hydroxide need not be considered an interference so long as solutions have higher fluoride activities than hydroxide activities. In fact, hydroxyl ion may be used to advantage in masking aluminum in cryolite or samples containing aluminum fluoride. Conveniently,the pH is between 11 and 12 when a sample fused with 3–6 g of sodium carbonate is dissolved in 250 ml of water. This simplifies the determination by eliminating the need for buffering or pH adjustment.

The most stable operation of the electrode (*i.e.*, optimum response time and repeatability, and least sensitivity to stirring rate) was found in the 100–1,000 p.p.m. range of fluoride. One feature of the direct potentiometric fluoride determination is that precision of measurement is the same regardless of the fluoride concentration provided that the electrode response is Nernstian[6]. Because of the logarithmic relationship, one millivolt difference in measurement represents a 4% relative difference in fluoride whether on the 1–10 p.p.m. or 100–1,000 p.p.m. scale. The maximum precision for currently available expanded scale pH meters is ±0.1 mV or ±0.4% relative fluoride. For aluminum fluoride samples, ±0.4% of 65% fluoride is ±0.26% fluoride; thus the absolute precision attainable with present equipment is about 0.25% fluoride. As refinements are made in the measuring technique this level of precision may be improved.

Errors in measurement have been primarily due to two basic factors: reference electrode problems and absorption effects. Reference electrode problems include irreproducible junction potentials caused by clogging of fiber or ceramic plugs and changes in ionic strength of samples caused by high leak rates from sleeve-type electrodes. Presently an Orion sleeve-type silver–silver chloride electrode with a filling solution similar in ionic strength to a buffered sample is used. Special care must be taken to avoid rapid leak rates. Absorption problems appear to stem largely from retention of solutions in microscopic crevices of either electrode and are minimized by thorough washing between samples, preferably with immersion. Correction of these problems improves the response time of the electrode and virtually eliminates drifting.

## SUMMARY

The Orion fluoride electrode was used to measure major concentrations of fluoride in samples containing aluminum, calcium and silicon without prior separation. Liquid samples were mixed with a total ionic strength buffer and direct potentiometric readings were compared to a calibration curve. Samples of $AlF_3$, $Na_3AlF_6$, $CaF_2$, and $SiO_2$ (containing 20% fluoride) were fused with sodium carbonate and dissolved in water or a total ionic strength buffer. For samples containing alumina which may not be rendered soluble by a carbonate fusion, a borate–carbonate fusion was used. Interferences were masked by the addition of equal concentrations of the interfering ion during the preparation of the standards. Results are shown for various samples analyzed by this technique and by the Willard–Winter distillation and titration. The direct method is accurate to within ±3% of the amount present.

## RÉSUMÉ

L'électrode fluorure Orion permet de mesurer des concentrations en fluorure dans des échantillons contenant aluminium, calcium et silicium sans séparation préalable. Les échantillons sont mélangés avec un tampon à force ionique totale; les lectures potentiométriques directes sont comparées à une courbe de calibrage. Les échantillons $AlF_3$, $Na_3AlF_6$, $CaF_2$ et $SiO_2$ (renfermant 20% de fluorure) sont fondus avec du carbonate de sodium et dissous dans l'eau ou un tampon à force ionique totale, les échantillons contenant de l'alumine doivent être fondus avec un mélange borate–carbonate. Les interférences sont évitées par addition de l'ion gênant, lors de la préparation des étalons. La précision de cette méthode directe est de ±3%.

## ZUSAMMENFASSUNG

Die Orion-Fluoridelektrode wurde benutzt, um grössere Konzentrationen an Fluorid in aluminium-, calcium- und siliciumhaltigen Proben ohne vorherige Trennung zu messen. Flüssige Proben wurden mit einem Gesamtionenstärke-Puffer versetzt und die potentiometrischen Messergebnisse mit einer Eichkurve verglichen. Proben von $AlF_3$, $Na_3AlF_6$, $CaF_2$ und $SiO_2$ (mit 20% Fluorid) wurden mit Natriumcarbonat geschmolzen und in Wasser oder einem Ionenstärkepuffer gelöst. Bei aluminium-

oxidhaltigen Proben, die durch einen Carbonataufschluss nicht löslich werden, wurde eine Borat–Carbonat-Schmelze benutzt. Störungen wurden unterbunden, indem zu den Standardproben gleiche Konzentrationen der störenden Ionen hinzugefügt wurden. Es werden die Ergebnisse verschiedener Proben vorgelegt, die nach dieser Methode und mittels Willard–Winter-Destillation und Titration analysiert worden sind. Die direkte Methode hat eine Genauigkeit von ±3% der vorhandenen Menge.

## REFERENCES

1 M. S. Frant and J. W. Ross, Jr., *Science*, 154 (1966) 1553.
2 J. J. Lingane, *Anal. Chem.*, 39 (1967) 881.
3 R. A. Durst, *National Bureau of Standards, Technical Note No. 455*, Oct. 1968, p. 100.
4 J. C. Van Loon, *Anal. Letters*, 1 (1968) 393.
5 A. Ringbom, *Complexation in Analytical Chemistry*, Interscience, New York, 1963, Table A.5, p. 353.
6 T. S. Light, in R. A. Durst, *Ion-Selective Electrodes*, N.B.S. Spec. Publ. No. 302, 1969.

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

# APPLICATION OF SILICONE RUBBER-BASED GRAPHITE ELECTRODES FOR CONTINUOUS FLOW MEASUREMENTS

## PART I. GENERAL RELATIONSHIPS

E. PUNGOR, ZS. FEHÉR* AND G. NAGY*
*Department of Analytical Chemistry, University of Chemical Industries, Veszprém (Hungary)*

(Received April 20th, 1970)

Recently, PUNGOR AND SZEPESVÁRY reported on the application of silicone rubber-based graphite electrodes in voltammetry[1]. They summarized the various types of graphite electrode and showed that the silicone rubber-based graphite electrodes could be readily applied for the determination of many organic and inorganic compounds in the potential range of $-0.5$ to $+1.5$ V (*vs.* S.C.E.) in stationary solutions. The electrodes showed memory effects only when the surface of the electrode had deteriorated either by the formation of a metal coating or by the deposition of a non-conducting polymer; these interfering reactions were only encountered in a few cases. Thus, it was considered worthwhile to employ the silicone rubber-based graphite electrodes in a number of analytical determinations, for these sensors have a well-defined surface area so that a high degree of accuracy is attainable.

In industrial practice, it is often desirable to determine the concentration of a given component in the reacting mixture, or in by-pass systems of the reacting mixture, instead of analysing samples taken intermittently from the reactor.

Many reports are available in the literature concerning the polarographic analysis of continuous flow systems. The parameters of the analysis have been studied in many cells for various types of electrodes. Unfortunately, no general idea can be obtained from the literature data regarding the parameters that affect the analysis. Opinions on the relationship between the flow rate and the current intensity are contradictory; this relationship is obviously very complicated when a dropping mercury electrode is used, as in this case the surface of the electrode changes as a function of time. Moreover, the form of the mercury drop can also be distorted to a certain extent depending on the flow rate. Among others WILSON AND SMITH[2], MANN[3], JURA[4], and MANCY AND OKUN[5] have investigated this phenomenon. MANCY AND OKUN showed that the flow rate influenced the shape of the drop and the drop time, and found that the current intensity is proportional to the 2.2-power of the flow rate.

According to KIMLA AND ŠTRAFELDA[6], the expression is more complex, namely:

$$i = 5840\, n c_0 D^{2/3} (mt)^{4/9} \cdot$$
$$v^{1/3} (1 + 1.86 D^{1/3} (mt)^{-1/9} v^{-1/3} + 0.00332 D^{-1/3} m^{4/9} t^{-5/9} v^{-2/3})$$

where $i$ is the current intensity, $n$ is the number of the electrons taking part in the

---

[*] Permanent address: United Works of Pharmaceutical and Diatetic Products, Budapest, Hungary.

electrochemical process, $c_0$ is the concentration of electroactive component, $m$ is the weight of mercury flowing from the capillary per second, $t$ is the drop time, $v$ is the flow rate, and $D$ is the diffusion coefficient.

The application of the conventional dropping mercury electrode in continuous measurements is hindered by the fact that the capillary undergoes various changes during the measurements. For example, in the determination of the oxygen content of water it becomes covered by calcium carbonate; moreover, the electrode is very sensitive to mechanical effects. Another disadvantage of this method is that the analysis requires a large amount of mercury and its cleaning is very troublesome. Attempts have been made to employ a horizontal dropping mercury electrode[7,8] or a dropping electrode provided with a large aperture[9]. However, the difficulties could not be eliminated completely by these modifications.

NOVAK[10] introduced the stationary mercury electrode in order to eliminate some of the drawbacks of the dropping mercury electrode. The author pointed out the advantages offered by the large surface of the electrode.

ZAVORKA AND ŠTRAFELDA[11] worked out a method to remove continuously the metal components amalgamating the electrode.

Among the solid electrodes, platinum electrodes were the first to be employed in flowing media. MÜLLER[12] found that the current intensity varied linearly with the concentration, while it was proportional to the logarithm of the flow rate, if a platinum electrode was used. JORDAN AND JAVICK[13] gave the following equation for the current intensity of a platinum electrode in the case of laminar flow:

$$i = 4\, nFAcV^{1/2}\, D^{2/3}\, (27)^{1/2}\, L^{1/2}\, \nu^{1/6}$$

where $nF$ is the number of coulombs flowing through the cell, $A$ is the effective surface area, $c$ is the concentration, $D$ is the diffusion coefficient, $\nu$ is the kinematic viscosity, $L$ is the length of generatrix of the conical electrode, and $V$ is the rate of flow (cm s$^{-1}$).

GURINOV AND GORBACHEV[14] employed platinum ring-electrodes in a flowing stream. They proved that in the case of laminar flow, the JORDAN–JAVICK relation is valid and the current is proportional to the square root of the flow rate. However, in the case of turbulent flow, a linear relationship was found between the current intensity and the flow rate.

KIMLA AND ŠTRAFELDA[15] studied the correlation between the current intensity and the rate of flow in the case of a cylindrical platinum electrode which was arranged parallel to the direction of the flow. The equation is as follows:

$$i = 0.618 \cdot 10^6\, nc_0 a^{2/3} l^{2/3} D^{2/3} v^{1/3} \{\log(b/a) - 1\}^{-1/3} \cdot$$
$$[1 + 0.556\, a^{-2/3} l^{1/3} D^{1/3} v^{-1/3} \{\log(b/a) - 1\}^{1/3}]$$

where $i$ is the current intensity, $a$ is the radius of the electrode, $l$ is the length of the electrode, $b$ is the radius of tube, in which the solution is streaming, $D$ is the diffusion coefficient, $n$ is the number of electrons taking part in electrochemical reaction, $c_0$ is the concentration of electroactive component, and $v$ is the linear flow rate of the solution.

Carbon electrodes were first employed by NOVAK[16] in streaming media.

Diffusion in the boundary layer between the solid surfaces and the streaming solution was theoretically discussed by LEVICH[17]. According to LEVICH, the thickness of the diffusion layer depends on the rate of flow ($U$) by a function $U^{-n}$, and the diffusion current varies accordingly as a function of $U^{-n}$; $n$ is constant in a certain range of flow rate and its numerical value varies according to the shape of the solid surface. For example, in the case of a sphere sedimenting slowly in a streaming liquid, $n$ is equal to 1/3 when the flow is laminar, but $n$ is equal to 1/2 in the case of a planar electrode placed parallel to the direction of flow, and in the case of a rotating disc electrode.

In continuous measurements an important problem is the proper selection of the reference electrode, which should be unpolarizable even after long periods of time. It is also desirable that the reference electrode need not be separated from the solution by a diaphragm, because the latter can considerably increase the resistance of the cell. According to NOVAK[18], conventional electrodes of the second kind are not suitable as reference electrodes for continuous voltammetric measurements because they are rather rapidly polarized; consequently, he employed a dropping mercury electrode as the reference electrode.

In the case of high flow rates, the dropping mercury electrode cannot be used. In such cases, NOVAK used a platinum foil in a streaming solution containing iron(II) and iron(III) ions[19]. This electrode can be employed both as cathode and anode.

A silver/silver chloride reference electrode has been employed in flowing potassium chloride or sodium chloride solution by BLAEDEL AND STROHL[20,21] as well as by LE PETIT AND THIELEMANN[22].

The aim of this work was to study the applicability of the silicone rubber-based graphite electrodes developed by PUNGOR AND SZEPESVÁRY[1] for analysis in flowing media.

## EXPERIMENTAL

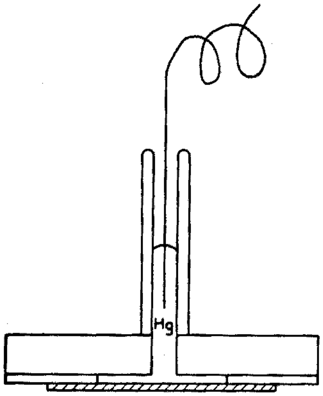
A Radelkis Polarograph Type OH 101/1 was employed for the measurements.

The effect of the surface area was investigated in a static electrolyte. The electrode shown in Fig. 1 had surface areas ranging from 0.13 to 9 cm$^2$. The surface area of the electrode was changed by gradually coating the silicone rubber layer with a film of $n$-cetyl alcohol. Microelectrodes with different surface areas were used to study the effect of the surface area of the electrode on the voltammetric current when the area was smaller than 0.13 cm$^2$. The microelectrode consisted of a capillary of 0.5–1.5 mm in diameter with a tip made of a silicone rubber layer filled with graphite. The capillary tube was filled with mercury to ensure electric contact. The determination of the surface area was simple in the case of large electrodes, whereas a microscope was necessary in the case of the microelectrodes.

The equipment employed for the measurements in flowing media is shown in Fig. 2. A silicone rubber-based graphite electrode and a Ag/AgCl electrode were placed in a tube, through which flowed the electrolyte to be investigated. The flow of solution was obtained by a hydrostatic method. Constant pressure was ensured by suitable level controllers, while various valves served for varying the rate of flow. The latter was determined by measuring the volume of liquid leaving the cell.

The intensity of the voltammetric current was recorded at constant potential selected on the basis of the voltammetric wave.

The supporting electrolyte was prepared from reagent-grade potassium chloride and the model substance chosen for the investigation was Propylon hydrochloride {3,4-dihydroxy-α-(isopropylaminomethyl)-benzyl alcohol hydrochloride}. The compound is a product of the United Works of Pharmaceutical and Diatetic Products.



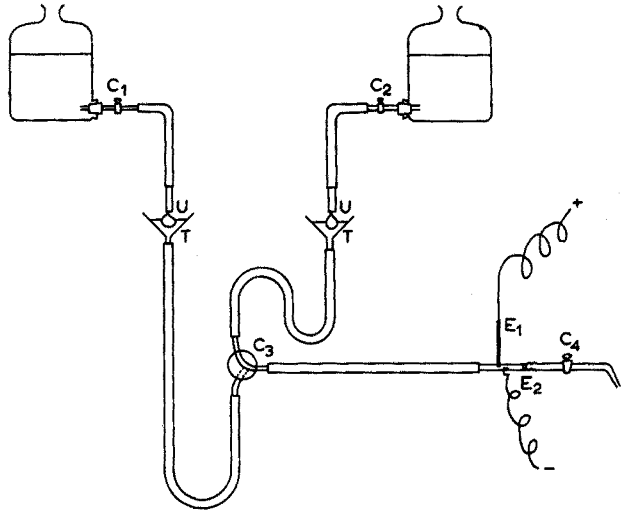


Fig. 1. Construction of an indicator electrode of large surface area.

Fig. 2. Apparatus for measurements in flowing media. ($E_1$) Indicator electrode; ($E_2$) reference electrode; ($C_1$, $C_2$, $C_3$, $C_4$) stopcocks. The left-hand reservoir contains 0.1 $M$ KCl and the right-hand reservoir 0.1 $M$ KCl + sample. U are floats, T are funnels.

## RESULTS AND DISCUSSION

### *Relation between the current intensity and the surface area of the electrode in stationary solution*

Figure 3 shows the voltammetric wave of Propylon in a stationary electrolyte. The electrode was polarized from 0 V (*vs.* Ag/AgCl electrode) towards positive potentials. When the current intensity was plotted *vs.* the concentration of the Propylon solutions over the range $1–7 \cdot 10^{-4}\,M$, a straight-line relationship was found, the current increasing from 2 to 12 μA over the above range. Similar measurements were performed with electrodes of various surface areas and the current constants were calculated. The latter ($k = i_p c^{-1}$, where $i_p$ is the current intensity and $c$ is the concentration of the electroactive component in the solution) were plotted *vs.* the surface area of the electrode as shown in Fig. 4 and Table I; the relation obtained with electrodes of small surface areas is also shown as an inset.

The experimental results can be explained as follows:

According to the RANDLES–SEVČIK equation,

$$i = kAn^{3/2}\,v^{1/2}\,c \qquad (1)$$

where $i$ is the current intensity, $k$ is a constant, $A$ is the surface area, $v$ is the rate of polarization, $c$ is the concentration, and $n$ is the number of electrons.

According to this equation, the current intensity varies linearly with the surface of the electrode. This was proved to be valid for indicator electrodes of surface area of 1–9 cm². In the interpretation of the whole curve obtained experimentally, the spherical diffusion also should be taken into account. The active points of the electrode surface are partly on the more or less convex surface and partly on the edges of the silicone rubber membrane layer. The surface area of the electrode is thus greater than can be measured geometrically. These surfaces which cannot be measured, also influence the current intensity through spherical diffusion. This spherical diffusion cannot be taken into account by considering the radius of the curvature of the surface, but it can be considered by the so-called equivalent radius ($r_2$) and its corresponding surface area ($A_2$).

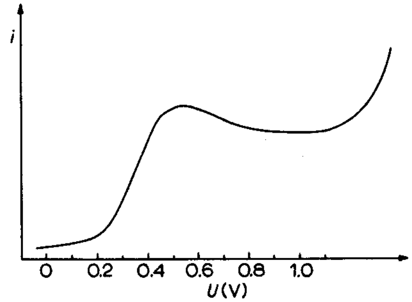


Fig. 3. Voltammetric wave of Propylon in stationary electrolyte. Supporting electrolyte, $10^{-1}$ *M* KCl; sensitivity, $1 \cdot 10^{-7}$ A mm$^{-1}$; rate of polarization, 2 V min$^{-1}$.

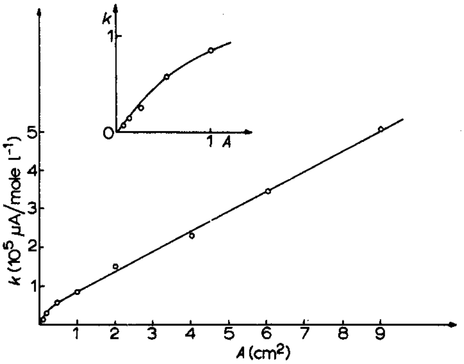


Fig. 4. Dependence of the voltammetric current constant on the geometrical surface area of the electrode.

TABLE I

RELATIONSHIP BETWEEN SURFACE AREA AND VOLTAMMETRIC CURRENT CONSTANT

| *Surface area (mm²)* | *Voltammetric current constant ($\mu A$ $M^{-1}$)* |
|---|---|
| 0.333 | 572 |
| 0.827 | 1500 |
| 1.160 | 1873 |
| 2.413 | 1235 |
| 2.907 | 2500 |
| 3.240 | 2970 |

Thus the amount of the electroactive component, which diffuses to the electrode surface in the unit of time is:

$$\frac{\mathrm{d}N}{\mathrm{d}t} = k_1 Dc\left(\frac{A_1}{r_1} + \frac{A_2}{r_2} + \frac{A_1+A_2}{(\pi Dt)^{1/2}}\right) \tag{2}$$

where $k_1$ is a constant, $D$ is the diffusion coefficient of the electroactive component in the solution, $c$ is the concentration of the electroactive component in the solution, $t$ is the time of the diffusion transport, $A_1$ is the surface area corresponding to the geometrical radius ($r_1$), and $A_2$ is the surface area belonging to the equivalent radius ($r_2$).

Equation (2) indicates that in general the voltammetric current intensity is influenced by the parameters of the membrane layer through three factors. Consequently the value of the current constant cannot be determined by measuring the geometrical surface area alone. Table I shows that if the geometrical surface area is increased, then the current constant is not necessarily increased.

Equation (2) can be simplified by using electrodes of different surface areas, shown in Fig. 1. In this case:

$$r_1 \rightarrow \infty \tag{3}$$

Thus, eqn. (2) can be rewritten:

$$\frac{\mathrm{d}N}{\mathrm{d}t} = k_1 Dc \left(\frac{A_2}{r_2} + \frac{A_1 + A_2}{(\pi Dt)^{1/2}}\right) \tag{4}$$

It is obvious, that the edges are determined by the surface area $A_1$ as follows:

$$A_2 = k_2\, A_1^{1/2} \tag{5}$$

where $k_2$ is a constant.

In this case $r_2$ can be considered as a constant so if $k_2 \cdot r_2^{-1} = k_3$, then

$$\frac{\mathrm{d}N}{\mathrm{d}t} = k_1 Dc \left(k_3 A_1^{1/2} + \frac{A_1 + k_2 A_1^{1/2}}{(\pi Dt)^{1/2}}\right) \tag{6}$$

In conclusion, it can be stated that the amount of an electroactive component which diffuses to the electrode surface, varies as a function of the geometrical surface of the electrode and can be described by means of eqn. (6).

The shape of the function written in eqn. (6) is the same as that of curve of the current constant *vs.* surface area (Fig. 4).

The above considerations show that even electrodes of equal surface areas may have different current constants, thus in these cases the constant employed in the appropriate determination has to be evaluated experimentally.

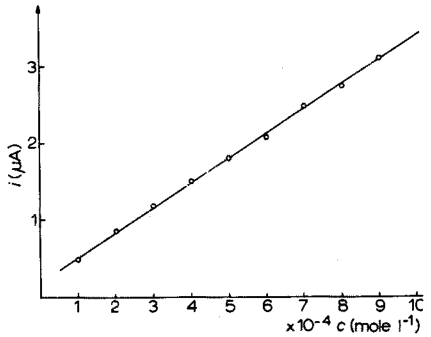
### *Measurements in flowing media*

The cells used for the measurements were characterized by the hold-up, *i.e.* the volume of the liquid flowing through the cross-section of the cell during the time elapsed from the moment when the electroactive solution entered the cell to the moment when the total value of the signal was attained. This volume was approximately equal to 0.35 ml and was found to be independent of the rate of flow (up to 0.06 ml $s^{-1}$) in the case of polyethylene cells which were found best for the measurements.

The stability of the measuring cell was also checked; it was found that neither the potential of the reference electrode nor the performance of the indicator electrode changed even during 8 h of continuous measurements.

The relationship between the current intensity and the concentration of the solution is of great importance from an analytical viewpoint. The results of the measurements carried out at constant potential are shown in Fig. 5. From these, it is apparent that the method is suitable for analytical determinations in a flowing electrolyte, when the flow rate is constant.

The results obtained for the relation between the current intensity and the rate of flow at constant Propylon concentration and constant potential are shown in Fig. 6. Analysis of this curve showed that the relationship between the current intensity and the square root of the flow rate is linear (Figs. 7 and 8). These results are in good agreement with LEVICH's theoretical results obtained for a planar electrode placed parallel to the direction of the stream.



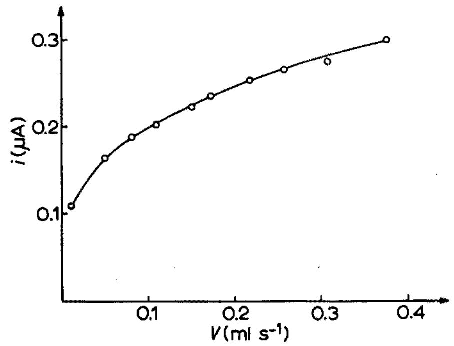
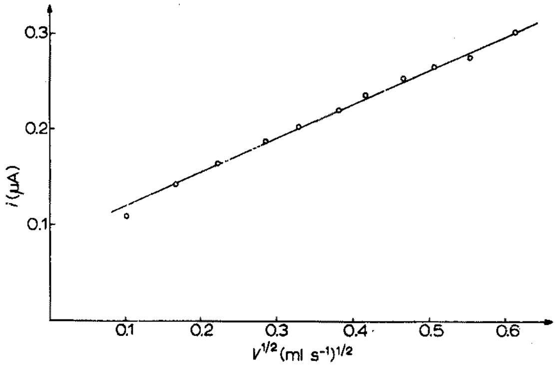


Fig. 5. Voltammetric calibration curve for Propylon in flowing media. Potential, $+0.7$ V; sensitivity, $8\cdot10^{-8}$ A mm$^{-1}$; rate of flow, 1.0 ml s$^{-1}$.

Fig. 6. Dependence of the voltammetric current on the flow rate. Concentration of Propylon, $10^{-4}$ *M*; potential, $+0.75$ V; sensitivity, $4\cdot10^{-9}$ A mm$^{-1}$.



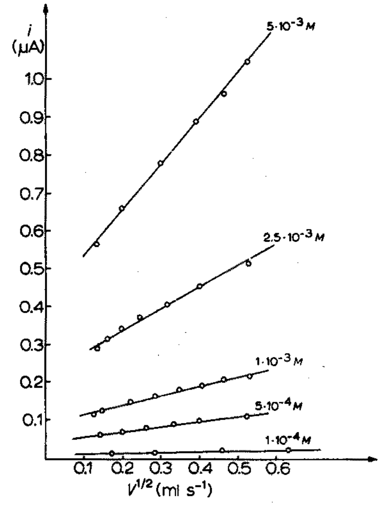


Fig. 7. Dependence of the voltammetric current on the square root of the flow rate. Conditions as for Fig. 6.

Fig. 8. Dependence of the voltammetric current on the square root of the flow rate in solutions of various concentrations. Potential, $+0.75$ V; sensitivity (A mm$^{-1}$), $1\cdot10^{-9}$; $1.5\cdot10^{-9}$; $3\cdot10^{-9}$; $8\cdot10^{-9}$; $1.5\cdot10^{-8}$.

The results prove that the voltammetric current is diffusion-controlled and that the relationship can be used for measurements of unknown flow rates.

## SUMMARY

The behaviour of the silicone rubber-based graphite electrode was studied. The relationship between the surface area of the electrode and the voltammetric current constant was established. The applicability of the silicone rubber-based graphite electrode in the continuous analysis of electrolyte flows was also investigated. At constant potential, the current exhibited a linear dependence on the concentration of the depolarizer and on the square root of the flow rate.

## RÉSUMÉ

Une étude est effectuée sur le comportement des électrodes de graphite caoutchouc silicone. On établit la relation entre surface de l'électrode et constante de courant voltammétrique. On examine également les possibilités d'application de ces électrodes pour l'analyse en continu. A potentiel constant, le courant est fonction de la concentration, linéairement, et de l'écoulement, à la racine carrée.

## ZUSAMMENFASSUNG

Das Verhalten der Silicongummi-Graphitelektrode wurde untersucht. Die Beziehung zwischen Elektrodenoberfläche und voltammetrischer Stromkonstante wurde ermittelt. Ausserdem wurde die Anwendbarkeit der Silicongummi-Graphitelektrode in der kontinuierlichen Analyse strömender Elektrolyte untersucht. Bei konstantem Potential zeigt der Strom eine lineare Abhängigkeit von der Konzentration des Depolarisators und von der Quadratwurzel der Fliessgeschwindigkeit.

## REFERENCES

1 E. PUNGOR AND É. SZEPESVÁRY, *Anal. Chim. Acta*, 43 (1968) 289.
2 L. D. WILSON AND R. J. SMITH, *Anal. Chem.*, 25 (1953) 218.
3 C. K. MANN, *Anal. Chem.*, 29 (1957) 1385.
4 W. H. JURA, *Anal. Chem.*, 26 (1954) 1121.
5 K. H. MANCY AND D. A. OKUN, *Anal. Chem.*, 32 (1960) 108.
6 A. KIMLA AND F. ŠTRAFELDA, *Collection Czech. Chem. Commun.*, 29 (1964) 2913.
7 L. ŠERAK, *Z. Phys. Chem.*, (1958) 84.
8 C. P. TYLER AND J. H. KARCHMER, *Anal. Chem.*, 31 (1959) 499, 509.
9 R. BRIGGS, F. S. DAVIES, G. VAN DIJKE AND G. KNOWLES, *Chem. Ind. (London)*, (1957) 223.
10 J. V. A. NOVAK, *Collection Czech. Chem. Commun.*, 21 (1956) 662.
11 J. ZAVORKA AND F. ŠTRAFELDA, *Chem. Listy*, 51 (1957) 2374.
12 O. H. MÜLLER, *J. Am. Chem. Soc.*, 69 (1947) 2992.
13 J. JORDAN AND R. A. JAVICK, *J. Am. Chem. Soc.*, 80 (1958) 3846.
14 YU. S. GURINOV AND S. V. GORBACHEV, *Zh. Fiz. Khim.*, 38 (1964) 2245.
15 A. KIMLA AND F. ŠTRAFELDA, *Collection Czech. Chem. Commun.*, 31 (1966) 1189.
16 J. V. A. NOVAK, *Collection Czech. Chem. Commun.*, 25 (1960) 3098.
17 V. G. LEVICH, *Physicochemical Hydrodynamics*, Englewood Cliffs, 1962.
18 J. V. A. NOVAK, *Collection Czech. Chem. Commun.*, 20 (1955) 1076.
19 J. V. A. NOVAK, *Collection Czech. Chem. Commun.*, 20 (1955) 1095.
20 W. J. BLAEDEL AND J. H. STROHL, *Anal. Chem.*, 33 (1961) 1631.
21 W. J. BLAEDEL AND J. H. STROHL, *Anal. Chem.*, 36 (1964) 445.
22 G. LE PETIT AND H. THIELEMANN, *Chem. Tech. (Berlin)*, 17 (1965) 479.

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

# THE COULOMETRIC GENERATION OF LOWER OXIDATION STATES OF VANADIUM

G. A. BRYDON* AND G. F. ATKINSON
*Department of Chemistry, University of Waterloo, Waterloo, Ontario (Canada)*

(Received February 9th, 1970)

The oxidation–reduction chemistry of vanadium is rather complicated, for the metal possesses several common oxidation states. In acidic solution, vanadium(V) and (IV) are moderately strong oxidizing agents, while vanadium(III) and (II) are reducing agents. The standard electrode potentials for the half-reactions in acid solution of the common oxidation states are[1]:

$$VO_2^+ + 2\,H^+ + e^- = VO^{2+} + H_2O \qquad E^0 = +1.00\ V$$

$$VO^{2+} + 2\,H^+ + e^- = V^{3+} + H_2O \qquad E^0 = +0.36\ V$$

$$V^{3+} + e^- = V^{2+} \qquad E^0 = -0.26\ V$$

In the absence of dissolved oxygen, vanadium(V), (IV) and (III) are stable in acid solution, while vanadium(II) is unstable with respect to oxidation by hydrogen ion. Both vanadium(III) and (II) are susceptible to air oxidation, the latter being oxidized very rapidly.

As LINGANE has recently emphasized[2], this versatile redox chemistry of vanadium permits a large number of possibilities for detection and determination of the element. From an alternative viewpoint, vanadium furnishes a number of potential redox reagents. All four of the common oxidation states have been recommended as volumetric reagents, of which the most important are the pentavalent and divalent states[3,4].

The controlled-current coulometric generation of vanadium species as redox titrants has not been extensively studied. DAVIS[5] determined permanganate with vanadium(IV) coulometrically generated from a vanadium(V) precursor. The use of vanadium(III) as a coulometric titrant for iron(III), vanadium(V), manganese(VII) and chromium(VI) has been reported, the reductant being generated at a mercury cathode from a sodium acetate–hydrochloric acid buffer solution[6]. The controlled-potential oxidation and reduction of vanadium has been studied by MEITES *et al.*[7,8] and more recently by RIGDON AND HARRAR[9].

Controlled-current coulometry is used for the *in situ* generation of titrants, eliminating the preparation and storage of standard solutions. This is especially advantageous in dealing with species which are less stable because of their strength as oxidants and reductants. To attain high current-generation efficiency, it is usually necessary to stabilize such species by complexation and pH control. Examination of the Nernst equation shows that if a reduced species is complexed preferentially to

---

* Present address: Dept. of Chemistry, University of South Florida, Tampa, Fla. 33620, U.S.A.

the oxidized member of its couple, the resulting potential is shifted to less reducing values and thus the likelihood of reduction of solvent is decreased. This increases the current efficiency of the coulometric generation process.

In this study of the generation of vanadium(III) and (II) species, the effects of cathode material, complexants, and acidity upon current efficiencies have been examined.

## EXPERIMENTAL

### *Reagents*

Solutions of vanadium(IV) were prepared from vanadyl sulfate $VOSO_4 \cdot 2H_2O$ (Fisher Scientific Co.) and standardized by titration with cerium(IV) sulfate by the method of SRIRAMAM AND RAO[10]. All other reagents were of ACS or Analysed Reagent grades. Nitrogen was purified by passing it through two vanadium(II) chloride towers and a deionized water spray trap. All solutions were prepared with deionized water.

### *Apparatus*

The Leeds and Northrup 7961 coulometric titration cell kit was used for quantitative experiments as in a previous study[11]. The cell was modified to provide a mercury pool cathode by joining a downward-pointing male Luer fitting to the bottom close to the edge of the 100-ml beaker. To this was attached a 25-mm length of 18-gauge platinum needle tubing with Kel-F Luer terminations, followed by a length of similarly fitted Teflon tubing of 1.6 mm internal diameter leading to a levelling bulb. Electrical contact was made to the platinum tubing. When a genera-

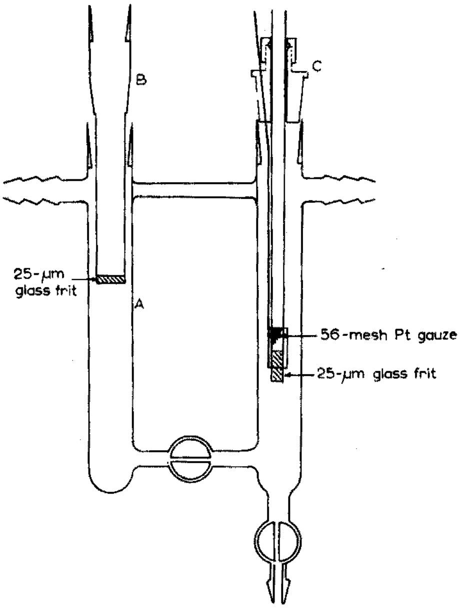


Fig. 1. Schwartz tube electrolytic cell. (A) Cell body, (B) auxiliary electrode compartment, (C) working compartment stopper assembly.

tion experiment was to be followed by a volumetric titration in the generating cell, the mercury surface was lowered into the bore of the glass Luer fitting and a drop of carbon tetrachloride was inserted on top of it to preclude any reaction with mercury.

Preparative electrolyses for qualitative observation and testing of products were performed on a smaller scale in a cell made from a Schwartz absorption tube (Kontes Glass Co., Vineland, N.J., K-89150). This cell (Fig. 1) could also be operated with either a platinum electrode or a mercury pool.

The source of electrolysis current was a Sargent Model IV Coulometric Current Source, which had been calibrated. A Honeywell Model 620 Digital Voltmeter was connected directly to platinum and saturated calomel electrodes for potentiometric measurements. Measurements of pH were made with a Leeds and Northrup 7401-A1 meter and glass and silver–silver chloride microelectrodes.

### *Procedures*

The predominant oxidation state in each solution could be identified by the characteristic colour. The reaction of each solution with iron(III) and copper(II) was also tested, since vanadium(III) is oxidized by iron(III), while vanadium(II), but not vanadium(III), reduces copper(II) to the metal.

Current efficiencies were determined by passing a measured amount of charge, and then titrating the reduced vanadium species formed with air-free standard iron(III) chloride. These titrations were followed potentiometrically at a platinum electrode.

Formal potentials were determined by reducing a known quantity of vanadyl sulfate to vanadium(II) by exhaustive electrolysis in 0.5 *M* perchloric acid at a mercury cathode and high current density, then purging the solution of hydrogen with nitrogen. A three-fold molar excess of air-free vanadyl sulfate was next added, giving a solution equimolar in vanadium(IV) and (III). An excess of complexing agent was added, and the pH was varied by adding air-free 5 *M* sodium hydroxide until precipitation occurred. Solution potentials were followed as before at a platinum electrode. Temperatures were maintained at $25 \pm 1°$.

## RESULTS AND DISCUSSION

A number of possible complexing reagents were examined under various conditions of acidity and in the presence of platinum and of mercury cathodes, to compare their ability to support efficient generation of vanadium(III) or (II) and their ability to stabilize these reductants. The results presented in Table I show that little success was attained in generating either species in unbuffered solutions less than 0.1 *M* in strong acid, regardless of electrode material. Only in 1 *M* potassium oxalate solution was successful reduction obtained: with a platinum cathode, a green solution of vanadium(III) was formed, from which a brown hydrolysis product later precipitated. At a mercury cathode, in the presence of sulfuric acid, the solution went through green to the intense reddish-brown reported by LINGANE AND MEITES for vanadium(II) oxalate solutions[12].

Platinum was found to be an unsatisfactory cathode material for the efficient reduction of vanadium(IV) solutions. A wide range of current densities was used by

TABLE I

SURVEY OF COULOMETRIC REDUCTION OF VANADIUM(IV) IN THE PRESENCE OF VARIOUS REAGENTS

| *Initial solution* | | | | *Cathode* | | *Product* |
|---|---|---|---|---|---|---|
| *Reagent* | *(M)* | *$VOSO_4$ (M)* | *pH* | *Pt* | *Hg* | |
| *Conditions giving no reduced vanadium species* | | | | | | |
| None | | 0.086 | 2.4 | | × | Hydrolytic solids |
| $Na_2SO_4$ | 1.0 | 0.05 | | × | | Hydrolytic solids |
| KCl | 0.2 | 0.05 | | | × | Hydrolytic solids |
| EDTA | 0.14 | 0.07 | 6.0 | × | | Hydrolytic solids |
| $H_2SO_4$ | 0.1, 3.8 | 0.05 | | × | | Reduction of $H^+$ |
| *Conditions giving vanadium(III) species* | | | | | | |
| $K_2C_2O_4$ | 1.0 | 0.05 | | × | | Green solution, then brown precipitate |
| Kojic acid | 0.15 | 0.05 | 2.0 | × | | Green solution |
| $H_2SO_4$ | 0.1 | 0.043 | | | × | Green solution, then brown precipitate |
| EDTA[a] | 0.14 | 0.07 | 3.8 | | × | Hydrolytic solids |
| EDTA<br>$K_2SO_4$ | 0.5<br>0.05 | 0.05 | 9.5 | | × | Hydrolytic solids |
| SSA[b] | 0.12 | 0.04 | 1.1, 1.4, 2.2 | × | | Green solutions |
| *Conditions giving vanadium(III) and vanadium(II) species* | | | | | | |
| $K_2C_2O_4$<br>$H_2SO_4$ | 1.0<br>0.2 | 0.5 | | | × | Reddish-brown solution |
| SSA | 0.2 | 0.05 | | | × | Violet solution |
| HCl | 0.1 | 0.05 | | | × | Violet solution |
| $HClO_4$ | 1.0 | 0.02 | | | × | Violet solution |

[a] EDTA = ethylenediaminetetraacetic acid, disodium salt.
[b] SSA = 5-sulfosalicylic acid.

selecting different currents and electrode areas. Vanadium(III) was generated only from oxalate, sulfosalicylic acid, and kojic acid solutions, and even in these media the titrations with iron(III) showed no current efficiencies greater than 10%. In no case was evidence of vanadium(II) generation obtained.

By contrast, both vanadium(III) and (II) could be generated at the mercury cathode in all but neutral and weakly-complexing media. Current efficiencies, though low, were higher than those on platinum and reached 46% when vanadium(III) was generated in sulfosalicylic acid at pH 1.1.

A group of experiments was performed to determine formal potentials of the vanadium(IV)/(III) system directly in the presence of several complexing agents. Figure 2 shows these potentials as a function of pH for systems equimolar in vanadium(IV) and (III). Taking the values obtained in 0.5 *M* perchloric acid solution (which is negligibly complexing) as reference, the largest increase in the observed potential was produced by phosphate, although precipitation occurred at a lower pH in this system. Sulfosalicylic acid also gave an increase in potential. Acetate produced a slight decrease, which at first sight is surprising since an acetate–hydrochloric acid buffer was reported to be a satisfactory medium for coulometric titrations with vanadium(III)[6]. A possible explanation is that the chloride ion in the buffer used stabilized vanadium(III) relative to vanadium(IV).

The results of the formal potential experiments confirm that phosphoric acid could be an effective stabilizer of vanadium(III). Previous workers have noted that vanadium(III) solutions are stable in air for 2 h in 8–12 *M* phosphoric acid solution[13].

A more detailed study of the generation efficiencies of vanadium(III) and (II) in phosphoric acid at a mercury cathode was undertaken. Comparisons were made with a similar perchloric acid medium which is non-complexing. In most determinations, current sufficient to produce 600 $\mu$eq of reduced species at 100% efficiency was passed through a solution containing 500 $\mu$moles of vanadium(IV). Thus, both vanadium(III) and (II) should theoretically be produced, so that both overall reductive current efficiency, and the ratio of vanadium(III) to vanadium(II) can be observed.

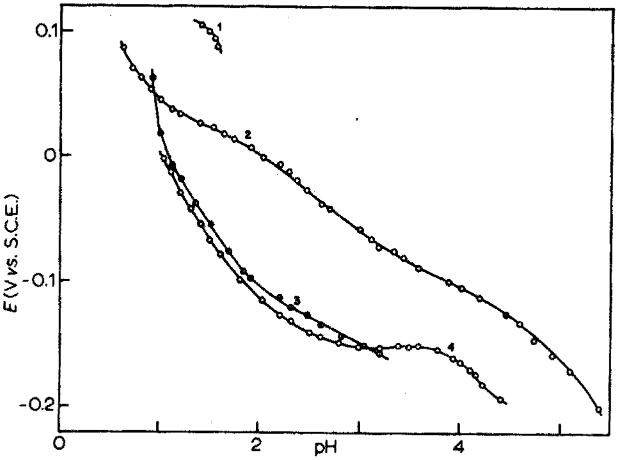


Fig. 2. Formal potentials of the vanadium(IV)/(III) couple in the presence of complexing agents. (1) 3:1 molar excess of sodium dihydrogen phosphate, (2) 2:1 molar excess of 5-sulfosalicylic acid, (3) no complexing agent, (4) 3:1 molar excess of sodium acetate.

TABLE II

GENERATION CURRENT EFFICIENCIES FOR VANADIUM(III) AND (II) IN PHOSPHORIC AND PERCHLORIC ACID MEDIA AT VARIOUS CURRENT DENSITIES

| *Electrolyte* | | *Current density ($mA\ cm^{-2}$)* | *Overall generation efficiency (%)* | *Fraction generated as vanadium(III)* |
|---|---|---|---|---|
| *$HClO_4$ (M)* | *$H_3PO_4$ (M)* | | | |
| 0.5 | | 2.9 | 66.7 | 0.95 |
| | 0.5 | 0.6 | 43.6 | 1.0 |
| | 0.5 | 0.6 | 37.6 | 1.0 |
| | 0.5 | 2.9 | 82.3 | 0.96 |
| | 0.5 | 5.8 | 81.2 | 0.94 |
| | 0.1 | 0.6 | 49.3 | 1.0 |
| | 0.1 | 0.6 | 46.1 | 1.0 |

Results in Table II show that higher current densities favour higher current efficiencies. Efficiencies at low current density decrease somewhat with increasing phosphoric acid concentration. Not unexpectedly, the precision obtained in duplicate determinations was poor at these low efficiencies[14]. The lower current densities necessitate longer generation times, and instability of the generated species is most likely to cause the low efficiencies noted.

In agreement with previous work[13], vanadium(III) in phosphoric acid solutions was found to be exceptionally stable to air. The characteristic bright green colour was visible for several days in solutions in open containers. The violet vanadium(II) species were very unstable to air and their colour disappeared in a few seconds of exposure.

Phosphoric acid offers substantial promise for the stabilization of reduced states of vanadium. None of the efficiencies thus far obtained are sufficient for practical coulometric generation of these external to the site of ultimate use, but there are indications that further studies, including the effect of current density, in higher phosphoric acid concentrations, are worthwhile.

This work was supported by the National Research Council of Canada. One author (G.A.B.) was the holder of a Province of Ontario Graduate Fellowship.

## SUMMARY

The controlled-current coulometric generation of vanadium(III) and (II) has been studied as a function of cathode material, pH, and composition of the precursor electrolyte. Some formal potentials of the vanadium(IV)/(III) couple have been measured. The current efficiency of vanadium(III) generation was greatest at higher current densities at a mercury cathode in the presence of phosphoric acid.

## RÉSUMÉ

On a effectué une étude sur la coulométrie à courant contrôlé du vanadium(III) et (II), en fonction de la cathode, du pH et de la composition de l'électrolyte. Le rendement du vanadium(III) formé est plus grand à des densités de courant plus élevées, à une cathode de mercure, en présence d'acide phosphorique.

## ZUSAMMENFASSUNG

Die stromkontrollierte coulometrische Erzeugung von Vanadin(III) und -(II) ist als Funktion des Kathodenmaterials, des pH-Wertes und der Elektrolytzusammensetzung untersucht worden. Einige formale Potentiale des Vanadin(IV)/(III)-Paars sind gemessen worden. Die Stromausbeute bei der Vanadin(III)-Erzeugung war am grössten bei höheren Stromdichten an einer Quecksilberkathode in Gegenwart von Phosphorsäure.

## REFERENCES

1 L. G. Sillén and A. E. Martell, *Stability Constants*, Spec. Publ. No. 17, The Chemical Society, London, 1964.
2 J. J. Lingane, *Analytical Chemistry of Selected Metallic Elements*, Reinhold, New York, 1966, p. 127.
3 I. M. Kolthoff and R. Belcher *Volumetric Analysis, Vol. 3*, Interscience, New York, 1957.
4 A. Berka, J. Vulterin and J. Zyka, *Newer Redox Titrants*, Pergamon, Oxford, 1965.
5 D. G. Davis, *Anal. Chem.*, 31 (1959) 1460.
6 T. C. Tso and P. L. Chu, *Hua Hsueh Hsueh Pao*, 31 (1965) 86.
7 L. Meites and S. A. Moros, *Anal. Chem.*, 31 (1959) 23.
8 Y. Israel and L. Meites, *J. Electroanal. Chem.*, 8 (1964) 99.
9 L. P. Rigdon and J. E. Harrar, *Anal. Chem.*, 41 (1969) 1673.
10 K. Sriramam and G. G. Rao, *Talanta*, 13 (1966) 1468.
11 G. F. Atkinson and G. A. Brydon, *Anal. Chim. Acta*, 46 (1969) 309.
12 J. J. Lingane and L. Meites, *J. Am. Chem. Soc.*, 69 (1947) 1021.
13 G. Rao and L. S. A. Dikshitulu, *Talanta*, 10 (1963) 295.
14 J. J. Lingane, *Electroanalytical Chemistry*, 2nd Edn., Interscience, New York, 1958, p. 450.

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

# THE TITRIMETRIC DETERMINATION OF MERCURY(II) WITH THIOACETAMIDE*

BARBARA COULTER AND DAVID G. BUSH
*Research Laboratories, Eastman Kodak Company, Rochester, N. Y. 14650 (U.S.A.)*

(Received March 2nd, 1970)

Halides interfere with most titrimetric methods for mercury[1-3], since they form very stable complexes with mercury(II)[4]. There is no interference from halides when the mercury is titrated with sulfide ions, yielding the extremely insoluble mercury(II) sulfide. Stable thioamides[5,6] are used as a convenient source of sulfide ions for this titration.

ANDREASOV *et al.*[5] report the potentiometric titration of mercury in alkaline solution with thiobenzamide as a titrant. BUSH *et al.*[6] from this Laboratory suggested the use of thioacetamide as a reagent for the potentiometric titration of silver. This paper extends the use of this reagent to the titration of mercury.

The hydrolysis of thioacetamide is promoted by either hydrogen or hydroxyl ions in solution and leads ultimately to the formation of hydrogen sulfide or sulfide ion, depending on the pH[7,8]. When thioacetamide is added to an alkaline solution, the precipitation of mercury(II) sulfide occurs rapidly enough to permit the use of this reagent for the potentiometric titration of mercury(II). Because of the exceedingly low solubility of mercury(II) sulfide, there is a very large change in the potential of a silver sulfide indicator electrode at the equivalence point. If mercury(II) is present in the original solution as the slightly dissociated (ethylenedinitrilo)-tetraacetic acid (EDTA) or iodide complexes, the magnitude of the potential break at the end-point is somewhat diminished but remains satisfactory for accurate volumetric work.

The procedure is recommended for the determination of mercury in organic compounds as well as of those mercury salts which are directly soluble in alkaline EDTA. Organomercury compounds which are not soluble in alkaline EDTA may be dissolved in nitric acid after Schöniger combustion[2].

## EXPERIMENTAL

### *Apparatus*

The measurements were recorded on a Metrohm Potentiograph Model E 436 with auxiliary head Model E 436E, used with a Beckman Model 39170 fiber-tip saturated calomel electrode and a silver sulfide electrode. The latter is made by immersing a Beckman 39261 silver billet electrode or a pure silver rod into an alkaline solution of thioacetamide for 20 min. It is cleaned weekly with a commercial scouring powder to remove the sulfide coating which builds up. A Thomas-Ogg Model 11 oxygen flask igniter was used for the Schöniger combustion.

---

* Presented at the Anachem Conference, Detroit, Mich., October 5, 1967.

### *Reagents*

*Buffer solution, pH 5.* Mix 0.1 *M* potassium acid phthalate and 0.05 *M* trisodium phosphate solutions in the ratio of 50:24 (v/v), and add 0.5 g/l of powdered thymol.

*Thioacetamide stock solution, 0.025 M.* Dissolve 1.9 g of thioacetamide in 1 l of pH 5 buffer solution. This solution is stable, decreasing in titre by about 1% per month. Dilute 200 ml of this solution to 1 l with the pH 5 buffer to provide a 0.005 *M* standard solution.

*(Ethylenedinitrilo)tetraacetic acid (EDTA) solution, 0.1 M.* Dissolve 37.2 g of disodium EDTA in 1 l of water.

*Gelatin, 1.2% solution.* Dissolve 12 g of gelatin in hot water, 0.5 g of thymol and dilute to 1 l.

*Mercury standard, 0.005 M.* Dilut-IT mercury analytical concentrate ampoules (J. T. Baker No. 4783) were diluted to 100 ml. If desired, any mercury salt may be used and standardized with thiocyanate[1].

### *Procedures*

*Soluble samples.* To a solution containing 5–15 mg of mercury and 30 ml of 0.1 *M* EDTA (disodium salt) add 20 ml of 2 *M* sodium hydroxide and 20 ml of 1.2% gelatin; titrate the resulting solution with 0.005 *M* thioacetamide using the calomel and silver sulfide electrodes. The thioacetamide concentration can be adjusted for samples containing more or less than the suggested amount of mercury. This method can be applied to organic and inorganic mercury compounds which are soluble in alkaline EDTA solutions.

*Insoluble organic samples.* Enclose samples containing 5–15 mg of mercury in a combustible wrapper and place in the sample holder of a Schöniger combustion flask sufficiently large to insure complete burning of the sample (*e.g.* a 500-ml flask was used for 30-mg samples). After addition of about 10 ml of concentrated nitric acid and flushing of the flask with oxygen, insert the stopper and ignite the wrapper. When the flask has cooled, rinse the stopper, flask neck, and holder with hot nitric acid or *aqua regia*. Reflux the contents for 15 min, cool, and transfer to a beaker. After neutralization of the solution with sodium hydroxide, apply the same procedure as for soluble compounds.

### *Standardization of thioacetamide solution*

To 10.0 ml of the 0.005 *M* standard mercury solution, add 30 ml of 0.1 *M* EDTA, 20 ml of 2 *M* sodium hydroxide, 20 ml of 1.2% gelatin, and 20 ml of water. Titrate the resulting solution with 0.005 *M* thioacetamide to the inflection point of the titration curve.

## DISCUSSION

### *Experimental variables*

Figure 1 illustrates the titration curves obtained and shows the effect of variations in alkalinity on the titration curve. Alkalinities of 0.4 *M* and above result in identical curves with a large potential break at the equivalence point.

The EDTA added to these samples performs a dual function: (*a*) it complexes the mercury(II) and prevents the precipitation of mercury(II) oxide; and (*b*) it prevents the precipitation of most common metal sulfides. FLASCHKA[9] has shown that EDTA prevents the precipitation of the sulfides of a number of metals, including copper, cadmium, zinc, cobalt, and nickel. Varying the EDTA concentration from $1 \cdot 10^{-3}$ *M* (about 3 times the mercury concentration) to $3 \cdot 10^{-2}$ *M* (about 90 times the mercury concentration) has little effect on the shape of the titration curve.

It is advisable to make the mercury sample alkaline just before titration. Alkaline EDTA solutions of mercury which stand for several hours before titration tend to give low results.

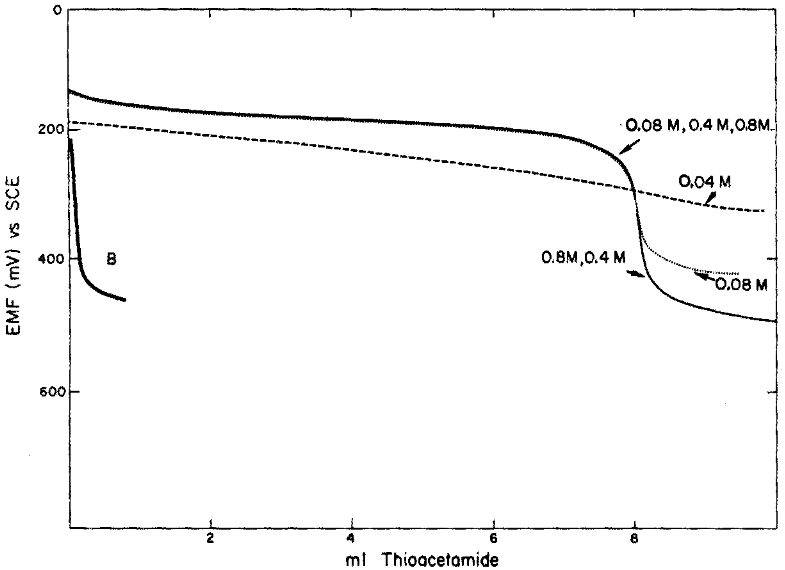


Fig. 1. Effect of alkali. Curves obtained on titration of 100-ml samples where $[Hg^{2+}] = 3.8 \cdot 10^{-4}$ *M*, [EDTA] = 0.015 *M*, [OH] = variable as indicated, B = titration blank.

The silver sulfide electrode comes to equilibrium with the solution very rapidly and little time is required between additions of the reagent. Most of the titrations reported in this paper were done on the Metrohm titrator and required 10 min for a 10-ml titration. In the absence of gelatin, the mercury(II) sulfide formed by the reaction tends to agglomerate and form a loose coating on the electrode surface, which, if left undisturbed, may slow the electrode response. Addition of gelatin keeps the precipitate suspended in solution.

The Schöniger combustion of mercury samples deposits reduced mercury and mercury salts on the walls of the combustion flask. In most cases, a 15-min refluxing with nitric acid[2] completely solubilizes the sample. The combustion of organomercury compounds containing chlorine, however, often produces a white precipitate (probably mercury(I) chloride), which is insoluble in hot nitric acid. In this instance, *aqua regia* is required to effect solution. When this treatment is necessary, combustion flags of quartz are preferred to platinum flags, which are somewhat soluble in *aqua regia*. The dissolved platinum is precipitated by sulfide ion constituting an interference in the method.

*Effect of halides*

Chloride or bromide ions, even in great excess, have no effect on the titration. Iodide ions, especially when present in large excess, alter the shape of the titration curve (Fig. 2). Even when present in a 32-fold excess over mercury, however, iodide ion does not decrease the accuracy of the titration.

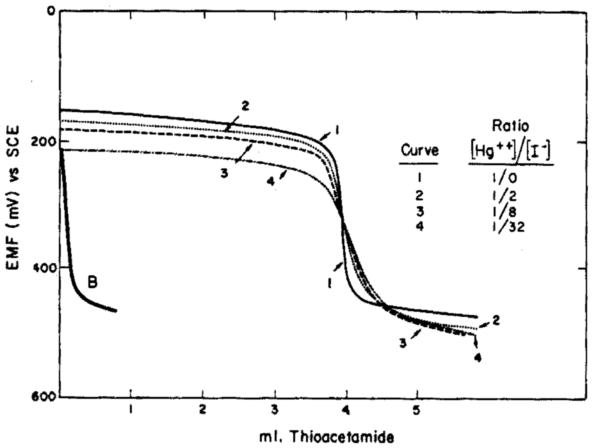


Fig. 2. Effect of iodide. Curves obtained on titration of 100-ml samples where $[Hg^{2+}] = 2.5 \cdot 10^{-4}$ *M*, [EDTA] = 0.03 *M*, [OH] = 0.4 *M*, $[I^-]$ = variable as indicated, B = blank titration.

RESULTS

In replicate standardizations of 0.005 *M* thioacetamide with 0.05 mmole of mercury(II), 10.08, 10.11, 10.08, and 10.04 ml of thioacetamide were required. The average is 10.08 ml with a standard deviation of 0.03 ml.

Six mercury compounds were analyzed, each in quadruplicate. The first three were readily soluble in alkaline EDTA and the last three required Schöniger combustion before analysis. The results are summarized in Table I.

These results indicate that the relative standard deviation of the method is

TABLE I

RESULTS OF DETERMINATION OF MERCURY(II) WITH THIOACETAMIDE

| *Compound* | *% Mercury* | | |
|---|---|---|---|
| | *Results*[a] | *Std. dev.* | *Theory* |
| Mercury(II) chloride | 73.2 | 0.38 | 73.9 |
| Mercury(II) oxide | 94.3 | 0.36 | 92.6 |
| Mercury(II) thiocyanatocobaltate | 40.6 | 0.08 | 40.8 |
| Mercury(II) cyclohexanebutyrate (NBS Standard No. 1064) | 36.2 | 0.31 | (36.2)[b] |
| Chloromercuribenzoic acid | 56.5 | 0.55 | 56.2 |
| 2,5-Dichloro-3,6-dihydroxy-*p*-benzoquinone, mercury(II) salt | 49.9 | 0.74 | 49.2 |

[a] Average of 4 determinations.

[b] Theoretical assay for this compound is 37.2% mercury; 36.2 is the assay (± 0.36%) furnished by NBS for this sample.

about 1%. Since the average of the analyses for mercury(II) cyclohexanebutyrate (NBS standard 1064) is exactly the same as that reported by NBS, the relative error of the method is also 1%.

It has been our experience that the Schöniger combustion can be incomplete with certain samples, leading to irregular, low results. In this instance, mixing the original sample with potassium perchlorate will increase the combustion temperature so that reaction is complete. This technique was applied to the analysis of chloromercuribenzoic acid.

Studies in this Laboratory indicate that silver[6] and platinum (see DISCUSSION) are the only common metals that precipitate in the presence of EDTA and, therefore, interfere with the method.

None of the common anions (like nitrate, phosphate, sulfate, acetate, halides) interfere. Cyanide, however, interferes with the potentiometric detection of the endpoint even though it does not prevent the precipitation of mercury(II) sulfide.

The authors are grateful to Miss NANCY L. MILLER, Mr. E. WILLIAM ROBESON, and Mr. ANTHONY J. BRANCATO for preliminary work on the method. They are also indebted to Dr. EDWIN P. PRZYBYLOWICZ for his helpful discussions.

## SUMMARY

A rapid method is described for the direct titration of mercury(II) in the presence of halide ions, which cause interference in classical titrations. The mercury(II), in an alkaline solution as the (ethylenedinitrilo)tetraacetic acid (EDTA) complex, is titrated potentiometrically with thioacetamide and a silver sulfide–calomel electrode pair. Organomercury compounds which are not soluble in alkaline EDTA may be titrated after Schöniger combustion. The relative error of the method is 1%.

## RÉSUMÉ

Une méthode rapide est décrite pour le titrage direct du mercure(II) en présence d'ions halogénures, gênant les titrages classiques. Le mercure(II), en solution alcaline, sous forme de complexe EDTA (acide éthylènedinitrilotétracétique) est titré potentiométriquement avec la thioacétamide à l'aide d'électrodes sulfure d'argent–calomel. Les composés organomercuriques, insolubles dans l'EDTA alcalin peuvent être titrés après combustion Schöniger. L'erreur relative est de 1%.

## ZUSAMMENFASSUNG

Es wird eine schnelle Methode für die direkte Titration von Quecksilber(II) in Gegenwart von Halogenidionen beschrieben, die bei klassischen Titrationsverfahren Störungen verursachen. Das in alkalischer Lösung als Äthylendinitrilotetraessigsäure(EDTA)-Komplex vorliegende Quecksilber(II) wird potentiometrisch mit Thioacetamid und einem Silbersulfid–Kalomel-Elektrodenpaar titriert. Organische Quecksilberverbindungen, die in alkalischem EDTA nicht löslich sind, können nach einer Schöniger-Verbrennung titriert werden. Der relative Fehler des Verfahrens ist 1%.

## REFERENCES

1 I. M. KOLTHOFF, P. J. ELVING AND E. P. SANDELL (Editors), *Treatise on Analytical Chemistry*, Part II, Vol. 3, Interscience, New York, 1961, p. 278.
2 P. GOUVERNEUR AND W. HOEDEMAN, *Anal. Chim. Acta*, 30 (1964) 519.
3 B. C. SOUTHWORTH, J. H. HODECKER AND K. D. FLEISCHER, *Anal. Chem.*, 30 (1958) 1152.
4 L. G. SILLÉN, *Stability Constants of Metal-Ion Complexes*, Spec. Publ. No. 17, The Chemical Society, London, 1964, pp. 292, 326, and 341.
5 L. M. ANDREASOV, E. I. VAIL, V. A. KREMER, Z. N. CHERNYAEVA AND S. A. REZNICHENKO, *Izv. Vysshikh Uchebn. Zavedenii Khim. i Khim. Tekhnol.*, 10 (1967) 743.
6 D. G. BUSH, C. W. ZUEHLKE AND A. E. BALLARD, *Anal. Chem.*, 31 (1959) 1368.
7 C. N. REILLEY, *Advances in Analytical Chemistry and Instrumentation*, Interscience, New York, 1960, p. 298.
8 D. C. TAYLOR, D. M. SMITH AND E. H. SWIFT, *Anal. Chem.*, 36 (1964) 1924.
9 H. FLASCHKA, *Z. Anal. Chem.*, 137 (1952) 107; *Chemist-Analyst*, 44 (1955) 2.

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

# DETERMINATION OF CARBON BY NON-AQUEOUS TITRATION AFTER COMBUSTION IN A HIGH-FREQUENCY INDUCTION FURNACE

## APPLICATION TO ROCKS, STONY METEORITES AND METALLURGICAL SAMPLES*

JOY G. SEN GUPTA
*Geological Survey of Canada, Ottawa 4, Ontario (Canada)*

(Received March 31st, 1970)

For studying geological processes, it is necessary to know the carbon content of a large number of rock samples; this requires a sufficiently rapid, widely applicable and accurate method of determining carbon. The conventional gravimetric method involves collection of carbon dioxide, evolved during combustion (total carbon) or acid treatment (carbonate carbon) of the sample, in Ascarite; for determining small amounts of carbon in rocks, this method suffers from some uncertainty because it involves measuring a small difference in weight (*i.e.* a fraction of a mg) for an absorption tube which may weigh over 100 g, and the weighing conditions tend to be critical. Thermal conductivity measurements, as incorporated in some commercial carbon analyzers, are rapid and accurate but involve expensive and sophisticated equipment.

Many aqueous and non-aqueous titrimetric procedures have been proposed (see a recent review by DAVIES[1]) as alternative methods of determining the final product in carbon analysis. The conventional aqueous absorbents for carbon dioxide are sodium hydroxide and baryta, but the latter is preferred because barium carbonate is sparingly soluble. However, LINDNER[2] found that absorption of large amounts of carbon dioxide in baryta was incomplete and BELCHER *et al.*[3] noted that acidimetric titration of excess of baryta after carbon dioxide absorption led to significant errors greater than those of the gravimetric method.

Various non-aqueous titrimetric methods for determining carbon dioxide are available. A simple procedure involving the use of pyridine containing a small amount (0.6% w/w) of monoethanolamine as absorbent was proposed by BLOM *et al.*[4,5] who used it for the determination of carbon in steel[5] and organic compounds[6]. In this method, carbon dioxide reacts with monoethanolamine forming hydroxyethylcarbamic acid, which is directly titrated with sodium methylate in presence of thymol blue as the indicator.

An attempt to adapt the titration technique of BLOM *et al.*[4,5] for determining carbon dioxide evolved by heating various geological and metallurgical samples in an induction furnace was not successful. Difficulties were found from back-up of the pyridine caused by excessive back-pressure developed during combustion, and

---

* This paper was presented at the joint American Chemical Society, Chemical Institute of Canada Meeting (Division of Analytical Chemistry), May 25–29, 1970, Toronto, Ontario (Canada).

removal of absorbent from the receiver[4] at the high oxygen pressures needed to avoid back-up. Moreover, a fine white precipitate of sodium methyl carbonate was formed during combustion of some samples containing medium or high carbon contents; the precipitate adhered to vessel walls, obscured the end-point and clogged the buret tip.

An alternative approach was therefore made to utilize this method. The modification involved the use of a series of two receivers (as used for sulphur[7,8]) containing pyridine or acetone, monoethanolamine (0.6% v/v), an excess of sodium methylate and phenolphthalein indicator. Phenolphthalein was used because it gave a more distinct end-point than thymol blue. For samples with very high carbon contents, pyridine or acetone in the above solution was replaced by a 1:1 mixture of acetone and methanol. Carbon dioxide is consumed by sodium methylate either as such and/or as the carbamic acid derivative. The excess sodium methylate is then back-titrated by a standard methanolic solution of benzoic acid.

The pyridine method worked well for most silicate rocks, stony meteorites and steels ($<1\%$ C), but had the disadvantage of toxicity and obnoxious odour. Moreover, low results were obtained in pyridine medium for samples containing $>1\%$ C. Acetone either alone (for 0–10 mg C) or in conjunction with methanol (for determining 10–30 mg C in some samples such as limestone, dolomite, silicon carbide, etc.) served as a more effective and cheaper absorbent.

Induction heating was preferred to resistance heating for the determination of total carbon. With dual apparatus assemblies, two determinations could be completed in about 10 min by the induction heating procedure and 25 min by the acid evolution method (excluding the time for weighing the sample and preparation of solutions).

Although a method was required for accurately determining carbon primarily in geological materials, the procedures for total carbon as described in this paper were tested also for other available standard materials, *e.g.* metallurgical samples.

## EXPERIMENTAL

### *Equipment*

*Induction furnace and parts.* A Leco high-frequency induction furnace model 522 (220 V) equipped with a two-combustion tube unit was used. A Leco silica combustion tube with built-in jet (#550-212) was joined with a polyvinyl tube to the "right-angle bend" (part #550-119). A Leco dust trap (#501-10), a sulphur trap (#503-33) and a catalyst furnace (#507-000) were used on each side of the furnace. Leco heavy-duty crucibles (#528-35 or 528-120), covers with holes (#528-40) and iron chips (#501-077) were required. A tube (like an empty Leco sulphur trap) packed with magnesium perchlorate was used as a water drier, and a gas washing bottle (Fisher Scientific Co., #11-184) was employed as an empty trap (*cf.* Fig. 1).

Figures 1 and 2 show the apparatus used. All connections were made by polyvinyl (Nalgon) tubing and joints were sealed with Kronig Cement (Fisher Scientific Co.).

### *Reagents and solutions*

Analytical grade Celite (diatomaceous silica) (Johns-Manville Product, Fisher

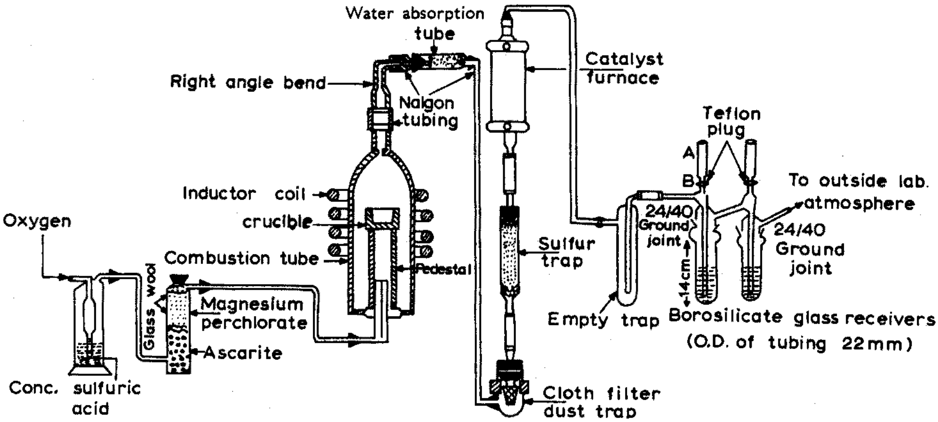


Fig. 1. Determination of total carbon by combustion in a high-frequency induction furnace and non-aqueous titration.

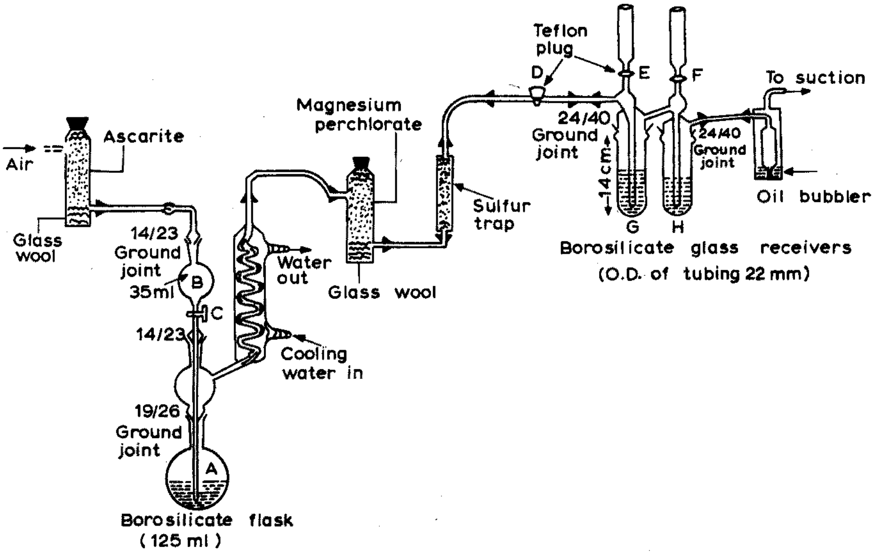


Fig. 2. Determination of carbonate carbon by acid evolution of $CO_2$ and non-aqueous titration.

Scientific #C-211) was freed from carbon impurity by igniting it with occasional stirring in a quartz dish at 1200°.

Vanadium pentoxide powder (certified reagent, Fisher Scientific Co.) was used.

*Standard benzoic acid solution.* For a 0.1 *M* solution, dissolve 1.2216 g of benzoic acid crystals ("Baker Analyzed" reagent, 99.97%), in methanol (A.C.S. grade) in a 100-ml volumetric flask and dilute to volume with the same solvent. Prepare a 0.5 *M* solution analogously.

*Sodium methylate solution.* Dissolve appropriate amounts of sodium methylate (Fisher, purified reagent) in methanol in a polyethylene beaker to make *ca.* 0.1 or 1 *M* solutions as required and store in tightly stoppered polyethylene bottles.

Both standard benzoic acid (0.1 *M*) and sodium methylate (0.1 *M*) solutions are stable for several weeks. However, 1 *M* sodium methylate solution should be freshly prepared, as some precipitate settles out after a few days. If during preparation of 1 *M* sodium methylate solution in methanol there is an undissolved residue, it should be filtered through a dry Whatman #40 filter paper. A methanolic 1% (w/v) solution of phenolphthalein was used.

### *Determination of total carbon by the induction furnace method (Fig. 1)*

As both sides of the furnace are capable of independent operation, two determinations are carried out simultaneously.

*Procedure 1. Recommended for silicate rocks, stony meteorites and metallurgical samples.* Weigh the sample (0.5 g for most silicate rocks having $>0.1\%$ $CO_2$ and 1.0 g for samples containing $<0.1\%$ $CO_2$; for metallurgical samples, the weight should be 0.2 g for 0.5–5.0% C and 0.5 g for 0–0.5% C) and transfer it to a crucible. For rocks, clays and stony meteorites add 1.5 g of iron chips and 0.5 g of vanadium pentoxide. For metallurgical samples, reduce the weight of iron chips by an amount equal to weight of the sample and add 0.5 g of vanadium pentoxide. Mix well with a narrow nickel spatula and brush off any adhering particles into the crucible. Cover with a crucible cover, place the crucible on the pedestal of the induction furnace and introduce it into the combustion tube by raising the locking mechanism handle. Pass a moderate current of oxygen (3–5 bubbles per sec) for 2–3 min.

Place 10ml of acetone (or pyridine for $<1\%$C) containing 0.6%(v/v) monoethanolamine in each of the two receivers and add 6 drops of phenolphthalein indicator to each. Depending on the amount of carbon dioxide to be expected, add 0.5–10 ml of 0.1 *M* sodium methylate (*e.g.* 1.0 ml per 4.4 mg $CO_2$, plus 1.0 ml in excess) to the first receiver and 0.5–1.0 ml of the same to the second receiver. In all cases add a known excess (equivalent to 0.5–1.0% more carbon dioxide than will actually be present in the sample being analyzed) of sodium methylate solution to the first receiver.

Connect the receivers (see Fig. 1), and increase the flow of oxygen (1–1.5 l $min^{-1}$) through the system and turn on the furnace. After the initial back-pressure has diminished, adjust the oxygen flow through the receiving solutions to about 2–3 bubbles per sec. If during the combustion of a sample of unknown carbon content, the pink solution in the first receiver becomes colourless, then add a measured excess of sodium methylate solution to funnel A of the first receiver (*cf.* Fig. 1). Allow the methylate solution to enter the first receiver by momentarily opening the stopcock B (Fig. 1) while applying a gentle suction at the end of the second receiver by means of a rubber bulb. Close the stopcock B immediately and pass oxygen as usual. For very accurate results this determination should be repeated after taking adequate amount of sodium methylate solution (as determined by the preliminary determination) into the first receiver.

It has been observed that for satisfactory results the maximum plate current reading should be between 350 and 400 mA.

After combustion for about 10 min, disconnect the receivers and transfer the contents to a 125-ml conical flask by washing with a small quantity of methanol. Any solid particle separating out in the solution during combustion will dissolve in methanol. Wash the inside of the glass tube by opening the Teflon plugs B and C (Fig. 1) and running a small quantity of methanol through the funnels. Titrate immediately with 0.1 *M* benzoic acid to the colourless end-point, using a 10-ml microburet.

Carry out the blank determination and standardization of sodium methylate as follows: take 1.5 g of iron chips and 0.5 g of vanadium pentoxide in a crucible, mix with a nickel spatula and cover the surface with 0.3 g of Celite. Put on the lid, place on the pedestal of the induction furnace and pass oxygen as usual. Add 1.5 ml and 0.5 ml of *ca.* 0.1 *M* sodium methylate solution to the first and the second receiver, respectively, each containing the same amount of the solvent and the indicator as used above and carry out the combustion for 10 min. In this determination caution is needed in controlling the flow of oxygen. During the first few seconds of combustion, oxygen is consumed very rapidly by iron chips, so that the absorbent solutions tend to back-up into the connecting tubes; the flow rate of oxygen must be increased immediately this back-up starts so that the forward flow of oxygen is maintained. The flow of oxygen should then be decreased to 2–3 bubbles per sec. Celite provides a silica matrix, which prevents fast consumption of oxygen by iron chips and hence reduces the possibility of back-up.

After combustion for 10 min, transfer the solutions and titrate immediately as described above.

To standardize the sodium methylate solution, immediately add 2 ml of that solution to the colourless titrated blank solution and again titrate with 0.1 *M* benzoic acid to a colourless end-point. The standardization is done in this manner so that the titration is carried out in a volume of acetone (or pyridine) and methanol similar to that used in other titrations.

Calculations are done in the conventional manner with due allowance for the blank.

*Procedure 2. Recommended for carbonate rocks or carbides.* Accurately weigh the sample (0.1–0.2 g for limestone or dolomite, and 0.1 g for silicon carbide) and transfer it to a crucible. Add 1.5 g of iron chips and 0.5 g of vanadium pentoxide and proceed as recommended in the first paragraph of Procedure 1.

Take 20 ml of a mixture of 1:1 acetone and methanol containing 0.6% (v/v) monoethanolamine in each of the two receivers, add 6 drops of phenolphthalein indicator to each, and depending on the "expected" amount of carbon dioxide, add 1–3 ml of 1 *M* sodium methylate (*e.g.* 1 ml per 44 mg $CO_2$, plus 0.5 ml in excess) to the first receiver and 0.5 ml to the second receiver. Connect up the apparatus as above and burn the sample for 15 min. After combustion, transfer the solution to a 125-ml conical flask by washing the receivers and tubes with methanol. Any solid formed in the first receiver during combustion will dissolve at this stage. Titrate with 0.5 *M* benzoic acid (in methanol) to a colourless end-point, using a 10-ml microburet.

Determine the blank by using the identical crucible, cover, flux (1.5 g Fe, 0.5 g $V_2O_5$, 0.3 g Celite) and solvent mixture (*cf.* Procedure 1).

Standardize the sodium methylate solution (1 *M*) against benzoic acid solution (0.5 *M*) in the titrated blank solution, as described above.

### *Determination of carbon dioxide by the acid evolution method*

The non-aqueous titration method as described above has also been applied to the determination of carbon dioxide evolved by the action of acid on rocks and minerals.

TABLE I

DETERMINATION OF TOTAL CARBON IN ROCKS AND CLAY BY PROCEDURE I—COMPARISON OF THE RESULTS OBTAINED IN PYRIDINE AND ACETONE MEDIA

| *Sample* | *% Carbon (total) calculated as carbon dioxide* | | |
|---|---|---|---|
| | *Pyridine medium (this work)* | *Acetone medium (this work)* | *Gravimetric value* |
| G-1 (Granite)[a] | 0.12 | 0.12 | 0.11[c] |
| G-2 (Granite)[a] | 0.09 | 0.08 | 0.08[d] |
| GSP-1 (Granodiorite)[a] | 0.13 | 0.12 | 0.11[d] |
| AGV-1 (Andesite)[a] | 0.04 | 0.04 | 0.01[d] |
| PCC-1 (Peridotite)[a] | 0.17 | 0.18 | 0.18[d] |
| DTS-1 (Dunite)[a] | 0.07 | 0.08 | 0.07[d] |
| BCR-1 (Basalt)[a] | — | 0.02 | 0.02[d] |
| GA (Granite)[b] | 0.17 | 0.18 | |
| GH (Granite)[b] | 0.16 | 0.19 | |
| BR (Basalt)[b] | 0.92 | 0.94 | |
| Amphibolite | 0.27 | — | 0.24[e] |
| Metagabbro metadiorite | 0.37 | — | 0.40[e] |
| Bentonite | 0.73 | — | 0.66[e] |
| Epidote amphibolite | 0.78 | — | 0.83[e] |
| Slate-argillate composite | 0.90 | — | 1.00[e] |
| Diabase | 1.82 | 2.10 | 2.10 |
| Siltstone | 2.00 | 2.10 | 2.14 |
| Skarn | 3.20 | — | 3.10[e] |
| Clay | 19.01 | 19.54 | 19.68[e] |

[a] U.S.G.S. (Washington) rock standard.
[b] French (Nancy) rock standard.
[c] Hoefs[9].
[d] $CO_2$ by Peck's method as reported by Flanagan[10].
[e] Independent operator (G.S.C.).

TABLE II

DETERMINATION OF TOTAL CARBON IN STONY METEORITES AND STANDARD METALLURGICAL SAMPLES BY PROCEDURE I—COMPARISON OF THE RESULTS OBTAINED IN PYRIDINE AND ACETONE MEDIA

| *Sample* | *Total carbon (%)* | | |
|---|---|---|---|
| | *Pyridine medium (this work)* | *Acetone medium (this work)* | *Gravimetric or certified value* |
| *Stony meteorites* | | | |
| Bruderheim | 0.05 | 0.04 | 0.04[a] |
| Peace River | 0.03 | 0.04 | 0.04[b] |
| Benton | 0.06 | — | 0.04[c] |
| Dresden | 0.08 | 0.08 | 0.07[c] |
| Abee | 0.41 | 0.42 | 0.38[d] |
| *Metallurgical samples* | | | |
| Basic open-hearth steel (NBS 15a) | 0.11 | 0.11 | 0.11 |
| Ferroboron (NBS 172) | 0.22 | 0.235 | 0.234 |
| Bessemer steel (NBS 10b) | 0.36 | 0.37 | 0.363 |
| Cr–V steel (NBS 30d) | 0.35 | 0.36 | 0.36 |
| Bessemer steel (NBS 22) | 0.55 | 0.583 | 0.59 |
| Mo–W steel (NBS 132) | 0.78 | 0.80 | 0.80 |
| Basic open-hearth steel (NBS 16a) | 0.91 | 0.94 | 0.99 |
| Spiegeleisen (NBS 66a) | 4.14 | 4.30 | 4.39 |

[a] Baadsgaard *et al.*[11].
[b] Baadsgaard *et al.*[12].
[c] Independent operator (G.S.C.).
[d] Dawson *et al.*[13].

*Procedure 3. Recommended for rocks.* Connect the apparatus as shown in Fig. 2. Normally two determinations are carried out simultaneously with two such apparatus assemblies.

Depending on the carbonate content, accurately weigh 0.5–1.0 g of the rock sample (see Procedure 1 for weight) and transfer it to the flask A. Add 30 ml of pre-boiled and cooled distilled water and connect to the apparatus (Fig. 2). Keep stopcocks C and D open and E closed and apply suction at the end tube of the first receiver (G). After 10 min close the stopcocks C, D, E and F.

Pipette 10 ml of acetone (containing 0.6% monoethanolamine) into each of the receivers G and H, add 6 drops of phenolphthalein indicator and depending on the carbon dioxide content of the sample, add 1–10 ml of 0.1 *M* sodium methylate solution (*e.g.* 1.0 ml per 4.4 mg $CO_2$, plus 1.0 ml excess) to the receiver G and 1 ml to the receiver H. Connect the receivers to the system and apply gentle suction at the end of the oil bubbler (*cf.* Fig. 2). Add 30 ml of 1:1 hydrochloric acid to funnel B and close the lid. Open stopcock D first and then C and allow the acid to trickle into the flask A. Allow cold water to circulate through the condenser. Heat the contents of flask A to boiling by an electric heating mantle, boil for 5 min and remove the heat. During the first few seconds of heating, it may be necessary to move the heating mantle up and down to prevent excessive heating and back-up of the solution into flask B. Continue the suction for additional 15 min at the rate of 1–2 bubbles per sec.

Disconnect receivers G and H and transfer the contents into a 125-ml flask by washing with small amount of methanol. Wash also the inside and outside of the tubes (G, H) with about 1–2 ml of methanol and collect the washings in the 125-ml flask. Titrate immediately with 0.1 *M* benzoic acid to the colourless end-point.

Determine the blank in each apparatus by following the above procedure for the sample. In order to standardize sodium methylate, add 2 ml of the *ca.* 0.1 *M* sodium methylate solution to the flask containing the titrated blank solution and titrate with 0.1 *M* benzoic acid to the colourless end-point.

*Procedure 4. Recommended for clay (high carbonate content), limestone and other carbonates.* For the determination of carbon dioxide in clay, limestone and other carbonates, the weight of the sample, the concentrations of sodium methylate and benzoic acid and the nature of the absorbing solutions are the same as given under Procedure 2. The operating procedures for sample, blank and standardization of 1 *M* sodium methylate are as described under Procedure 3.

## RESULTS AND DISCUSSION

The total carbon values for various samples as obtained by the induction furnace using different solvents are given in Tables I–III. Table IV gives the results obtained in the acetone medium by the acid evolution method, and Table V provides some data on the reproducibility of the methods. Tables I and II indicate that for most rocks, stony meteorites and steels the total carbon values obtained in pyridine or acetone medium are similar to the gravimetric values. In general, the acetone solvent is superior to pyridine for samples containing >1% total carbon. It is also free from the obnoxious odour and poisonous character of pyridine. The main criticism levelled against acetone is its flammability[1,4], but no difficulty was en-

TABLE III

DETERMINATION OF TOTAL CARBON (%) IN LIMESTONES, DOLOMITE AND SILICON CARBIDE—COMPARISON OF T
RESULTS OBTAINED IN PYRIDINE, ACETONE, AND ACETONE + METHANOL (1:1) MEDIA

| *Sample* | *C (total) by Procedure 1* | | *C (total) by Procedure 2* | *C (total)* |
|---|---|---|---|---|
| | *Pyridine medium* | *Acetone medium* | *Acetone + methanol (1:1) medium* | *Certified value* |
| Argillaceous limestone (NBS 1a) | 32.74[a] | 33.53[a] | 35.86[a] | 35.77[a] |
| Argillaceous limestone (NBS 1b) | — | 39.10[a] | 40.50[a] | 40.40[a] |
| Dolomite (NBS 88) | 43.8[a] | 46.64[a] | 47.52[a] | 47.54[a] |
| Silicon carbide (NBS 112) | 27.46 | 28.61 | 29.16 | 29.19 |

[a] Calculated as $CO_2$.

TABLE IV

DETERMINATION OF CARBON DIOXIDE IN ROCKS, CLAY AND LIMESTONE BY THE ACID EVOLUTION METHOD (BY PROCEDURES 3 AND 4)

| *Sample* | *% Carbon dioxide* | |
|---|---|---|
| | *This work* | *Others* |
| G-2 (Granite) | 0.08 | 0.08[a] |
| GSP-1 (Granodiorite) | 0.10 | 0.11[a] |
| AGV-1 (Andesite) | 0.02 | 0.01[a] |
| PCC-1 (Peridotite) | 0.18 | 0.18[a] |
| DTS-1 (Dunite) | 0.07 | 0.07[a] |
| BCR-1 (Basalt) | 0.02 | 0.02[a] |
| GA (Granite) | 0.06 | 0.12[b] |
| GH (Granite) | 0.11 | 0.14[b] |
| BR (Basalt) | 0.83 | 0.87[b] |
| Epidote amphibolite | 0.66 | 0.68[c] |
| Siltstone | 2.03 | 2.04[c] |
| Clay | 18.97 | 18.95[c] |
| NBS 1a (Argillaceous limestone) | 33.55 | 33.54[d] |

[a] $CO_2$ by PECK's method as reported by FLANAGAN[10].
[b] GOVINDARAJU[14].
[c] Independent operator (G.S.C.).
[d] NBS certified value.

TABLE V

REPRODUCIBILITY OF RESULTS IN ACETONE MEDIUM

| *Sample* | *C (total) as $CO_2$ (%) (induction furnace, Procedure 1)* | *% $CO_2$ (acid evolution method, Procedure 3)* |
|---|---|---|
| BCR-1 (Basalt) | 0.02, 0.02, 0.02, 0.02, 0.02 | 0.02, 0.02 |
| AGV-1 (Andesite) | 0.04, 0.04 | |
| GA (Granite) | | 0.05, 0.06 |
| GH (Granite) | | 0.11, 0.11 |
| Diabase | 2.10, 2.10, 2.12 | 1.90, 1.91 |
| Siltstone | 2.08, 2.10 | 2.02, 2.02, 2.03 |

countered in using it with the induction heating. However, as a precautionary measure in the induction heating, an empty trap was used between the catalyst furnace and the receivers to retain the liquid in case any back-up occurred during combustion. This was not necessary for the acid evolution method. However, the use of a heating mantle instead of a gas burner in the acid evolution method reduced the fire hazard.

Table III (Procedure 1) shows that considerable loss occurs when pyridine is used as a solvent for the determination of total carbon in limestone, dolomite and silicon carbide. The use of acetone improves the results substantially but they are still not quantitative (see Table III, Procedure 1).

BRAID *et al.*[15] obtained the best retention of carbon dioxide in a solution of dimethylformamide which contained 5% (v/v) of monoethanolamine. However, dimethylformamide has a harmful vapour and is expensive. Experiments were performed for the same samples as in Table III, with 5% monoethanolamine in acetone as the absorbent, but the results obtained were the same as those given in Table III (under Procedure 1) for acetone containing 0.6% monoethanolamine. There was therefore no advantage in increasing the concentration of monoethanolamine.

In extending Procedure 1 to high carbon contents in limestone, dolomite and silicon carbide (Table III), difficulties were encountered because of low sample weight (inhomogeneity in samples and poor coupling in the induction heating), and the necessity of using large volumes of sodium methylate solution (which caused indicator fading). If the sample weight and the concentration of sodium methylate were increased, respectively, to 0.5 g and 1 *M*, then difficulty was experienced in the acetone solvent owing to separation of solid sodium methyl carbonate. However, when a 1:1 mixture of acetone and methanol containing 0.6% monoethanolamine was used as the solvent and the sample weights for carbonate ores and silicon carbide were restricted to a maximum of 0.2 g and 0.1 g, respectively, then quantitative recoveries were obtained (Table III).

Although addition of Celite to the sample during combustion in the induction furnace was not necessary for most of the samples analyzed, it proved helpful to use 0.3 g of it on the surface of certain special rock samples to prevent a vigorous reaction with oxygen and to facilitate smoother combustion.

In the case of the determination of carbon dioxide by the acid evolution method, difficulties developed with variable blanks when propane gas burners were used for heating the sample; possibly some carbon dioxide from the propane combustion products leaked into the absorption system, causing variable blanks. When electric heating mantles were used low and reproducible blanks were obtained.

It is of interest to note that at the request of Dr. J. A. MAXWELL, a Principal Investigator of lunar materials in the Geological Survey of Canada, the writer used Procedure 1 to determine the total carbon contents of three lunar materials (rock chips, samples 10017-29 and 10020-30, and dust sample 10084-132) collected by Apollo 11 astronauts. The total carbon content of each of these samples was found to be 0.014% (MAXWELL *et al.*[16] reported these data up to the second decimal place, *i.e.* 0.01%C). The writer's data on sample 10084 agree well with other data (around 0.015%C) on the same sample obtained by combustion plus manometric (KAPLAN AND SMITH[17]) and $^{13}C/^{12}C$ isotope ratio mass spectrometric (EPSTEIN AND TAYLOR[18]) methods.

The author thanks Mr. S. ABBEY for encouragement in this work and for critically reading the manuscript.

## SUMMARY

Suitable non-aqueous titration methods have been developed for the determination of total carbon in silicate and carbonate rocks, stony meteorites and metallurgical samples by a high-frequency induction furnace. The method has been extended to the determination of carbon dioxide in rocks, clay and limestones by the acid evolution method. A conventional receiver with a buret for continuous titration was unsuitable in the induction heating procedure; and was replaced by two connected borosilicate glass receivers in a closed system. Acetone either alone (for 0–10 mg C) or in 1:1 mixture with methanol (for 10–30 mg C) containing 0.6% (v/v) monoethanolamine and an excess of standard sodium methylate was found to be a better absorbent for carbon dioxide than pyridine. After reaction, the excess sodium methylate was back-titrated by a standard methanolic solution of benzoic acid with phenolphthalein as indicator. The method gives reliable results up to 47% total carbon dioxide.

## RÉSUMÉ

Des méthodes de titrage, en milieu non aqueux, sont présentées pour le dosage du carbone total dans des roches silicatées et carbonatées, des météorites pierreux et des échantillons métallurgiques, par un four-induction à haute fréquence. Ce procédé a également été appliqué au dosage d'anhydride carbonique dans des roches, de l'argile, des pierres calcaires. L'acétone pure (pour 0 à 10 mg C) ou mélangée au méthanol (pour 10 à 30 mg C) contenant 0.6% (v/v) de monoéthanolamine et un excès de méthylate de sodium standard constitue un absorbant pour l'anhydride carbonique meilleur que la pyridine. Après réaction, le méthylate de sodium en excès est titré en retour par une solution méthanolique d'acide benzoïque étalon, en présence de phénolphtaléine comme indicateur.

## ZUSAMMENFASSUNG

Es sind geeignete nichtwässrige Titrationsmethoden für die Bestimmung von Gesamtkohlenstoff in Silicat- und Carbonatgesteinen, Steinmeteoriten und metallurgischen Proben nach Verbrennung in einem Hochfrequenzinduktionsofen entwickelt worden. Die Methode ist auf die Bestimmung von Kohlendioxid in Gesteinen, Ton und Kalkstein nach der Methode der sauren Zersetzung erweitert worden. Eine herkömmliche Vorlage mit einer Bürette für kontinuierliche Titration war beim Induktionsheizungsverfahren ungeeignet und wurde durch zwei miteinander verbundene Borsilikatglas-Vorlagen in einem geschlossenen System ersetzt. Aceton, entweder allein (für 0–10 mg C) oder in einer 1:1-Mischung mit Methanol (für 10–30 mg C), mit einem Gehalt von 0.6 Vol.-% Monoäthanolamin und überschüssigem Natriummethylat war ein besseres Absorptionsmittel für Kohlendioxid als Pyridin. Nach der Reaktion wurde das nicht verbrauchte Natriummethylat mit einer methanolischen Benzoesäurelösung und Phenolphthalein als Indikator zurücktitriert. Die Methode ergibt zuverlässige Werte bis zu 47% Gesamt-Kohlendioxid.

## REFERENCES

1 D. H. Davies, *Talanta*, 16 (1969) 1055.
2 J. Lindner, *Mikrochem.*, 20 (1936) 209.
3 R. Belcher, J. H. Thompson and T. S. West, *Anal. Chim. Acta*, 19 (1958) 309.
4 L. Blom and L. Edelhausen, *Anal. Chim. Acta*, 13 (1955) 120.
5 L. Blom, J. A. Stijntjes, J. A. van de Vliervoet and A. J. Beeren, *Chim. Anal. (Paris)*, 44 (1962) 302.
6 L. Blom and M. H. Kraus, *Z. Anal. Chem.*, 205 (1964) 50.
7 J. G. Sen Gupta, *Anal. Chem.*, 35 (1963) 1971.
8 J. G. Sen Gupta, *Anal. Chim. Acta*, 49 (1970) 519.
9 J. Hoefs, *Geochim. Cosmochim. Acta*, 29 (1965) 399.
10 F. J. Flanagan, *Geochim. Cosmochim. Acta*, 31 (1967) 289.
11 H. Baadsgaard, F. A. Campbell and R. E. Folinsbee, *J. Geophys. Res.*, 66 (1961) 3574.
12 H. Baadsgaard, R. E. Folinsbee and G. L. Cumming, *J. Geophys. Res.*, 69 (1964) 4197.
13 K. R. Dawson, J. A. Maxwell and D. E. Parsons, *Geochim. Cosmochim. Acta*, 21 (1960) 127.
14 K. Govindaraju, unpublished results, communicated privately to S. Abbey.
15 P. Braid, J. A. Hunter, W. H. S. Massie, J. D. Nicholson and B. E. Pearce, *Analyst*, 91 (1966) 439.
16 J. A. Maxwell, S. Abbey and W. H. Champ, *Science*, 167 (1970) 530.
17 I. R. Kaplan and J. W. Smith, *Science*, 167 (1970) 541.
18 S. Epstein and H. P. Taylor, Jr., *Science*, 167 (1970) 533.

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

# A SIMPLE AND SENSITIVE COLORIMETRIC ASSAY OF BENZYLHYDRAZINE

TETSUO SATOH AND KAYOKO MOROI

*Department of Pharmacology and Toxicology, Institute of Food Microbiology, Chiba University, Chiba (Japan)*

(Received February 27th, 1970)

ROTH AND RIEDER[1] reported a fluorimetric assay of benzylhydrazine in 1962, but this method required complicated techniques although its sensitivity was excellent.

The quantitative assay method described in this paper is based on the formation of a colored compound with *p*-dimethylaminobenzaldehyde in the presence of both glacial acetic acid and metaphosphoric acid. On this basis, a method has been developed which is relatively simple, rapid, sensitive and specific, and is suitable for both clinical and research purposes.

## EXPERIMENTAL

### Reagents

*Metaphosphoric acid, 30%.* Reagent-grade material was dissolved in twice-distilled water from glass apparatus.

p-*Dimethylaminobenzaldehyde solution.* 1.0 g of *p*-dimethylaminobenzaldehyde was dissolved in a mixture of 20 ml of ethanol and 10 ml of glacial acetic acid. This solution was prepared freshly before use.

*Phosphate buffer.* pH 7.0, 0.2 *M*.

### Standard procedure

For the analysis of aqueous solutions of benzylhydrazine, 1.0 ml of 30% metaphosphoric acid and 1.0 ml of water were added to tubes containing 1.0 ml of the solution to be analyzed. The color was developed by adding 1.5 ml of *p*-dimethylaminobenzaldehyde solution with mixing. After standing for at least 30 min at room temperature, the absorbance was measured at 490 nm.

In the application of the present method to biological materials, deproteinization was performed by adding 3.0 ml of 30% metaphosphoric acid to the mixture containing 1.0 ml of phosphate buffer (pH 7.0), 0.5 ml of plasma or 1.0 ml of 30% tissue homogenates in isotonic potassium chloride solution, and water to a total volume of 3.0 ml. After standing for 20 min, samples were centrifuged at 3,000 r.p.m. for 10 min. Aliquots of resulting supernates were withdrawn and the color was developed by adding 1.5 ml of *p*-dimethylaminobenzaldehyde solution and water to a total volume of 4.5 ml. The absorbance was then measured at 490 nm as above.

## RESULTS AND DISCUSSION

### *Absorbance spectra*

The absorbance spectra of the colored solutions were investigated when *p*-dimethylaminobenzaldehyde solution, metaphosphoric acid and glacial acetic acid solutions were added to solutions containing either benzylhydrazine and isocarboxazid (Fig. 1A) or liver homogenate in the presence of one or both of benzylhydrazine and isocarboxazid (Fig. 1B). It can be seen from Fig. 1A that no interference was caused by isocarboxazid at the wavelength used for benzylhydrazine determination (490 nm), hence benzylhydrazine in mixtures containing isocarboxazid could be determined accurately.

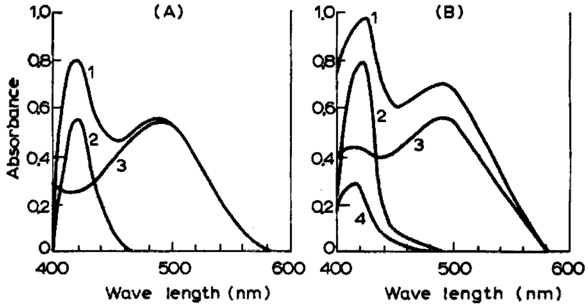


Fig. 1. Absorbance spectra. The spectra were obtained as follows. (A) Curve 1 represents a mixture of isocarboxazid ($5 \cdot 10^{-4}$ *M*) and benzylhydrazine ($1 \cdot 10^{-4}$ *M*); curves 2 and 3 represent isocarboxazid ($3 \cdot 10^{-4}$ *M*) and benzylhydrazine ($1 \cdot 10^{-4}$ *M*), respectively. These mixtures were not incubated.
(B) Curve 1 represents isocarboxazid ($3 \cdot 10^{-3}$ *M*) incubated with liver homogenate at 37° for 1 h; curve 2 represents isocarboxazid ($5 \cdot 10^{-4}$ *M*) and liver homogenate without incubation; curve 3 represents homogenate plus benzylhydrazine ($1 \cdot 10^{-4}$ *M*) and curve 4 homogenate alone.

As shown in Fig. 1B, absorbance caused by benzylhydrazine was observed when isocarboxazid was incubated with liver homogenate (curve 1); however, no absorbance was obtained from the same constituents without incubation (curve 2). These facts indicated that benzylhydrazine was formed from isocarboxazid by incubation with liver homogenate at 37°.

### *Standard curve*

When standard solutions of benzylhydrazine ranging from $1 \cdot 10^{-5}$ *M* to $5 \cdot 10^{-4}$ *M* were treated by the standard procedure given under EXPERIMENTAL, and the resulting absorbances were plotted against the amounts of benzylhydrazine, Beer's law was obeyed up to a final concentration of benzylhydrazine of $2 \cdot 10^{-4}$ *M* (24.4 $\mu$g ml$^{-1}$). The limit of detection for benzylhydrazine by this procedure was as low as $2 \cdot 10^{-5}$ *M* (2.44 $\mu$g ml$^{-1}$).

### *Optimal concentrations of metaphosphoric acid and glacial acetic acid*

Benzylhydrazine solutions containing increasing volumes of 30% metaphosphoric acid were added to *p*-dimethylaminobenzaldehyde solution prepared as in the standard method. The results shown in Fig. 2A indicate that maximum absorbance resulted from 1.0–2.0 ml of metaphosphoric acid. When the optimal amount of glacial acetic acid in the preparation of the *p*-dimethylaminobenzaldehyde solution for the development of the maximal color intensity was determined, 0.3–0.5 ml of the acid was found to give the best results (Fig. 2B). Under these conditions, changes in the pH values of the solutions did not affect the color development of benzylhydrazine.

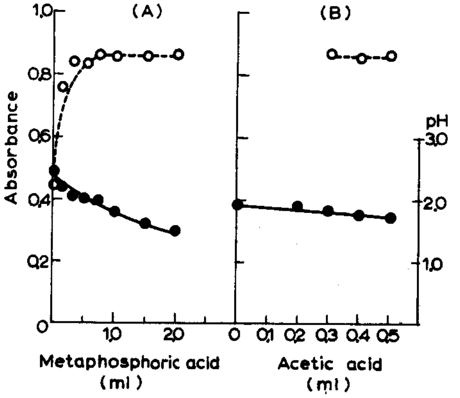


Fig. 2. Effects of the amounts of metaphosphoric acid and glacial acetic acid on color development. Color intensity developed (○) and changes in pH values (●) for each condition were measured.

TABLE I

EFFECTS OF HYDRAZINES, AMINES, AND TRYPTOPHAN ANALOGS ON THE COLOR DEVELOPMENT OF BENZYLHYDRAZINE

| *Compound* | *Concentration (M)* | *Absorbance maxima (nm)* | *Color intensity*[a] *(%)* |
|---|---|---|---|
| Benzylhydrazine | $1\cdot10^{-4}$ | 490 | 100 |
| Tryptophan | $1\cdot10^{-3}$ | — | 0 |
| Serotonin | $1\cdot10^{-3}$ | — | 0 |
| Tryptamine | $1\cdot10^{-3}$ | — | 0 |
| Tyramine | $1\cdot10^{-3}$ | — | 0 |
| Benzylamine | $1\cdot10^{-3}$ | — | 0 |
| Diphenylamine | $1\cdot10^{-3}$ | — | 0 |
| Diphenylcarbazide | $1\cdot10^{-3}$ | — | 0 |
| Phenylhydrazine | $1\cdot10^{-3}$ | 440 | 0 |
| Phenelzine | $1\cdot10^{-4}$ | 480 | 125 |
| Isocarboxazid | $3\cdot10^{-3}$ | 420 | 0 |
| Iproniazid | $1\cdot10^{-4}$ | — | 0 |
| Pheniprazine | $1\cdot10^{-4}$ | 430 | 7 |
|  | $1\cdot10^{-3}$ |  | 65 |

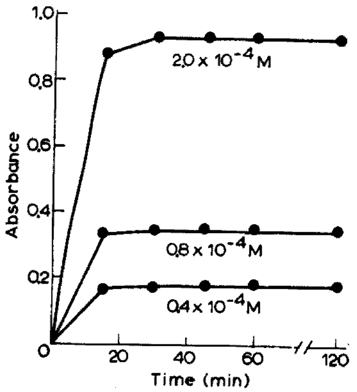
[a] Measured at 490 nm.

## *Selectivity*

The interference of nine compounds chemically related to benzylhydrazine and of three tryptophan analogs was investigated. Phenelzine ($1\cdot10^{-4}$ *M*) showed essentially the same color intensity as benzylhydrazine, and pheniprazine ($1\cdot10^{-3}$ *M*), to a lesser extent. The other compounds tested showed no interference at 490 nm under these conditions (Table I).

*Stability of color*

Experiments with aqueous solutions of benzylhydrazine, *i.e.*, $0.4 \cdot 10^{-4}$ *M*, $0.8 \cdot 10^{-4}$ *M* and $2.0 \cdot 10^{-4}$ *M* as final concentrations, showed (Fig. 3) that the absorbance of the colored compound formed with benzylhydrazine was stable from 30 min to at least 2 h after the beginning of the reaction at room temperature (20 ± 2°).



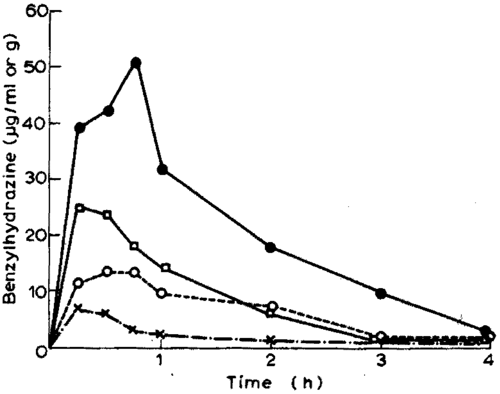


Fig. 3. Development and stability of color intensity. Three concentrations of benzylhydrazine, *i.e.*, $0.4 \cdot 10^{-4}$ *M*, $0.8 \cdot 10^{-4}$ *M* and $2.0 \cdot 10^{-4}$ *M* were used.

Fig. 4. Time course experiments of benzylhydrazine levels in rat plasma and tissues after intraperitoneal administration of isocarboxazid in doses of 50 mg $kg^{-1}$ body wt. Benzylhydrazine levels are shown as µg per ml of plasma (○) or g of tissues for liver (●), kidney (□) and brain (×). Values at each point represent means of at least three experiments.

TABLE II

RECOVERIES OF BENZYLHYDRAZINE ADDED TO TISSUE HOMOGENATES AND BLOOD
(Homogenates were prepared as described under EXPERIMENTAL)

| *Tissue* | *Isocarboxazid added (M)* | *Benzylhydrazine (µmole)* | | *Recovery (%)* |
|---|---|---|---|---|
| | | *Added* | *Found*[a] | |
| Liver | — | 0.05 | 0.049 | 98 |
| | — | 0.10 | 0.101 | 101 |
| | — | 0.25 | 0.242 | 97 |
| | $2.5 \cdot 10^{-4}$ | 0.10 | 0.102 | 102 |
| | $1.5 \cdot 10^{-3}$ | 0.10 | 0.101 | 101 |
| Brain | — | 0.05 | 0.049 | 98 |
| | — | 0.10 | 0.092 | 92 |
| | — | 0.25 | 0.245 | 98 |
| | $1.5 \cdot 10^{-3}$ | 0.10 | 0.100 | 100 |
| Kidney | — | 0.05 | 0.050 | 100 |
| | — | 0.25 | 0.249 | 98 |
| | $2.5 \cdot 10^{-4}$ | 0.10 | 0.103 | 103 |
| Blood | — | 0.05 | 0.049 | 98 |
| | — | 0.25 | 0.250 | 100 |
| | $2.5 \cdot 10^{-4}$ | 0.10 | 0.102 | 102 |

[a] All data were the results of triplicate samples.

*Recovery experiments*

Table II shows a summary of recoveries of known amounts of benzylhydrazine with and without isocarboxazid added to liver, kidney, brain homogenates and blood. The recoveries of added benzylhydrazine ranged from 92% to 103% with a mean recovery of 99.15%.

*Practical application of the present method to animal experiments*

The standard procedure was applied to the time course experiments of benzylhydrazine levels of rat after intraperitoneal administration of isocarboxazid in doses of 50 mg per kg body weight. On 0.5 ml of either plasma or 30% tissue homogenates of rats after sacrifice at appropriate times, the benzylhydrazine levels were estimated by the procedure described under EXPERIMENTAL. As illustrated in Fig. 4, plasma and tissue benzylhydrazine levels showed significant elevation between 15 and 45 min after treatment, and then returned gradually to the initial level at 4 h. Addition of either hydrochloric acid or perchloric acid instead of metaphosphoric acid in practical application failed to develop color from benzylhydrazine, hence it appeared that metaphosphoric acid may be required not only as deproteinizing agent but as an essential factor in the development of the color with benzylhydrazine.

As reported by SCHWARTZ[2,3] and KOECHLIN *et al.*[4], benzylhydrazine is an intermediate of isocarboxazid and this compound is well-known as a more potent monoamine oxidase inhibitor than the latter. It is possible to speculate that the pharmacological effects of isocarboxazid may be, in part, responsible for the action of benzylhydrazine.

The procedure described here has been used in this laboratory for a series of studies concerning the pharmacological activity of isocarboxazid. The selectivity of the present method was similar to that found in the fluorimetric assay[1]; moreover, the color intensity from benzylhydrazine in biological materials was not affected by the presence of isocarboxazid.

The proposed method has advantages over fluorimetry in terms of simplicity, rapidity and stability of color developed.

The authors are indebted to Professor K. MIYAKI, Director of this Institute, for his encouragement.

## SUMMARY

A new and simple procedure for the colorimetric determination of benzylhydrazine is described. It is based on the color development by *p*-dimethylaminobenzaldehyde in the presences of metaphosphoric acid and glacial acetic acid. The assay of microgram quantities of benzylhydrazine in plasma and tissues of rat treated with isocarboxazid is reported.

## RÉSUMÉ

Une nouvelle méthode simple est proposée pour le dosage colorimétrique de la benzylhydrazine. Elle est basée sur la coloration du *p*-diméthylaminobenzaldéhyde formé, en présence d'acide métaphosphorique et d'acide acétique glacial. On décrit les essais effectués avec des quantités de benzylhydrazine de l'ordre du microgramme dans le plasma et les tissus de rats traités avec de l'isocarboxazide.

## ZUSAMMENFASSUNG

Es wird eine neue und einfache kolorimetrische Methode zur Bestimmung von Benzylhydrazin beschrieben. Sie beruht wahrscheinlich auf der Bildung eines Metaphosphorsäurekomplexes von *p*-Dimethylaminobenzaldehyd mit Essigsäure. Eine Methode zur quantitativen Bestimmung von Mikrogramm-Mengen von Benzylhydrazinen in Blutplasma und Organen von Isocarboxazid-behandelten Ratten wird angegeben.

## REFERENCES

1 M. Roth and J. Rieder, *Anal. Chim. Acta*, 27 (1962) 20.
2 M. A. Schwartz, *J. Pharmacol. Exptl. Therap.*, 130 (1960) 157.
3 M. A. Schwartz, *Proc. Soc. Exptl. Biol. Med.*, 107 (1961) 613.
4 B. A. Koechlin, M. A. Schwartz and W. E. Oberhaensli, *J. Pharmacol. Exptl. Therap.*, 138 (1962) 11.

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

# THE DETERMINATION OF RHENIUM IN SEA WATER

A. D. MATTHEWS AND J. P. RILEY
*Department of Oceanography, The University, P.O. Box 147, Liverpool L69 3BX (England)*

(Received April 25th, 1970)

Rhenium is one of the rarest elements, and for this reason little is known of its geochemistry, even in igneous rocks, in which its average concentration is probably *ca.* $5 \cdot 10^{-8}$ %[1]. Even less information is available about its occurrence in the marine environment. Pacific Ocean surface water has been found[2] to contain 0.007–0.011 $\mu$g Re $l^{-1}$. The larger algae appear[2,3] to contain 0.01–0.02 $\mu$g Re $g^{-1}$. No data at all are available for the occurrence of the element in recent marine sediments. For this reason it was decided to carry out a survey of the marine geochemistry of the element.

When the present investigation was commenced nothing was known about the concentration of rhenium in sea water, and as it was expected that its concentration would be very low, it was decided to determine it by neutron activation analysis. Subsequently, SCADDEN[2] has successfully used this technique for this purpose. However, since her procedure differs in many ways from that developed in the present work, and gives a radiochemically less pure product, it was decided to publish the present method.

In nature there are two stable isotopes of rhenium, rhenium-185 and rhenium-187 which possess large thermal neutron capture cross-sections of 100 and 75 barns, and on thermal neutron activation give rise to rhenium-186 ($t_{\frac{1}{2}}$ = 88.8 h) and rhenium-188 ($t_{\frac{1}{2}}$ = 16.7 h) respectively. Rhenium-186 activity was used in the present work because of its more convenient half-life. This nuclide is also produced by two other reactions: $^{184}W(n,\gamma)^{185}W \xrightarrow[74d]{\beta^-} {}^{185}Re(n,\gamma)^{186}Re$ and $^{186}Os(n,p)^{186}Re$. Calculation showed that no interference in the determination of rhenium would be caused by either tungsten or osmium at their sea water concentrations.

### *Preconcentration of rhenium*

Since the concentration of rhenium in sea water is low, it is necessary to concentrate it from a relatively large volume of sample before the neutron activation. This separation also serves to separate the element from major elements such as sodium and chlorine which would give rise to undesirably high activities. Since SCADDEN[2] used a relatively high neutron flux, only small sample volumes were required (*ca.* 1 l) and she was therefore able to use a solvent extraction procedure or preconcentration. However, in the present work it was necessary to use 15-l samples because the neutron flux available was only *ca.* 1/20 of that used by SCADDEN; this ruled out the use of a solvent extraction method because of the difficulty of extracting the large volumes of sea water.

A survey was made of possible methods for concentrating rhenium. Coprecipitation with aluminium and iron(III) hydroxides or with hydrous manganese dioxide proved unsuccessful, practically no rhenium being carried by any of these precipitates. The perrhenate ion is known to be adsorbed from hydrochloric acid medium by strongly basic ion-exchange resins[4,5], and the possibility of using this technique for the concentration of rhenium from sea water was therefore investigated. For this purpose, 6-mm diameter exchange columns filled to a depth of 10 cm with the chloride form of Deacidite FF resin (50–100 mesh) were used. Preliminary experiments showed that rhenium which had been adsorbed on the resin column could not be eluted with 60 ml of 2 *M* nitric acid. However, it could be removed quantitatively (>99.8%) with 90 ml of either 4 *M* or 6 *M* nitric acid. Since 4 *M* nitric acid gave the sharper elution curve, it was adopted as the eluting agent. Aliquots (3 l) of filtered sea water were spiked with *ca.* 0.2 $\mu$Ci of $^{186}$Re (*ca.* 0.2 $\mu$g Re) and acidified to molarities in the range 0.1–2.0 *M* with hydrochloric acid. The acidified sea water was allowed to pass through the ion-exchange columns at flow rates of *ca.* 5 ml min$^{-1}$. Each column was then eluted with 90 ml of 4 *M* nitric acid and the recovery of rhenium was assessed radiochemically. It was found that rhenium could be recovered quantitatively (>99%) from acified sea water over the hydrochloric acid molarity range 0.1–2.0 *M*. However, only *ca.* 80% could be recovered from sea water which had not been acidified. In all subsequent work the samples were brought to 0.1 *M* with respect to hydrochloric acid.

TABLE I

PERCENTAGES OF ELEMENTS RETAINED BY DEACIDITE FF FROM SEA WATER 0.1 *M* WITH RESPECT TO HYDROCHLORIC ACID, AND PERCENTAGES OF TOTAL ELUTED WITH 90 ml OF 4 *M* NITRIC ACID

| *Element* | *Percentage retained* | *Percentage of total present in 4 M nitric acid eluate* |
|---|---|---|
| Ag | 100 | 45 |
| Au(III) | 95 | 4 |
| Bi | 99 | 38 |
| Cd | 60 | 60 |
| Fe(III) | 8.5 | 1.5 |
| Ga | 3 | 1 |
| In | 19 | 19 |
| Mn(II) | 0 | 0 |
| Mo(VI) | 95 | 55 |
| Pt(VI) | 86 | 6 |
| Re(VII) | 100 | 100 |
| Sb(III) | 33 | 33 |
| U | — | 1 |

The resin will take up several other elements from the acidified sea water. Many of these will be eluted by the passage of 90 ml of 4 *M* nitric acid, and will be present during the neutron activation. The behaviour of a number of elements during the ion-exchange process, under the conditions described above, was therefore investigated radiochemically. It was found (Table I) that appreciable amounts of some of them would be present in the 4 *M* nitric acid eluate. The most important of these is molybdenum which, on activation with thermal neutrons, gives rise to technetium-99m, via the process $^{98}\mathrm{Mo}(\mathrm{n},\gamma)^{99}\mathrm{Mo} \xrightarrow{\beta} {}^{99\mathrm{m}}\mathrm{Tc}$. This reaction is significant because the concentration of molybdenum in sea water is *ca.* 1000 times greater than that of rhenium and because technetium very closely resembles rhenium in its properties. Technetium-99m is also produced during nuclear fission of uranium. However, since more than 99% of the uranium present in the sea water is removed during the ion-exchange process, the amount of $^{99m}$Tc produced in this way will be insignificant in the analysis.

### *Neutron activation of the rhenium concentrate*

The 4 *M* nitric acid eluate containing the rhenium must be evaporated to a very small volume before irradiation with neutrons. Although rhenium is comparatively volatile from acid solutions, radiochemical tests showed that no loss of the element occurred if the evaporation was carried out on the water bath, or with a heating block at a temperature not exceeding 110°. In order to induce sufficient activity for precise counting, and to enable the radiochemical purity of the rhenium-186 to be checked, the irradiation was carried out for 50 h in a flux of $3.7 \cdot 10^{12}$ $cm^{-2}$ $sec^{-1}$, at the Joint Universities Reactor at Risley, Lancs.

### *Radiochemical separation scheme*

In addition to the desired rhenium-186 activity, the irradiated concentrate contains many other induced activities arising from the irradiation of either other elements also concentrated during the anion-exchange processes, or impurities introduced by reagents, the ion-exchange resin or from the apparatus. Earlier workers have mainly used conventional, and often complex, radiochemical separation schemes[6–9] to remove such activities when using neutron activation analysis for the determination of rhenium in geochemical materials. In an attempt to simplify the analysis an investigation has been made of the behaviour of rhenium during anion exchange from non-aqueous media. The versatility of such systems for the separation of metals has been demonstrated by KORKISCH[10] and by FRITZ AND RETTIG[11]. KORKISCH AND HAZAN[12] have studied the distribution coefficients of 23 elements (excluding rhenium) between Dowex 1-X8 and mixtures of 6 and 12 *M* hydrochloric acid with 12 organic solvents. From the point of view of the present work, the most promising of these were 95% formic acid–5% 12 *M* hydrochloric acid and 95% acetone–5% 12 *M* hydrochloric acid. It was thought that it might be possible to adsorb rhenium from formic acid–hydrochloric acid medium onto an anion exchanger. Since the distribution coefficients of most metals in this system are lower than with aqueous hydrochloric acid, it was hoped that an effective separation of rhenium might be obtained. It was also thought that the adsorbed rhenium might be readily eluted by an acetone–hydrochloric acid medium.

The ion-exchange behaviour of rhenium in the above mixtures was therefore investigated. Aliquots (10 ml) of 95% formic acid–5% 11.3 *M* hydrochloric acid were spiked with perrhenate ion (15 mg Re) containing *ca.* 0.2 $\mu$Ci $^{186}$Re. The solutions were allowed to flow through 5 cm × 0.2 $cm^2$ columns of Dowex 1-X8 (100–200 mesh) which had been previously washed with 50 ml of the same mixture. The columns were then eluted with 75 ml of the formic acid–hydrochloric acid mixture and washed with 25 ml of water. It was found radiochemically that rhenium was retained quantitatively by the resin, and that it was not removed to any significant extent ($<0.05\%$) during the washing process. However, it could be quantitatively eluted by means of 45 ml of a 95:5 (v/v) mixture of acetone and 11.3 *M* hydrochloric acid (it proved necessary to carry out this final elution at *ca.* 0° in order to prevent the formation of gas bubbles in the column).

The data of KORKISCH AND HAZAN[12] suggested that although the above procedure would separate most other elements from rhenium, the separation of gallium, indium and gold would be incomplete. It was found that gallium and indium could be removed by eluting the column with 45 ml of aqueous 0.5 *M* hydrochloric acid before eluting rhenium with the acetone–hydrochloric acid mixture. This stage was therefore incorporated in the procedure. The behaviour of 18 elements in the complete ion-exchange scheme was tested by radio-tracer techniques, and it was found that rhenium was separated completely from all but technetium and gold (Table II). In addition, alkali and alkaline earth metals, rare earth elements, aluminium, copper, nickel, thorium and uranium are known not to be retained by Dowex-1 from formic acid–hydrochloric acid medium[12]. The separation scheme is therefore almost specific for rhenium.

TABLE II

PERCENTAGES OF ELEMENTS ELUTED FROM DOWEX 1-X8 COLUMNS BY CONSECUTIVE USE OF VARIOUS ELUTING AGENTS

| *Element* | *35 ml formic acid–HCl (95:5, v/v)* | *45 ml 0.5 M aqueous HCl* | *45 ml acetone–HCl (95:5, v/v)* |
|---|---|---|---|
| Ag | 0.9 | 2.5 | 0 |
| Au(III) | 0.0 | 22 | 20 |
| Bi | 0.0 | 2 | 0 |
| Cd | 74 | 8.5 | 0 |
| Ce(III) | 100 | 0 | 0 |
| Co(II) | 100 | 0 | 0 |
| Cr(III) | 100 | 0 | 0 |
| Fe(III) | 97.5 | 2.5 | 0 |
| Ga | 68 | 32 | 0 |
| In | 2 | 98 | 0 |
| Mn(II) | 0 | 0 | 0 |
| Mo(VI) | 10 | 0 | 0 |
| Pb(II) | 60 | 9 | 0 |
| Pt(VI) | 2.5 | 1 | 0 |
| Re(VII) | 0 | 0 | 100 |
| Sb(III) | 86 | 6 | 0 |
| Sn(IV) | 80 | 20 | 0 |
| Tc(VII) | 0 | 0 | 80 |
| Zn | 90 | 10 | 0 |

The failure of the ion-exchange scheme to separate rhenium from the closely related element technetium was disadvantageous in the present instance. This was so because molybdenum, which accompanies rhenium through the pre-concentration stage, gives rise to the radionuclide $^{99m}$Tc indirectly on neutron irradiation (see above p. 456). Methods for bringing about a separation of these two group VII elements were therefore investigated. Both rhenium and technetium in their heptavalent oxidation states can be extracted from a 5 *M* sodium hydroxide medium by means of methyl ethyl ketone. GERLIT[13] has stated that if technetium is first reduced to the non-extractable tetravalent state with hydrazine, the extraction is selective for rhenium. When this method was investigated, it was found that if the hydrazine

LE III

ENTAGE EXTRACTION OF ELEMENTS FROM 5 *M* SODIUM HYDROXIDE MEDIUM INTO METHYL ETHYL KETONE
IE PRESENCE OF HYDROXYLAMINE HYDROCHLORIDE[a]

| | $Ag^+$ | $Au^{3+}$ | $Bi^{3+}$ | $Cd^{2+}$ | $Fe^{2+}$ | $Ga^{3+}$ | $In^{3+}$ | $Mo^{6+}$ | $Pb^{2+}$ | $Pt^{6+}$ | $Sb^{3+}$ | $Tc^{7+}$ | $Zn^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| entage ction | 8.0 | 0.01 | 2.0 | 0.01 | 0.01 | 0.01 | 3.5 | 0.1 | 1.8 | 1.5 | 0.1 | 0.01 | 0.7 |

ing three extractions with 15, 5 and 5 ml of methyl ethyl ketone.

content of the solution was high enough to inhibit extraction of technetium completely, the extraction of rhenium was less than 50% efficient. It was thought that failure to extract rhenium was caused by its partial reduction to the tetravalent state by the hydrazine. However, if hydroxylamine hydrochloride was substituted for hydrazine a satisfactory separation could be obtained. Thus, an 80% extraction of rhenium and negligible ($<0.01\%$) extraction of technetium resulted when 15 ml of 5 *M* sodium hydroxide containing perrhenate (15 mg Re) and pertechnetate was extracted with 15 ml of methyl ethyl ketone in the presence of 0.5 g of hydroxylamine hydrochloride. The recovery of rhenium could be increased to 98% by carrying out two further extractions with 5-ml aliquots of the ketone. This extraction procedure was therefore adopted and employed in the analytical scheme immediately following the neutron activation stage. The extraction of other elements which are retained as chloro-anions by Deacidite FF was investigated and it was observed (Table III) that rhenium was satisfactorily separated from several of them.

## EXPERIMENTAL

Water and acids used in the analysis were purified by distillation through a silica still.

Counting of the tetraphenylarsonium perrhenate precipitates was carried out with an end-window Geiger tube coupled to an EKCO preamplifier (type N558) and scaler (type 530F).

### *Ion-exchange column*

Wash Deacidite FF resin (50–100 mesh) with a current of water to remove "fines" and then digest it twice on the water bath with 2 *M* hydrochloric acid. Wash the resin with water and fill a 0.6-cm diameter ion-exchange column to a depth of 10 cm with it.

### *Elution reagents*

*Formic acid–hydrochloric acid reagent.* Mix 950 ml of 90% formic acid with 50 ml of concentrated hydrochloric acid (s.g. 1.18).

*Acetone–hydrochloric acid reagent.* Mix 475 ml of acetone with 25 ml of concentrated hydrochloric acid (s.g. 1.18).

### *Determination of rhenium in sea water*

Immediately after collection, filter 15 l of the sea water through a Millipore HA filter (0.45 μm) and treat it with 238 ml of constant-boiling hydrochloric acid.

Allow the filtered water to pass through the column of ion-exchange resin at a flow-rate not exceeding 5 ml $min^{-1}$. Wash the column with 50 ml of water and elute rhenium with 90 ml of 4 *M* nitric acid; collect the eluate in a silica flask. Evaporate the eluate slowly to *ca.* 1.5 ml and transfer it quantitatively to a silica irradiation capsule, using a small volume of water for washing. Place the capsule in an oven at 90° and evaporate the solution to *ca.* 0.2 ml, taking care to avoid contamination. Cool the capsule in liquid nitrogen and seal it using an oxyhydrogen torch. To prepare the blank, pass 238 ml of constant-boiling hydrochloric acid through a column of Deacidite FF (rhenium is quantitatively adsorbed from 6.5 *M* hydrochloric acid). Wash the column with 50 ml of water, elute with 90 ml of 4 *M* nitric acid and proceed as described above.

Place the capsules containing the sample and blank into an aluminium can, together with others containing known amounts of rhenium as potassium perrhenate (0.10 and 0.20 $\mu$g Re) dissolved in 0.2 ml of 4 *M* nitric acid, and corresponding blanks consisting of 0.2 ml of 4 *M* nitric acid. Irradiate in a thermal neutron flux of not less than $3 \cdot 10^{12}$ n $cm^{-2}$ $sec^{-1}$ for not less than 50 h. After completion of the irradiation, allow the can to cool for two days before commencing the radiochemical separation.

*Radiochemical separation of rhenium*

Cool the ampoules containing the samples and the corresponding blanks in liquid nitrogen and open them at the constriction. Transfer their contents quantitatively to silica beakers using concentrated nitric acid. Add to each as a carrier, 15 mg of rhenium as potassium perrhenate and sufficient 2 *M* sodium hydroxide solution to make the solution slightly alkaline. Evaporate the solution to dryness on the hotplate. Take up the residue in 15 ml of 5 *M* sodium hydroxide, transfer the solution to a 50-ml separating funnel and add 0.5 g of hydroxylamine hydrochloride. Extract three times with methyl ethyl ketone (15 ml, 5 ml, 5 ml) shaking on each occasion for 5 min. Wash the combined organic phases with 5 ml of 5 *M* sodium hydroxide solution. Transfer the ketone phase to a beaker and evaporate it to dryness on the water bath in a current of air.

Take up the residue in 5 ml of formic acid–hydrochloric acid reagent and pass the solution through a 5×0.5 cm column of Dowex-1 (100–200 mesh) which has previously been washed with 50 ml of the formic acid–hydrochloric acid reagent. Elute the column with a further 35 ml of this reagent, followed by 25 ml of water and 45 ml of aqueous 0.5 *M* hydrochloric acid. Reject these eluates. Cool the column in iced water and elute rhenium with 45 ml of acetone–hydrochloric acid reagent. Collect the eluate in a beaker containing 10 ml of water. Evaporate the acetone on the water bath. Adjust the pH of the resultant liquid to 8.5 by cautious addition of 2 *M* ammonia solution and add 1 ml of a 0.05 *M* aqueous solution of tetraphenylarsonium chloride. Heat the solution to 80° for 10 min to assist the precipitate to become granular. Filter the cold solution through a tared membrane filter and wash it with 4–5 ml of water. Transfer the filter to a tared planchette and dry in an oven at 110° for 30 min. When cool, weigh to determine the chemical yield of the separation process. Count the rhenium-186 activity of the precipitate with an end-window counter.

To standardize the procedure, open the irradiated capsules containing known amounts of rhenium, dissolve their contents in water, add 15 mg of rhenium, as potassium perrhenate and precipitate and count the tetraphenylarsonium perrhenate as described above. Carry out a corresponding reagent blank. Confirm the identity of the induced activity of the precipitate from the sample by measuring its half-life and aluminium absorption curve and comparing these with those of the standard.

## RESULTS

The precision of the procedure was tested by performing 6 replicate analyses on 10-l aliquots of a sample of sea water from the Menai Straits (Cl=*ca.* 34.0°/oo). These showed an average rhenium content of 0.057 $\mu$g $l^{-1}$, with a coefficient of variation of ±7%. The accuracy of the method was examined by analyzing 10-l

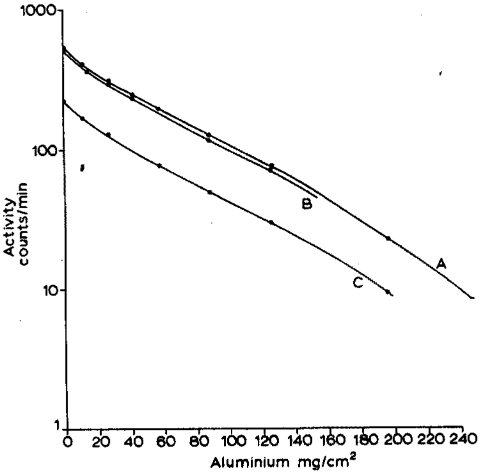


Fig. 1. Aluminium absorption curves for separated rhenium-186 activity. (A) Rhenium standard; (B) rhenium-186 activity from sample of Irish Sea water; (C) rhenium-186 activity from water from 250 m at Discovery Station 6998.

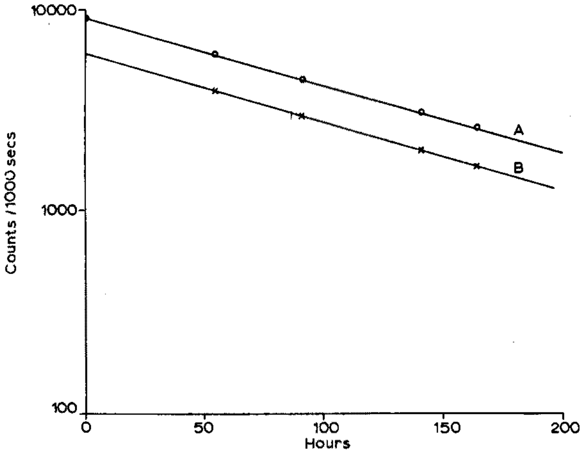


Fig. 2. Decay curve (A) of separated rhenium-186 from sample taken at 250 m at Discovery Station 6998. (B) Decay curve of irradiated rhenium standard.

aliquots of sea water both alone, and spiked with 0.25 $\mu$g of rhenium. These analyses showed the recovery of the added rhenium to be 99%.

In order to establish the general level of rhenium in the Atlantic analyses were carried out on water collected at Discovery Station 6998 (Lat. 27° 28.5'N, Long. 14°45.5'W, sonic depth 3547 m). Concentrations of 8.0, 5.9 and 6.7 ng $l^{-1}$ were found at depths of 250, 500 and 1000 m respectively. These values are similar to those found by SCADDEN for surface waters of the Pacific.

The identity and radiochemical purity of the rhenium-186 from the samples was confirmed by measurement of the half-life and by determining the aluminium absorption curve. The results (Figs. 1 and 2) for water taken at a depth of 250 m at Discovery Station 6998 are typical of those obtained. They suggest that the sample is radiochemically pure and indicate a half-life of $89.5 \pm 0.6$ h for the activity; this is in satisfactory agreement with the literature value[14] of 89 h for the half-life of rhenium-186.

The authors wish to thank Mr. J. HEMMINGWAY for assistance in the neutron activation of the samples. They are also grateful to the Captain and crew of R.R.S. Discovery for help in the collection of samples, and to Dr. J. D. BURTON for assistence in counting the samples.

## SUMMARY

A neutron activation procedure has been developed for the determination of rhenium in sea water. Anion exchange with Deacidite FF is used as a preconcentration stage. Rhenium is eluted with 4 *M* nitric acid and submitted to irradiation with thermal neutrons. Rhenium-186 is separated from other induced activities by solvent extraction and by an almost specific ion-exchange process employing mixed aqueous–organic solvent. Finally, rhenium is precipitated as tetraphenylarsonium perrhenate for determination of chemical yield and counting. Water from intermediate depths in the Atlantic was found to contain 6–8 ng Re $l^{-1}$.

## REFERENCES

1 D. F. C. MORRIS AND E. L. SHORT, in K. H. WEDEPOHL, *Handbook of Geochemistry*, Vol. II-1, p. 75.
2 E. M. SCADDEN, *Geochim. Cosmochim. Acta*, 33 (1969) 633.
3 R. FUKAI AND W. W. MEINKE, *Limnol. Oceanog.*, 7 (1962) 186.
4 F. C. NACHOD, *Ion exchange, Theory and Applications*, Academic Press, New York, 1949, p. 220.
5 K. A. KRAUS AND F. NELSON, *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva*, 7 (1956) 113.
6 G. W. LEDDICOTE, *The Radiochemistry of Rhenium*, NAS-NS 3028 Clearing House for Federal Scientific and Technical Information, Dept. of Commerce, Springfield, Va., U.S.A., 1961.
7 D. F. C. MORRIS AND F. W. FIFIELD, *Talanta*, 8 (1961) 612.
8 J. W. MORGAN, *Anal. Chim. Acta*, 32 (1965) 8.
9 K. ISHIDA, R. KURODA AND K. KAWABUCHI, *Anal. Chim. Acta*, 36 (1966) 18.
10 J. KORKISCH, *Mikrochim. Acta*, (1964) 816.
11 J. S. FRITZ AND T. A. RETTIG, *Anal. Chem.*, 34 (1962) 1562.
12 J. KORKISCH AND I. HAZAN, *Talanta*, 11 (1964) 1157.
13 J. P. GERLIT, *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva*, 7 (1956) 145.
14 P. C. KOCH, *Activation Analysis Handbook*, Academic Press, New York, 1960.

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

# POLAROGRAPHY OF SOME SULPHUR-CONTAINING COMPOUNDS

## PART XV*. POLAROGRAPHIC AND SPECTRAL INVESTIGATION OF ACID-BASE EQUILIBRIA IN AQUEOUS SOLUTIONS OF SUBSTITUTED 2-THIOBARBITURATES

W. F. SMYTH AND G. SVEHLA
*Department of Chemistry, The Queen's University of Belfast, Belfast (Northern Ireland)*
P. ZUMAN**
*Department of Chemistry, The University of Birmingham, Birmingham 15 (England)*

(Received March 19th, 1970)

Thiobarbiturates in the form of sodium salts find their principal use as intravenous anaesthetics. For the assay of the most commonly used, sodium 5-ethyl-5'-(1-methylbutyl)thiobarbiturate (Thiopentone sodium, Thiopental, Pentothal, etc.), the British Pharmacopoeia[1] recommends titration with hydrochloric acid, extraction by chloroform and weighing. Titrimetric methods[2] which are based on oxidation by iodine in alkaline media[3] or chloramine T[4], are more dependable than oxidation by bromate[3], or precipitation of a silver salt[3] and re-titration of excess of silver. Direct titration of thiopentone by silver nitrate with potentiometric or amperometric control in neutral media gives high results[5]. Spectrophotometric determination in the presence of cobalt salts[6] shows limited sensitivity and specificity[7].

Like other sulphur-containing compounds[8], thiobarbiturates have shown[9] anodic polarographic waves corresponding to formation of slightly soluble mercury compounds. The adsorption phenomena involved were shown to depend on the structure of the thiobarbiturate to such a degree that it was possible to distinguish between some derivatives. Anodic waves in 0.1 *M* sodium hydroxide were used for quantitative analysis of pharmaceutical preparations[10]. Polarographic results were in good agreement especially with iodimetric titration and a reasonable agreement was also found for argentimetric procedures. Results obtained by bromate oxidations were erratic and frequently substantially different from those obtained by all three other methods.

Application of polarographic methods based on anodic waves can be somewhat limited by adsorption phenomena occurring above a certain concentration. For this reason attention has been given to polarographic reduction waves of some thiobarbiturates, with the aim of providing an alternative analytical method for some pharmaceutical preparations. The possibility of using cathodic waves of thiobarbitu-

---

* Part XIV: *Anal. Chim. Acta*, 41 (1968) 63.

** Present address: Department of Chemistry, Clarkson College of Technology, Potsdam, N.Y., U.S.A.

rates for analysis of pharmaceuticals has been mentioned[11], but so far as is known, no report has been published and even the question whether the cathodic wave corresponds to a reduction or to hydrogen evolution catalysis (like those observed for thiocytosine[12]) has not been decided.

This paper deals with the polarographic characteristics of some 5,5′-dialkyl-substituted 2-thiobarbiturates including those with one alkyl group on the nitrogen in position 1. The behaviour of S-alkyl-substituted compounds as well as those disubstituted on both nitrogens in positions 1 and 3 differs to some extent, and will be discussed separately, together with some other derivatives. Some results concerning related compounds are considered here only when the reduction mechanism is discussed.

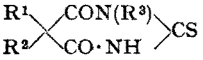
## EXPERIMENTAL

### *Apparatus*

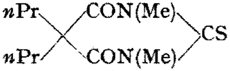
Polarographic curves were recorded using a Polarograph Polariter PO4 (Radiometer, Copenhagen) in conjunction with a Kalousek vessel with a saturated calomel electrode. The dropping electrode used had the following characteristics: outflow

TABLE I

HALF-WAVE POTENTIALS AND LIMITING CURRENTS OF SOME 5,5′-DIALKYL-2-THIOBARBITURATES AND SOME RELATED



($E_{\frac{1}{2}}$ is given as V *vs.* S.C.E. and limiting currents ($i_d$) in μA measured for $10^{-4}$ *M* solutions)

| *Cpd. no.* | *Substituents* | | | *0.1 M $H_2SO_4$* | | | | *Acetate buffer pH 4.6* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | *$R^1$* | *$R^2$* | *$R^3$* | *Cathodic* | | *Anodic* | | *Cathodic* | | *Anodic* | |
| | | | | $E_{\frac{1}{2}}$ | $i_d$ | $E_{\frac{1}{2}}$ | $i_d$ | $E_{\frac{1}{2}}$ | $i_d$ | $E_{\frac{1}{2}}$ | $i_d$ |
| I | Et | (1-Me)Pr | H | — | | — | | $-1.35$ | 0.31 | $+0.15$<br>$+0.22$ | 0.30<br>0.30 |
| II | Et | (1-Me)Bu | H | — | | — | | —[c] | | —[c] | |
| III | Allyl | Isobu | H | — | | — | | $-1.39$ | 0.27 | —[e] | |
| IV | Allyl | Cyclo hexen-2--yl | H | $-0.97^{a}$ | | $+0.05$<br>$+0.18$ | 0.25<br>0.25 | $-1.31$ | 0.30 | $+0.12$ | 0.27 |
| V | Pr | Pr | Pr | $-0.98^{a,b}$ | | — | | —[c] | | —[c] | |
| VI | Et | (1-Me)Pr | Me | — | | — | | $-1.36$ | 0.38 | $-0.02$ | 0.15 |
| VII | Allyl | (1-Me)Pr | Me | — | | — | | $-1.35$ | 0.40 | $-0.01^{d}$ | 0.15 |
| VIII | H | H | H | $-1.03^{a}$ | | —[f] | | — | | —[f] | |
| IX | (1-Me)Bu | H | H | $-0.9^{a}$ | | $+0.34^{g}$ | 0.6 | — | | $+0.17^{g}$ | 0.4 |
| X |  | | | — | | — | | $-1.27$ | 0.90 | $+0.05$ | 0.22 |
| XI |  | | | $-0.98$ | 1.0 | — | | $-1.19$ | 0.6 | $+0.24$ | 0.10 |

[a] Massive catalytic wave. [b] Despite precipitation, a cathodic wave was observed. [c] Precipitation observed for all concentrations investigated. [d] Number of anodic waves observed varies with concentration. [e] Two ill-developed waves. [f] Complexity of waves. [g] $E_{\frac{1}{2}}$ varies with concentration.

velocity $m = 1.73$ mg sec$^{-1}$, drop time $t_1 = 4$ sec at the potential of the saturated calomel electrode and at a mercury pressure $h = 80$ cm in 1 $M$ potassium chloride.

Controlled-potential electrolyses on the microscale were carried out with a dropping mercury electrode in 0.5–2 ml of solution stirred by the falling drops. A vessel designed by MANOUŠEK[13] with a reference electrode separated by sintered glass, an Agar bridge saturated with potassium chloride, and a device to keep the level of the falling mercury constant was used. This cell was connected to the polarograph and the potential set at a constant value. Macroscale controlled-potential electrolyses were carried out at a large mercury pool with a potentiostatted 3-electrode system.

Cyclic voltammetry experiments were done at a hanging mercury drop electrode with standard calomel as reference.

*Reagents*

Thiobarbituric acid derivatives (Table I) were obtained from a variety of sources (see p. 481). Thiopentone (IIa) is a sodium salt of compound II.

Aqueous stock solutions of the thiobarbiturates (usually $10^{-3}$–$5 \cdot 10^{-3}$ $M$) were prepared in deionised water containing a 2–3-fold molar excess of sodium hydroxide, where the acids were dissolved in the form of their sodium salts. The sodium salt used

SPECIES

| *Phosphate buffer pH 6.7* | | | | *Borate buffer pH 9.3* | | | | *0.1 M NaOH* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Cathodic* | | *Anodic* | | *Cathodic* | | *Anodic* | | *Cathodic* | | *Anodic* | |
| $E_{\frac{1}{2}}$ | $i_d$ | $E_{\frac{1}{2}}$ | $i_d$ | $E_{\frac{1}{2}}$ | $i_d$ | $E_{\frac{1}{2}}$ | $i_d$ | $E_{\frac{1}{2}}$ | $i_d$ | $E_{\frac{1}{2}}$ | $i_d$ |
| − 1.37 | 0.29 | + 0.07 | 0.28 | − 1.48 | 0.30 | − 0.06 | 0.30 | − 1.72 | 0.27 | − 0.25 | 0.15 |
| − 1.38 | 0.30 | + 0.09 | 0.27 | − 1.48 | 0.28 | − 0.06 | 0.28 | − 1.72 | 0.28 | − 0.24 | 0.13 |
| − 1.40 | 0.25 | + 0.06 | 0.25 | − 1.52 | 0.24 | − 0.13 | 0.24 | − 1.71 | 0.25 | − 0.26 | 0.11 |
| − 1.34 | 0.27 | + 0.05 | 0.32 | − 1.46 | 0.30 | − 0.13 | 0.30 | − 1.70 | 0.25 | − 0.35 | 0.12 |
| | | + 0.15 | 0.32 | | | 0.00 | 0.40 | | | − 0.24 | 0.30 |
| | | + 0.22 | 0.42 | | | + 0.08 | 0.32 | | | | |
| − 1.36[b] | | —[c] | | − 1.42[b] | | —[c] | | − 1.66 | 0.38 | − 0.31 | 0.14 |
| − 1.36 | 0.40 | − 1.15[d] | 0.15 | − 1.43 | 0.40 | − 0.3[d] | 0.15 | − 1.66 | 0.35 | − 0.31 | 0.15 |
| − 1.36 | 0.42 | − 0.13[d] | 0.15 | − 1.43 | 0.40 | − 0.32[d] | 0.15 | − 1.65 | 0.38 | − 0.30 | 0.15 |
| — | | + 0.01[d] | 0.30 | — | | − 0.09[d] | 0.32 | — | | − 0.22 | 0.40 |
| — | | + 0.07[d] | 0.4 | — | | − 0.09[d] | 0.42 | — | | − 0.27 | 0.40 |
| − 1.37 | 0.75 | + 0.05 | 0.20 | − 1.37 | 0.60 | + 0.05 | 0.20 | — | | − 0.24 | 0.36 |
| | | | | | | − 0.19 | 0.30 | | | | |
| − 1.37 | 0.25 | + 0.15 | 0.12 | — | | − 0.05 | 0.15 | — | | — | |
| − 1.65 | 0.25 | | | | | | | | | | |

(IIa) was dissolved directly in deionised water. Because of base-catalysed hydrolyses of thiobarbiturates in aqueous media, stock solutions had to be used within a few hours of preparation. (The stability of stock solutions of different derivatives was checked by observing any changes in their polarographic behaviour with time.) Typically, 5,5'-disubstituted thiobarbiturates were stable for up to 6 h whereas 1,5,5'-trisubstituted thiobarbiturates had to be used within 1 h.

Buffer solutions and all other supporting electrolytes were prepared from AnalaR-grade chemicals.

### *Experimental techniques*

In polarographic studies, 10 ml of the buffer or other supporting electrolyte was deaerated by a stream of nitrogen, the appropriate volume of the stock solution was added (usually 0.1–1.0 ml) and, after a brief flush with nitrogen, the $i$–$E$ curve was recorded at a slow rate of scanning (100 mV/min) to reduce the effects of hysteresis of the recording instrument. For the study of the dependence of wave height ($i_d$) on concentration, a suitable buffer was chosen and a consecutive addition method used, with brief flushes of nitrogen for deaeration and stirring between successive additions. The $i$–$E$ curves were recorded for each addition of stock solution and plots of diffusion current *versus* concentration of electroactive substance were constructed.

For the microcoulometric experiments, 0.5–2.0 ml of a $1\cdot10^{-3}$ $M$ solution of the examined compound in a suitable supporting electrolyte was transferred to the cell and the capillary was positioned so that its tip was just under the surface of the solution. The solution was deoxygenated, the $i$–$E$ curve recorded and a potential (usually corresponding to the limiting current) selected. The solution was discarded and replaced by the same quantity of a fresh solution. A voltage corresponding to the chosen potential was taken off the potentiometer and the change of current with time at this potential was recorded at a slow chart speed. After 10–20% conversion (required *ca.* 1 h), the electrolysed solution was replaced by the supporting electrolyte alone, in which the residual current was recorded in order to correct the measured limiting current. The logarithm of the diffusion current was plotted as a function of time[14] and from the slope the value of $n$ was calculated from $n=[4.5\cdot10^{-9}(i_d)_0]/[CV\cdot(\text{slope})]$, where $(i_d)_0$ is the limiting current at $t=0$, $C$ the molar concentration and $V$ the volume (in ml).

Preparative microelectrolysis was carried out with the same set-up. Below pH 7 the evolved gas was trapped in 0.1 $M$ sodium hydroxide and anodic waves in this alkaline solution were recorded either after chosen time intervals or at the end of electrolysis. Small aliquots sampled during electrolysis were diluted to $5\cdot10^{-5}$ $M$ and u.v. spectra were recorded.

For electrolyses above pH 10, where hydrogen sulphide is no longer volatile, an aliquot of the electrolysed solution was examined both polarographically and spectrophotometrically at various stages of electrolysis.

The macro-coulometric experiment was carried out also at a potential corresponding to the plateau of the wave. A mercury pool with a surface area of *ca.* 100 cm$^2$ was used as a working cathode. The counter electrode was a platinum wire separated from the cathode by a glass frit. The salt bridge contained agar–agar gel saturated with potassium nitrate and the upper part of the electrode contained saturated potassium nitrate solution. The reference electrode was a saturated calomel. The potentiostat was a Tacussel ASA-JH4T type instrument, used as a current integrator. A hydrazine microcoulometer[15] was also employed for measurement of quantity of electricity used, and the concentration decrease of the thiobarbiturate was followed by recording of polarographic curves of the thiobarbiturate in the electrolysis cell. For these polarographic measurements, a D.M.E. and the mercury pool electrode were used as indicator and reference electrodes.

## RESULTS AND DISCUSSION

### *Reduction process*

The number of reduction waves, their character and their half-wave potentials were found to be similar for all the substituted thiobarbiturates I–VII (Table I). Therefore, a more detailed examination was restricted to 5-ethyl-5′-(1-methylpropyl)-2-thiobarbituric (I) and 1-methyl-5-allyl-5′-(1-methylpropyl)-2-thiobarbituric (VII) acids, and it was only checked that the other compounds behaved analogously.

The reduction takes place in two steps, $i_1$ and $i_2$ (Figs. 1,2). The first reduction step in acidic media $i_1^{H_2A}$ corresponds to a four-electron process. At pH greater than about 3 the height of the wave $i_1^{H_2A}$ decreases in the shape of a dissociation curve until it reaches, at pH about 5.0, a value corresponding to a two-electron process.

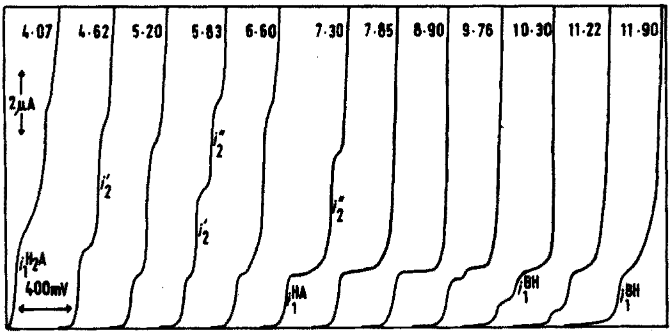


Fig. 1. pH Dependence of waves of $5 \cdot 10^{-4}$ *M* I: pH given on the polarogram; curves starting at −1.25 V; Britton–Robinson buffers.

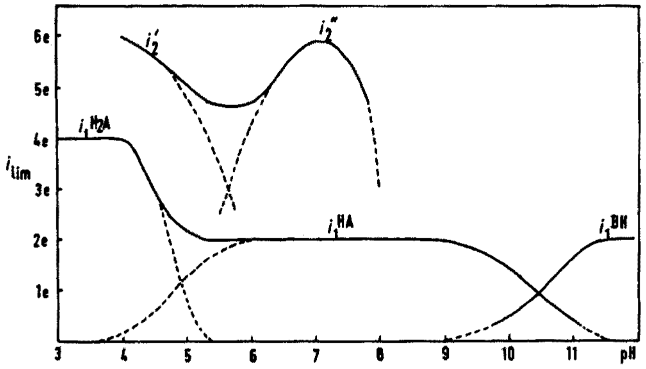


Fig. 2. pH Dependence of limiting currents of $5 \cdot 10^{-4}$ *M* I in Britton–Robinson buffers: (———) experimental values, (----) theoretical dissociation curves.

Shifts of half-wave potentials (Fig. 3a) indicate that the four-electron wave $i_1^{H_2A}$ decreases to zero in the shape of a polarographic dissociation curve with $pK_1'$ about 4.8 and a new two-electron wave $i_1^{HA}$ is formed. The height of this two-electron wave $i_1^{HA}$ remains pH-independent up to pH about 9. With further increase in pH, the height of wave $i_1^{HA}$ decreases in the shape of a polarographic dissociation curve with $pK_2' \simeq 10.5$. Another wave $i_1^{BH}$, is formed at the expense of wave $i_1^{HA}$ at more negative potentials, the total height remaining constant. The half-wave potentials of wave $i_1^{HA}$ are pH-independent at $pH < pK_2$ but are shifted towards more negative values at $pH > pK_2$ and those of wave $i_1^{BH}$ are pH-independent. The intersection of the two linear sections of the $i_1^{HA}$–pH plot at pH 7.4 is in reasonable agreement with the value $pK_2 = 6.9_8$ obtained potentiometrically and the value $pK_2 = 7.60$ obtained spectrophotometrically.

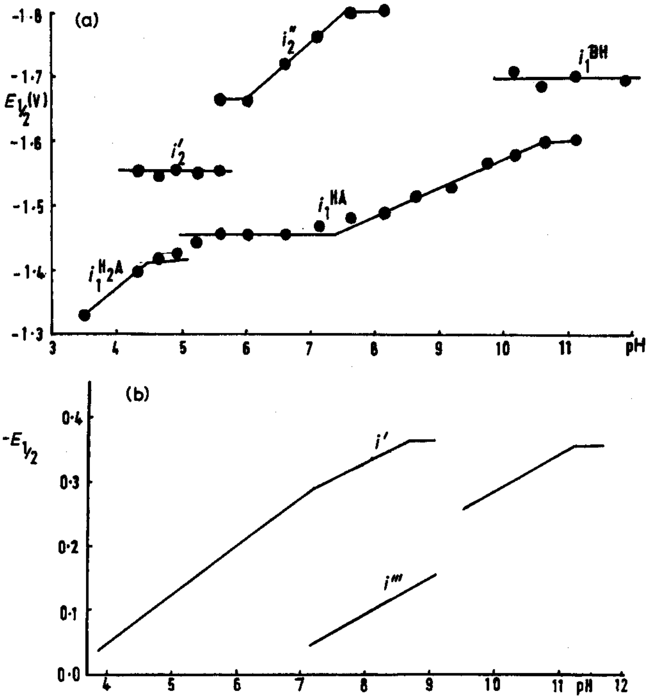


Fig. 3. (a) pH Dependence of half-wave potentials of cathodic waves of I ($5 \cdot 10^{-4}$ *M*) in Britton–Robinson buffers; (b) pH dependence of half-wave potentials of anodic waves of I ($10^{-4}$ *M*) in Britton–Robinson buffers.

The transfer of two electrons in the reduction taking place in wave $i_1^{HA}$ was confirmed by coulometry at a mercury pool electrode for thiopentone (IIa) at pH 8.9. In the electrode process hydrogen sulphide is evolved. This was confirmed by introduction of the liberated gas into a solution containing cadmium salts where cadmium sulphide was formed and by formation of a black precipitate at the surface of the mercury pool electrode.

The yield of hydrogen sulphide or sulphide ions depends on pH. At pH 3.8 the yield was only 10% (some losses by leakage and polymerization cannot be excluded);

at pH 6.9 the total amount of the sulphide formed in electrolysis was about 20%, whereas at pH 11.6 an equivalent of sulphides (*i.e.* practically 100% yield) was formed.

The two or three anodic waves observed had half-wave potentials very close to those of sulphide ions in alkaline media. The ratio of wave-heights and the limits above which the individual waves were concentration-independent, differed from those in pure solutions of sodium sulphide. For example, when the total wave-height corresponded to $5\cdot10^{-4}$ *M* sulphide, three waves were observed in the electrolysis product with half-wave potentials and ratios of wave-heights as observed for a $1\cdot10^{-3}$ *M* solution of sulphide, whereas in $5\cdot10^{-4}$ *M* sulphide only 2 waves were observed. This may be due either to the formation of some mercaptans or to the effect of the surface activity of some components of the reaction mixture.

Further, cyclic voltammetry, when the polarization was carried out to the potential of the limiting current of wave $i_1^{HA}$, showed on the reverse trace an anodic peak corresponding to mercury sulphide formation, different from the cathodic peak of the original thiobarbiturate (Fig. 4) corresponding to the reduction of the mercury salt.

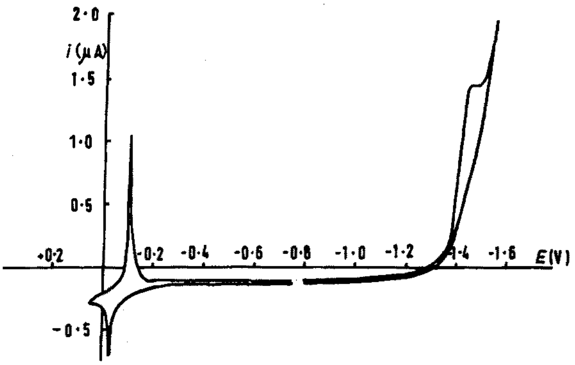


Fig. 4. Cyclic voltammetry of sodium thiopentone ($5\cdot10^{-4}$ *M*) at hanging mercury drop electrode in Britton–Robinson buffer pH 7.21.

The calculation of the number of electrons consumed was carried out either from the decrease of current of the cathodic wave with time during electrolysis or from the increase in volume of the evolved gas (Table II). Controlled-potential electrolyses with the dropping mercury electrode, carried out in small volumes (0.5–1.0 ml of the solution) gave linear log *i*–*t* plots.

The waves $i_1$ were a linear function of concentration from $1\cdot10^{-4}$ *M* to

TABLE II

MACROCOULOMETRIC DETERMINATION OF THE NUMBER OF ELECTRONS TRANSFERRED

($5\cdot10^{-3}$ *M* thiopentone sodium at $-1.75$ V (*vs.* S.C.E.) in Britton–Robinson buffer pH 8.9)

| *Time* | 0 | $t_1$ | $t_2$ | $t_3$ | $t_4$ |
|---|---|---|---|---|---|
| *A* (ml)[a] | 0 | 2.42 | 5.03 | 7.45 | 10.00 |
| *n* | — | 1.92 | 1.79 | $1.92_5$ | 2.03 |

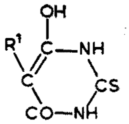
[a] Evolved gas.

$3 \cdot 10^{-3}$ $M$ over the entire pH range. Waves $i_1^{H_2A}$, $i_1^{HA}$ and $i_1^{BH}$ in the pH range where they reached the value corresponding to four- or two-electron transfer, respectively, were a linear function of the square root of mercury pressure and hence were diffusion-controlled. At pH about 11, when wave $i_1^{HA}$ was a small fraction of $i_1$, its wave-height was practically independent of mercury pressure and hence was kinetically controlled. Similarly, the plot of wave $i_1^{H_2A}$ (for $i_1^{H_2A} = 1.2\ i_1^{HA}$) as a function of $h_{Hg}^{\frac{1}{2}}$ indicated a kinetic component.

In the medium pH range, another wave $i_2$ was observed at more negative potentials, which corresponded to a transfer of another six electrons. The wave $i_2'$ observed at lower pH values decreased with increasing pH and was replaced by wave $i_2''$ which above pH 7 again decreased (Fig. 2). The $i$–pH plot (Fig. 2) gives values of the polarographic dissociation constants p$K_A'$ (between 5 and 6) and p$K_B'$ (between 7 and 8). Whereas the half-wave potential of wave $i_2'$ is practically pH-independent (Fig. 3a) that of wave $i_2''$ shows intersections of linear parts of the $E_{\frac{1}{2}}$–pH plot, corresponding to p$K_B \simeq 6$ and p$K_B' \simeq 7.5$.

The constant overall height of waves $i_2' + i_2''$ in the pH range 4–7 which corresponds to a six-electron process, together with the shifts of the half-wave potentials excludes the possibility that wave $i_2$ could correspond to catalytic hydrogen evolution. The wave was, on the other hand, so ill-developed that the effect of other parameters was not further studied. Below about pH 4 the wave was overlapped by the current of hydrogen evolution.

Unsubstituted 2-thiobarbituric acid (VIII) and 5-monoalkyl-2-thiobarbituric acid derivatives (IX) did not give any reduction waves in the available potential range.



VIII $R^1 = H$
IX $R^1 =$ alkyl

The anodic curves corresponding to mercury salt formation showed one or two waves according to pH and concentration (Fig. 3b) as has been observed for other thiobarbiturates[9]. At low pH values, adsorption phenomena occurred and limited the region in which the wave-height was a linear function of concentration; in 0.1 $M$ sodium hydroxide, the anodic waves were linearly proportional to concentrations up to $2 \cdot 10^{-3}$ $M$ for some compounds. The adsorption phenomena were even more developed for the N-alkyl compounds V–VII than for derivatives I–IV, but the differences between the two groups were not greater than the differences between various C-alkyl derivatives[9]. The anodic waves of compounds VIII and IX having one or two hydrogen atoms on the carbon in position 5 followed a similar pattern. As their reducibility was fundamentally different from that of compounds I–VII, it is obvious that another grouping is involved in reduction than in the formation of mercury salts which is responsible for the anodic waves.

1,3-Dimethyl-5,5'-di-*n*-propyl-2-thiobarbituric acid (X) gives at pH 8 to 9.5 one 2-electron reduction wave (the height of which decreases with increasing pH) in the shape of a dissociation curve with p$K_2' = 10.95$. Below pH 8 a gradual increase is observed with an inflexion point at about pH 6. At pH 4 the wave-height reaches a value corresponding approximately to a 3-electron reduction (Fig. 5a). The half-wave potential of the reduction wave is shifted in the pH range 2–6 by 0.085 V/pH and remains practically pH-independent at −1.37 V (*vs.* S.C.E.) in the pH range 6–12 (Fig. 5b).

Compound X also gives an anodic wave ($i_a$) at +0.05 V corresponding to a one-electron process, the height of which is pH-independent between pH 2 and 9.5. At higher pH values this wave is replaced by another, more negative wave ($i_a'$) increasing with pH in the form of a dissociation curve with p*K* 10.75 till at pH 12 it reaches approximately a value corresponding to a 2-electron process (Fig. 5a).

The polarographic behaviour of compound XI will be dealt with in a later paper.

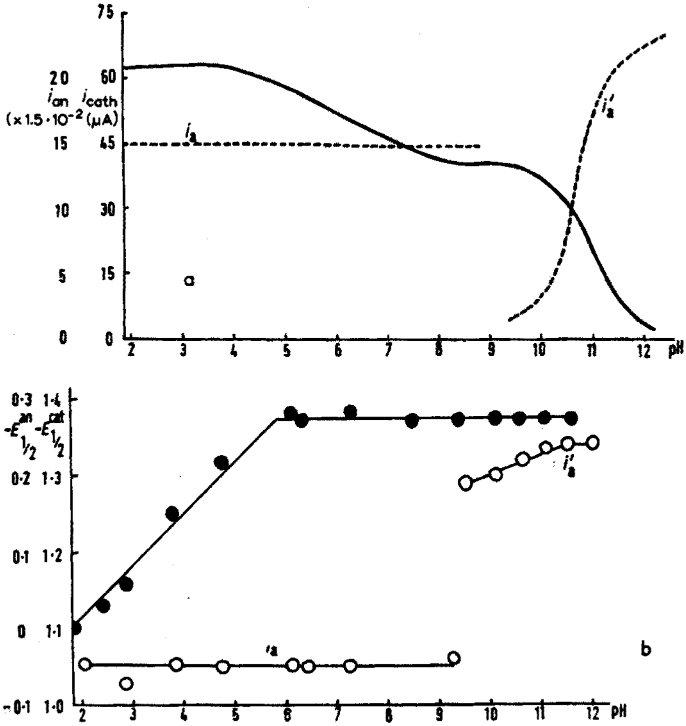


Fig. 5. (a) pH Dependence of anodic (----) and cathodic (———) limiting currents of $10^{-4}$ *M* X in Britton–Robinson buffers, 10% ethanol; (b) pH dependence of the half-wave potentials of the anodic (○) and cathodic (●) waves of $10^{-4}$ *M* X in Britton–Robinson buffers, 10% ethanol.

### *Electronic spectra*

The simplest spectral behaviour was shown by compound X which has no possibility of forming a thiolate form with C–S⁻ grouping. Compound X, bearing an alkyl group on each of the nitrogen atoms, gives at lower pH values than about 10, one intense absorption band at 285 nm accompanied by a shoulder at 258 nm. These bands do not change with acidity up to pH 1. As the compound has no possibility of forming an enol or enolate, both bands at 258 and 285 nm at lower pH values must correspond to two electronic transitions involving the same species.

Above pH 10, the band at 285 nm decreases and is replaced by a broad band (two overlapping bands) at 260 nm accompanied by a weak shoulder at 245 nm. The change of spectra with pH is accompanied by an isosbestic point at 250 nm, indicating that a simple acid–base equilibrium is involved. From the change of the extinction at 290 nm, it was possible to determine the p$K$ value (p$K$ = 10.5). The spectra were time-independent.

Relatively simple behaviour was shown also by compounds V–VII. In acidic media, a strong absorption band at 288 nm was accompanied by a weaker band at 250 nm. Above pH 7 these bands gradually decreased with increasing pH and were replaced by an intense band at 310 nm accompanied by a weaker band at 268–278 nm. In 0.1 $M$ sodium hydroxide and in more alkaline solutions the spectra changed with time owing to alkaline hydrolytic cleavage. At pH 7–9 there are four isosbestic points at 230 nm, 258 nm, 270 nm and 298 nm (Fig. 6). From the change in the absorbance at 315 nm, it was possible to determine the p$K$ value (p$K$ = 8.0 for VII and 8.10 for VI).

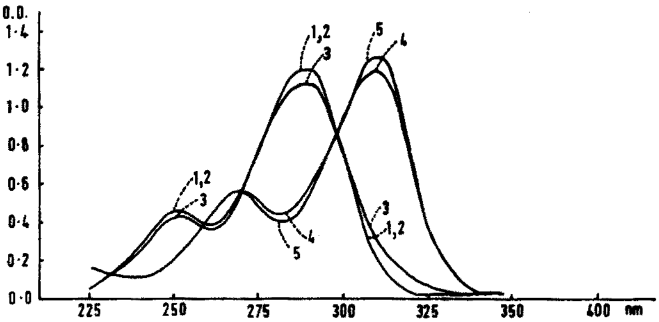


Fig. 6. pH Dependence of u.v. spectra of $5\cdot10^{-5}$ $M$ VII (1-cm cells): (1) 0.1 $M$ HCl, (2) acetate buffer pH 4.65, (3) phosphate buffer pH 7.3, (4) borate buffer pH 9.3, (5) 0.1 $M$ NaOH.

More complex changes were observed for the spectra of the disubstituted compounds I–IV and for 2-thiobarbituric acid (VIII) and its monoalkyl derivative (IX). At pH about 5 in solutions of the dialkyl derivatives I–IV, an absorption band at 292 nm predominated accompanied by a shoulder at 260 nm and a weaker band at 241 nm. Above pH 6 these bands decreased and were replaced by an intense band at 305 nm accompanied by a weaker band at 257 nm. The change of these bands corresponded to p$K$ = 7.60 (for compound I). In more strongly acidic media, below pH 2 an increase of bands at 288 nm (different from that at 292 nm, but overlapping) and at 240 nm was observed.

In alkaline media, above pH 11.5 an increase of the band at 305 nm was accompanied by formation of a shoulder at about 285 nm and decrease of the band at 257 nm. SATO[16] reports p$K$ 12.07 for the ethyl-(1-methylbutyl) derivative. The spectra in 1 $M$ sodium hydroxide were time-independent for at least 15 min.

Finally, the unsubstituted thiobarbituric acid VIII and monoalkyl derivative IX below pH 1 gave strong absorption bands at 283 nm accompanied by weaker bands at 235 nm. With increasing pH these bands were replaced by strong bands at 263 nm accompanied by shoulders at 280 nm and weaker bands at 243 nm. (For IX, these values were somewhat shifted, Table III.) This change corresponds to p$K$ 2.25 reported in the literature[16] and these bands predominated up to pH 10. (For IX, this p$K$ value was smaller than 2.) In strongly alkaline media these bands were replaced by a strong band at 236 nm, accompanied by a weaker band at 283 nm and a shoulder at 260 nm. These changes are in agreement with the value of p$K$ (10.72) reported previously[16].

All spectral data are summarised in Table III.

TABLE III

ELECTRONIC SPECTRA OF THIOBARBITURATES[a]

($\varepsilon \cdot 10^4$; b = broad; s = shoulder; d = decomposition)

| *Compound* | *$H_2A$* | | *HA* | | *BH* | | *B* | | *C* | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\lambda_{max}$ | $\varepsilon$ | $\lambda_{max}$ | $\varepsilon$ | $\lambda_{max}$ | $\varepsilon$ | $\lambda_{max}$ | $\varepsilon$ | $\lambda_{max}$ | $\varepsilon$ |
| I | 240 | 1.2 | 241 | 0.9 | 257 | 1.4 | 285s | 0.2 | — | |
| | $\underline{288}$ | 3 | 260s | 1.3 | $\underline{305}$ | 2.8 | $\underline{305}$ | 3 | | |
| | | | $\underline{292}$ | 2.3 | | | | | | |
| IV | 238 | 0.8 | 239 | 0.7 | 256 | 0.9 | 285s | 0.2 | | |
| | $\underline{288}$ | 2 | $\underline{294}$ | 2.0 | $\underline{307}$ | 2.8 | $\underline{307}$ | 3 | — | |
| VI | — | | 250 | 0.6 | 278 | 1.1 | d | | d | |
| | | | $\underline{288}$ | 2.2 | $\underline{308}$ | 2.5 | | | | |
| VII | — | | 250 | ≃0.6 | 268 | 1.0 | | | | |
| | | | $\underline{288}$ | 2.4 | $\underline{310}$ | 2.5 | d | | d | |
| VIII[c] | — | | 235 | 0.9 | — | | — | | 243 | 0.8 |
| | | | $\underline{283}$ | 2.4 | | | | | $\underline{263}$ | 1.8 |
| | | | | | | | | | 280s | ≃0.3 |
| IX[c] | — | | 240 | 0.5 | — | | — | | 239 | 1.0 |
| | | | $\underline{286}$ | 1.2 | | | | | $\underline{275}$ | 1.8 |
| | | | | | | | | | 290s | ≃0.2 |
| X | — | | 258s | ≃0.3 | — | | — | | 245s | ≃0.5 |
| | | | $\underline{285}$ | 2.2 | | | | | $\underline{260b}$ | >0.8 |

[a] Main spectral bands underlined.

[c] Forms D

| | | | | |
|---|---|---|---|---|
| VIII | $\lambda_{max}$ | $\underline{236}$ | 260s | $\underline{283}$ |
| | $\varepsilon \cdot 10^4$ | 1.8 | ~0.3 | 1.3 |
| IX | $\lambda_{max}$ | $\underline{234}$ | 265s | $\underline{288}$ |
| | $\varepsilon \cdot 10^4$ | 1.9 | ~0.1 | 1.3 |

### *Reduction scheme*

The polarographic reduction waves can be interpreted by means of the following scheme*

$$H_2A \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HA + H^+ \qquad pK_1 \tag{1}$$

$$HA \quad \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} BH + H^+ \qquad pK_2 \tag{2}$$

---

* Symbols $H_2A$, HA, BH, B, $P_i$, etc. are not intended to depict the unit charge of the species involved, *e.g.* $H_2A$ can be a bipositive or positive ion or a neutral molecule.

$$H_2A + 4e \xrightarrow{E_1^{H_2A}} P_1 \qquad i_1^{H_2A} \tag{3}$$

$$HA + 2e \xrightarrow{E_1^{HA}} H_2P_2 \qquad i_1^{HA} \tag{4}$$

$$H_2P_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} HP_2 + H^+ \qquad pK_A \tag{5}$$

$$HP_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} P_2 + H^+ \qquad pK_B \tag{6}$$

$$H_2P_2 + 6e \xrightarrow{E_2'} X_1 \qquad i_2' \tag{7}$$

$$HP_2 + 6e \xrightarrow{E_2''} X_2 \qquad i_2'' \tag{8}$$

$$BH + 2e \xrightarrow{E_1^{BH}} P_3 \qquad i_1^{BH} \tag{9}$$

For some compounds, where wave $i_2''$ decreases and then reaches a limiting value corresponding to a 2-electron process, it seems possible that a further reaction (10) can be involved.

$$P_2 + 2e \xrightarrow{E_2''} X_3 \qquad i_2'' \tag{10}$$

The spectra of 5,5'-dialkyl-2-thiobarbiturates in strongly alkaline media indicate the presence of another acid–base equilibrium:

$$BH \rightleftharpoons B + H^+ \qquad pK_3 \tag{11}$$

For the ranges of values of dissociation constants in the above scheme, the following approximate values are available: $pK_1 < 2$ (for I–IV) and $pK_1 < 0$ (for V–VII); $pK_2 = 7$–$8$; $pK_3 = 12$–$13$ (for I–IV, not observed for V–VII); $pK_A < 4$; $pK_B = 5$–$7$. Some available data for individual compounds are summarized in Table IV.

At pH < 3 the establishment of the equilibrium (1) is rapid and species $H_2A$ is reduced in a 4-electron step. Further reducibility of the reduction product of the 4-electron process cannot be distinguished because of the hydrogen evolution.

At pH 5.5–9.5, the establishment of the second dissociation step (2) is rapid and species HA is reduced in a 2-electron step. The product of this reduction $H_2P_2$ is reduced at lower pH values, when the protonation with rate constant $k_{-3}$ is fast, in a 6-electron step, like the conjugate base $HP_2$ at pH 6.5–8. Above pH 7 the protonation with rate constant $k_{-4}$ is no longer fast enough to transform all $P_2$ into $HP_2$ and wave

TABLE IV

VALUES OF EQUILIBRIUM DISSOCIATION CONSTANTS ($pK_2$) AND FORMAL POLAROGRAPHIC DISSOCIATION CONSTANTS ($pK_1'$, $pK_2'$) DETERMINED BY POTENTIOMETRY, SPECTROPHOTOMETRY AND FROM POLAROGRAPHIC MEASUREMENTS OF HALF-WAVE POTENTIALS AND LIMITING CURRENTS AS A FUNCTION OF pH

| *Compound* | $pK_1'$ | | $pK_2'$ | | $pK_2$ | | | *log* $k_{-2}$ |
|---|---|---|---|---|---|---|---|---|
| | $E_{\frac{1}{2}}$–*pH* | *i*–*pH* | $E_{\frac{1}{2}}$–*pH* | *i*–*pH* | $E_{\frac{1}{2}}$–*pH* | *Potentiometry* | *Spectrophotometry* | |
| I | $4.5_0$ | 4.8 | $10.5_5$ | $10.5_0$ | $7.4_0$ | $6.9_8$ | $7.6_0$[a] | $13.0_0$ |
| III | $4.2_5$ | $4.4_0$ | $10.5_5$ | $10.6_5$ | $7.0_5$ | $6.8_5$ | $7.1_0$[a] | $13.7_0$ |
| IV | $4.4_1$ | $4.8_0$ | $10.0_0$ | $10.3_3$ | $7.0_8$ | $6.8_0$ | $7.2_0$[a] | $12.7_5$ |
| VI | $5.2_5$ | 5.3[c] | $11.3_0$ | $11.1_5$ | $8.3_0$ | — | $8.1_0$[b] | $13.8_0$ |
| VII | $5.2_0$ | 5.3[c] | $11.2_0$ | $11.1_4$ | $8.2_0$ | — | 8.0[b] | $13.7_5$ |
| X | $\simeq 6$ | $\simeq 6$ | 11.3[d] | $10.9_5$<br>$11.7_5$[d] | — | — | 10.5 | — |

[a] $pK_3 = 12$–$13$. [b] Changes with time above pH 12 prevent determination of $pK_3$. [c] Owing to the absence of a complete "polarographic" dissociation curve, this value is very approximate. [d] Anodic wave.

$i_2''$ decreases. When form $P_2$ is reducible, this decrease is not complete but stops at a 2-electron process (10).

In the intermediate pH range 3–5.5 processes (3) and (4) compete and the wave height $i_1$ is limited by the rate of protonation with constant $k_{-1}$.

Above pH 12 only form B is reduced in a 2-electron step, the potential of which is pH-independent. The product of the electroreduction of this species $P_3$ is no longer electroactive.

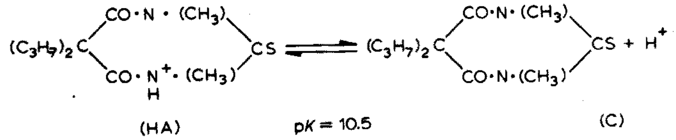
In the transitional range between pH 9.5 and 12, processes (4) and (9) also compete.

The shifts of half-wave potentials are in agreement with this interpretation; values for $pK_1'$ and $pK_2'$ from *i*–pH plots approximately agree with intersections on $E_{\frac{1}{2}}$–pH plots (Table IV) where intersections from smaller to greater slope correspond to the $pK_2$ value. For reaction (1), u.v. data for compounds I–IV indicate that the $pK_1$ value is 1–2, but as no more accurate data were available, no attempt was made to calculate the rate constant $k_{-1}$. From the difference of $pK_2'$ and $pK_2$, the value of the rate constant $k_{-2}$ was calculated[17]. Values of the order of $10^{13}$ (Table IV) indicate that protonation (2) proceeds at the surface of the dropping mercury electrode as a surface[18] rather than a volume reaction.

### *Structure of species involved in acid–base equilibria and polarographic reduction*

The spectroscopic and polarographic data indicate the presence of four different species in solutions of compounds I–IV: $AH_2$, AH, BH and B. It is possible to attribute $AH_2$ to monoprotonated, AH to unprotonated (or zwitterion), BH to monoanionic and B to dianionic forms, or $AH_2$ to diprotonated, AH to monoprotonated, BH to unprotonated (or zwitterion) and B to monoanionic forms. These alternatives can be distinguished as follows.

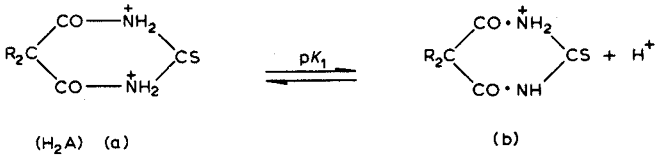
Substance X cannot form anionic forms bearing a C–S⁻ grouping and hence only one protonation can be involved:



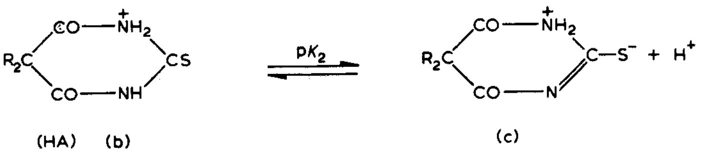
$$(C_3H_7)_2C\begin{matrix}CO\cdot N\cdot(CH_3)\\CO\cdot \underset{H}{N^+}\cdot(CH_3)\end{matrix}CS \rightleftharpoons (C_3H_7)_2C\begin{matrix}CO\cdot N\cdot(CH_3)\\CO\cdot N\cdot(CH_3)\end{matrix}CS + H^+ \quad (12)$$

(HA) $pK = 10.5$ (C)

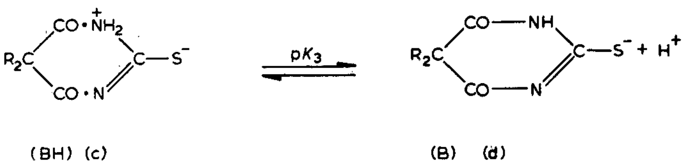
It is thus possible to conclude that the form of derivatives I–IV predominating in strongly acidic media is a diprotonated species and the three dissociation equilibria are:



(13)

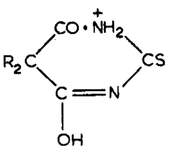


(14)

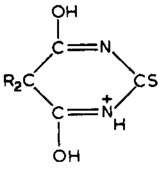


(15)

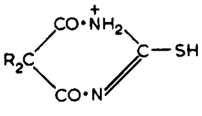
In eqns. (13)–(15) only one of the possible existing tautomeric forms is given, but it is assumed that the depicted structure corresponds to the predominant form. The attribution is based on comparison of electronic spectra. As the spectra of the form HA (b) of substances I–IV are similar to the spectra of the fully N-methylated compound X (Fig. 7) which cannot form enol or thioenol forms, it can be assumed that form HA is not (e), (f) or (g), but (b):



(e)



(f)



(g)

The presence of two absorbance bands in the N-dimethyl compound X at similar wavelengths and with a similar ratio of extinction coefficients as for compounds I–IV, indicates that the two bands at 240 and 290 nm cannot be attributed to keto and enol forms (as X cannot exist except in the keto form), but to two transitions involving the same species.

Because of the similarity of the spectra of forms $H_2A$ and HA for I–IV, it seems most logical to consider (a) as the predominant diprotonated form, but no corroborating evidence can be offered.

The spectra of form B showed strong absorbance bands in the region of 300 nm characteristic of anionic forms (d). Moreover, this spectrum was rather different from that of form C of compound X which cannot form anions of the type $C–S^-$.

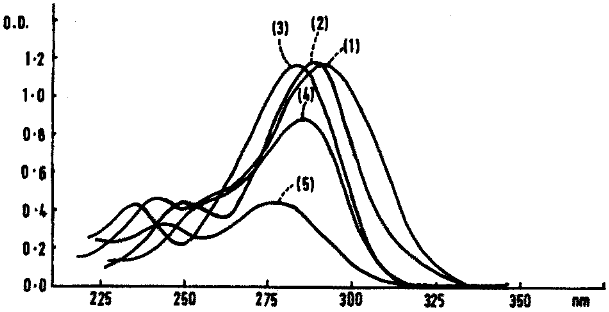
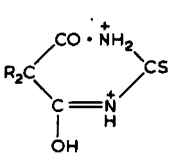


Fig. 7. Comparison of u.v. absorption spectra of the species HA for selected 2-thiobarbiturates of concentration $5 \cdot 10^{-5}$ *M*, except X which is $4 \cdot 10^{-5}$ *M*. (1) I, pH 2–7; (2) VII, pH 1–8; (3) VIII, pH <2; (4) X, pH 1–10; (5) XI, pH 1–4.

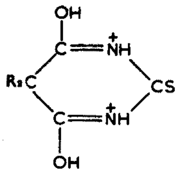
On the other hand, the spectra of form BH were considerably more like those of form B of compounds I–IV than like form C of substance X. Moreover, whereas for compound X the strongest absorbance band shifted with increasing pH to shorter wavelengths (which corresponds to the change of form HA to C), for compounds I–IV the change from HA to BH was accompanied by a shift of the strongest absorbance band to longer wavelengths. For these reasons, it is concluded that form BH for compounds I–IV is a zwitterion (c) rather than a neutral molecule.

Thus, for compounds I–IV, with increasing pH the diprotonated form is transformed consecutively into monoprotonated, zwitterion and anionic forms, the thiono–keto form predominating in acidic media and the thiolate–keto form in alkaline. For compounds V–VII, experimental evidence indicates only the presence of monoprotonated and zwitterion forms, whereas for compound X the monoprotonated form changes in alkaline media to the uncharged molecule.

The electroactive species is not necessarily the form predominating at a given pH in the bulk of the solution. From the limited evidence available on the nature of the 4-electron reduction products of the form $H_2A$, it is only possible to deduce that the reduction does not take place on the C=S group of the diprotonated form $H_2A$ (a), as little hydrogen sulphide is liberated. The disappearance of electroactive and of u.v.-absorbing species indicates that the primary electrolysis product is less conjugated than the oxidized form. Such a process can take place during a 4-electron reduction of the C=N double bond in the form (h) resulting in reductive cleavage of the ring, during two 2-electron processes attacking one C=N and one C=S bond in the form (h), or during two simultaneous 2-electron processes reducing the two C=N double bonds in form (j):



(h)

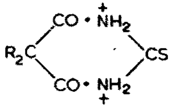
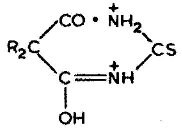
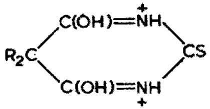
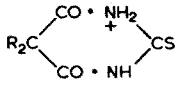
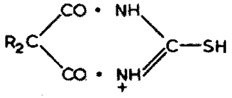
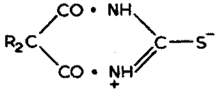
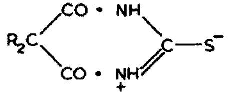
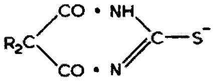
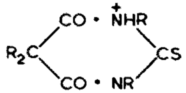
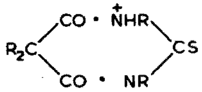
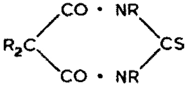


(j)

The hydrogen sulphide liberated is formed by a subsequent cleavage of the primary reduction product, which is not very fast in acidic media. Such an elimination reaction

TABLE V

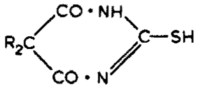
PREDOMINANT FORMS IN VARIOUS pH RANGES AND THE MOST PROBABLE ELECTROACTIVE FORMS

| *Form* | *Approximate pH range* | *Predominant structure* | *Wave* | *Approximate pH range* | *Most probable reducible forms* | *structure* | *bonds* |
|---|---|---|---|---|---|---|---|
| $H_2A$ | $< 1$ |  | $i^{H_2A}$ | $< 4$ | h |  | C = +NH + C = S |
| | | | | | j |  | 2C = +NH |
| HA | 2–7 |  | $i^{HA}$ | 6–9 | g |  | C = +NH |
| BH | 9–11 |  | $i^{BH}$ | 11–13 | c |  | C = +NH |
| B | $> 13$ |  | — | — | — | — | — |
| HA | 2–9 |  | $i^{HA}$ | 7–9 | HA |  | C = S |
| C | $> 11$ |  | — | — | — | — | — |

can hardly occur with the first of the above-mentioned reduction products which would be a thiourea derivative. But to decide between the two 2-electron reductions of C=N and C=S in (h) and two C=N bonds in (j), further identification of electrolysis products would be necessary.

The similar reduction pattern of the form HA derived for compounds I–VII and the S-methyl derivative XI as shown by a 2-electron process followed by a 6-electron uptake indicates that form (g) might be the electroactive species. As the anodic waves observed are again only a fraction of the equivalent concentration, it can be concluded that the reduction does not involve a nucleophilic substitution of the SH group in (g) by hydrogen. However, it cannot be distinguished if the ring is reductively split or the reduction attacks the C=N band in the electroactive species (g). The anodic waves being smaller than would be expected indicate that hydrogen sulphide is again generated in a chemical reaction after electroreduction. The cleavage of the primary electrolysis product, which appears to be less conjugated than the original compound there being no new waves (apart from indistinct waves in the region of the more negative wave $i_2$) and no intense u.v. absorbance bands formed, takes place faster in solutions of the reduction product formed at $i_1^{HA}$ than at $i_1^{H_2A}$.

Two-electron reduction of form BH offers the possibility of considering (c) or the uncharged form (k) as the electroactive species, but a further reduction of the product of the 2-electron transfer was not observed.



(k)

The reduction process might be a 2-electron cleavage of either the C–SH bond in (k) or the C=N double bond in (c) or (k), followed by a very fast elimination of $S^{2-}$ to account for the quantitative yield of sulphide.

For the N-alkyl derivatives V–VII the formation of the diprotonated form $H_2A$ and the anion B was not observed. The $pK_1$ is probably smaller than 0 and was not manifested in the studied pH range. Nevertheless, the increase in current below pH 4.4 indicates that the electroactive species in acidic media is again the diprotonated form, formed in protonation (13). Similarly, because of alkaline hydrolysis the pH region of existence of equilibrium (15) was not experimentally accessible. Hence, for the N-methylated compounds V–VII only establishment of equilibrium (14) was indicated.

Based on the similarity of the polarographic behaviour of forms HA and BH of compounds V–VII with the corresponding forms of compounds I–IV, it can be deduced that in wave $i_1^{HA}$ form (g), and in wave $i_1^{BH}$ form (c) or (k), are probably reduced in 2-electron steps.

The absence of reduction waves in solutions of unsubstituted 2-thiobarbituric acid (VIII) and its 5-monoalkyl derivatives (IX), is interpreted by predominance of enol forms and is discussed in detail at a later date.

For compound X which has a fixed keto–thiono structure the conjugate base, *i.e.* the unprotonated form C in eqn. (12), is not electroactive. Reduction of the monoprotonated form HA takes place in a 2-electron step, but contrary to compounds

I–VII, no consecutive processes were shown by the formation of more negative waves. This can be considered as supporting evidence for the above deduction that in the monoprotonated form of compounds I–VII the thiol form (g) rather than the thiono form (b) is reduced. The increase in current below pH 8 observed for compound X indicates the possibility of an uptake of a larger number of electrons than two by a diprotonated form. Further protonation before the electrode process proper is also evident from the $E_{\frac{1}{2}}$ shift below pH 6. In contrast to compounds I–IV, the product of the first 2-electron reduction of the diprotonated form must undergo, before further electron uptake, a chemical transformation which is not extremely fast and the rate of which governs the limiting current below pH 8.

The assumed predominant forms in solutions of varying acidity and the forms considered to be the most probably reduced tautomers are summarized with the most probably reducible bonds in Table V.

## ANALYTICAL APPLICATIONS

Borate buffer pH 9.3 (0.05 *M* borax) was found most suitable for the determination of substances I–VII by means of the cathodic wave. For compounds V–VII it is recommended to work with fresh stock solutions kept at 0° to prevent hydrolysis.

The dependence of limiting current on concentration was found to be linear for $10^{-3}$–$10^{-5}$ *M* solutions. The best values of the slopes of these linear plots together with the intercept and the correlation coefficient (*r*), each based on measurements of at least 25 wave-heights treated by regression analysis are given in Table VI.

The cathodic waves thus offer a wider concentration range than anodic waves[9] for most compounds. The heights of cathodic waves can also be measured

TABLE VI

RANGES OF ANALYTICAL APPLICATIONS

| *Substance* | *Range*[a] | *Slope*[b] | *Intercept*[c] | $r$[d] |
|---|---|---|---|---|
| I | $5 \cdot 10^{-6}$–$10^{-4}$ | 4.646 | −0.0096 | 0.9994 |
| | $10^{-4}$–$2 \cdot 10^{-3}$ | 4.232 | 0.0558 | 0.9999 |
| II-Na[e] | $10^{-5}$–$2 \cdot 10^{-4}$ | 3.619 | 0.1483 | 0.999 |
| | $1 \cdot 10^{-4}$–$4 \cdot 10^{-3}$ | 3.568 | 0.01257 | 0.999 |
| II | $5 \cdot 10^{-6}$–$2 \cdot 10^{-4}$ | 4.139 | −0.0088 | 0.9998 |
| | $5 \cdot 10^{-5}$–$2 \cdot 10^{-3}$ | 4.108 | −0.0145 | 0.9999 |
| III-Na[e] | $5 \cdot 10^{-6}$–$7.5 \cdot 10^{-4}$ | 3.25 | 0.01257 | 0.999 |
| IV | $5 \cdot 10^{-6}$–$2 \cdot 10^{-4}$ | 3.753 | −0.0052 | 0.9999 |
| | $10^{-4}$–$1.75 \cdot 10^{-3}$ | 3.836 | −0.029 | 0.9999 |
| V | $5 \cdot 10^{-6}$–$9 \cdot 10^{-5}$ | 4.095 | −0.0126 | 0.9995 |
| | $10^{-5}$–$2.6 \cdot 10^{-4}$ | 3.98 | −0.0047 | 0.9999 |
| VI | $5 \cdot 10^{-6}$–$1.25 \cdot 10^{-3}$ | 4.52 | 0.036 | 0.999 |
| VII | $5 \cdot 10^{-6}$–$10^{-3}$ | 4.36 | 0.0165 | 0.999 |

[a] Concentration range in moles $l^{-1}$.

[b] Slope of the calibration ($i$–conc.) curve in $\mu$A mmol$^{-1}$.

[c] Intercept with the current axis in $\mu$A.

[d] Correlation coefficient.

[e] Sodium salts—the slope is much lower owing to presence of sodium carbonate in the pharmaceutical preparation (6 parts of sodium carbonate added to 100 parts of the thiobarbiturate).

with a higher accuracy in most cases. When 2-thiobarbiturates are present in the sample with other electroactive substances the choice of using either cathodic waves in 0.05 *M* borax or anodic waves in 0.1 *M* sodium hydroxide will be made according to the properties of the other electroactive species, in particular whether they give more positive reduction waves or more negative anodic waves than thiobarbiturates. The cathodic wave must, nevertheless, be recommended for determination of 5,5′-dialkyl-1-alkyl-substituted 2-thiobarbiturates V–VII which undergo rapid hydrolysis in 0.1 *M* sodium hydroxide. On the other hand, for determination of unsubstituted 2-thiobarbituric acid VIII and its 5-monoalkyl derivatives (IX), it is necessary to use anodic waves as these compounds show no measurable reduction waves.

When 5,5′-dialkyl-2-thiobarbiturates with straight and branched alkyl groups are compared, anodic waves[9] enable differentiation between these two groups, whereas cathodic waves do not. On the other hand, this means that cathodic waves can be used for functional analysis of the NR·CS·NH grouping in substances of the type I–VII, as all substances give waves at similar half-wave potentials of comparable height.

We would like to thank Dr. E. F. Hersant (May and Baker Ltd., Dagenham, Essex) for samples II and III, Dr. Hackmack (Chemische Fabrik Promonta GMBH, Hamburg) for samples I and II, Dr. M. E. Peel (Allen and Hanburys Ltd., Ware, Herts.) for samples V, VI, VII, IX, and Dr. F. L. Rose (I.C.I. Ltd., Macclesfield, Cheshire) for sample X. One of us (W.F.S.) acknowledges the assistance given by Dr. G. Farsang and Dr. L. Ladanyi, Etvös Lorand University, Budapest, with the macroscale electrolysis and cyclic voltammetry. The authors thank Professor C. L. Wilson for his encouragement in this work and W.F.S. thanks the Northern Ireland Government for a maintenance grant.

## SUMMARY

Changes of u.v. absorption spectra and polarographic reduction waves with pH indicate in solutions of 5,5′-dialkyl-2-thiobarbiturates the presence of four different species: diprotonated ($AH_2$), monoprotonated (AH), zwitterion (BH) and anionic (B). Dissociation constants $pK_2$ were determined and values of $pK_1$ and $pK_3$ estimated. In attempts to elucidate the electroactive forms, some tautomers were excluded in the 4-electron reduction of $H_2A$ and 2-electron reductions of HA and BH, the electrolyses of which gave varying yields of hydrogen sulphide. The anion B gives no reduction waves. 1,5,5′-Trialkyl-2-thiobarbiturates show u.v. spectra and polarographic waves corresponding to forms HA and BH. 1,3-Dimethyl-5,5′-dipropyl-2-thiobarbiturate is reduced in the monoprotonated and possibly diprotonated form. Predominant forms in the bulk of the solution at various pH values and the most probable electroactive forms are discussed. Reduction waves of 5,5′-dialkyl- and 1,5,5′-trialkyl-2-thiobarbiturates in 0.05 *M* borax are suitable for analytical purposes.

## RÉSUMÉ

Une recherche est effectuée sur le comportement de solutions de 5,5′-dialcoyl-

2-thiobarbiturates en fonction du pH, par polarographie et spectrophotométrie u.v. D'autres 2-thiobarbiturates substitués ont été examinés. Les vagues polarographiques de réduction des 5,5'-dialcoyl et 1,5,5'-trialcoyl-2-thiobarbiturates, en milieu borax 0.05 *M*, conviennent à des fins analytiques.

## ZUSAMMENFASSUNG

Die Änderungen der u.v.-Absorptionsspektren und polarographischen Reduktionsstufen mit dem pH-Wert zeigen in Lösungen von 5,5'-Dialkyl-2-thiobarbituraten vier verschiedene Spezies an, nämlich die diprotonisierte ($AH_2$), monoprotonisierte (AH), zwitterionische (BH) und anionische Form (B). Die Dissoziationskonstanten $pK_2$ wurden bestimmt und die Werte von $pK_1$ und $pK_3$ geschätzt. Bei Versuchen zur Deutung der elektroaktiven Formen wurden einige Tautomere bei der 4-Elektronenreduktion von $H_2A$ und 2-Elektronenreduktion von HA und BH, deren Elektrolyse wechselnde Mengen an Hydrogensulfid ergaben, ausgeschlossen. Das Anion B gibt keine Reduktionsstufen. 1,5,5'-Trialkyl-2-thiobarbiturate zeigen den Formen AH und BH entsprechende u.v.-Spektren und polarographische Stufen. 1,3-Dimethyl-5,5'-dipropyl-2-thiobarbiturat wird in der monoprotonisierten und möglicherweise diprotonisierten Form reduziert. Die bei verschiedenen pH-Werten vorherrschenden Formen und die wahrscheinlichen elektroaktiven Formen werden diskutiert. Die Reduktionsstufen von 5,5'-Dialkyl- und 1,5,5'-Trialkyl-2-thiobarbituraten in 0.05 *M* Borax sind für analytische Zwecke geeignet.

## REFERENCES

1 *British Pharmacopoeia*, 1968, p. 1013.
2 G. Sandri and F. Lombardi, *Atti Accad. Sci. Ferrara*, 30 (1953) 27; *Chem. Abstr.*, 49 (1955) 2129.
3 H. Wojahn, *Arch. Pharm.*, 288 (1955) 1.
4 A. Berka and J. Zýka, *Cesk. Farm.*, 5 (1956) 335.
5 J. Čihalík, J. Doležal, V. Simon and J. Zýka, *Cesk. Farm.*, 2 (1953) 43.
6 E. Heise and K. H. Kimbel, *Arzneimittel-Forsch.*, 5 (1955) 149.
7 W. Awe and W. Winkler, *Arzneimittel-Forsch.*, 5 (1955) 518.
8 M. Březina and P. Zuman, *Polarography in Medicine, Biochemistry and Pharmacy*, Interscience, New York, 1958.
9 P. Zuman, *Collection Czech. Chem. Commun.*, 20 (1955) 649, 876, 883.
10 O. Mňoušek and P. Zuman, *Cesk. Farm.*, 4 (1956) 193; *Pharmazie*, 11 (1956) 530.
11 Private communication, Prague, 1958.
12 P. Zuman and M. Kuik, *Collection Czech. Chem. Commun.*, 24 (1959) 3861.
13 O. Mňoušek, private communication, Prague, 1966.
14 G. E. Gilbert and E. K. Rideal, *Trans. Faraday Soc.*, 47 (1951) 396.
15 J. A. Page and J. J. Lingane, *Anal. Chim. Acta*, 16 (1957) 175.
16 Y. Sato, *Nippon Kagaku Zasshi*, 78 (1957) 921; *Chem. Abstr.*, 54 (1960) 4598.
17 J. Koutecký and R. Brdička, *Collection Czech. Chem. Commun.*, 12 (1947) 337.
18 S. G. Majranovskij, *Catalytic and Kinetic Waves in Polarography*, Plenum Press, New York, 1968, p. 128.

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

# THE POLAROGRAPHY OF VANADYL SULFATE IN DIMETHYLFORMAMIDE*

CHARLES W. MANNING** AND WILLIAM C. PURDY
*Department of Chemistry, University of Maryland, College Park, Md. 20742 (U.S.A.)*
(Received March 18th, 1970)

The polarographic reduction of vanadium(IV) at a dropping mercury electrode (D.M.E.) gives rise to a number of waves. ISRAEL AND MEITES[1] have reported on these reductions in aqueous solution and have proposed explanations for the polarographic waves they observed. MICHLMAYR AND GUTMANN[2] studied the polarographic behavior of vanadium in dimethylformamide (DMF) but they offered no explanation for the waves they obtained.

In the present paper the polarographic behavior of vanadyl sulfate in DMF is discussed. Classical and fast-sweep polarographic, constant-potential coulometric, and spectrophotometric techniques are employed and mechanisms are proposed to explain the three waves obtained.

## EXPERIMENTAL

### *Reagents*

Vanadyl sulfate (Fisher Scientific Co.) was used without further purification. The DMF was distilled from phosphorus pentoxide at 82.5° and 55 mm of mercury, and was stored well isolated from the atmosphere. Tetraethylammonium perchlorate (TEAP; Eastman Kodak, Rochester, N.Y.) was recrystallized twice from water and dried in a vacuum oven at 60°.

Concentrated aqueous stock solutions of vanadyl sulfate were prepared and the pH was adjusted to 2 by the addition of sulfuric acid. The concentration of these stock solutions was determined by permanganate titration. In the polarographic studies, up to 150 $\mu$l of these aqueous solutions were diluted to 10 ml with 0.1 $M$ TEAP in DMF.

### *Apparatus*

The polarographic measurements were made with a Sargent Model XXI polarograph modified for three-electrode polarography as in the design of ANNINO AND HOGLER[3]. The polarographic cell was a water-jacketed beaker into which was placed a platinum-foil anode, a cadmium amalgam–cadmium chloride reference electrode[4], and the D.M.E. capillary which was constricted at the bottom. The solution to be studied was placed in the cell and purged with ultrapure nitrogen

---

* Taken in part from the Ph.D. Dissertation of CHARLES W. MANNING, University of Maryland, 1970.

** Present address: Rocky Mountain Arsenal, Colorado 80240.

(Southern Oxygen Co.) for 15 min before the run. During the polarographic run, an atmosphere of nitrogen gas was maintained above the test solution.

Coulometric studies were carried out with an instrument consisting of a Philbrick P45AU amplifier as the driver, a P65AU as the follower, and a SP65 as the integrator.

The Heath polarographic module was employed for the fast-sweep polarography. The scan was started remotely by a time-delay circuit triggered by the mercury drop. In some studies a hanging mercury drop electrode replaced the D.M.E.

Spectrophotometric studies were carried out in a Beckman DB Spectrophotometer.

## RESULTS AND DISCUSSION

Vanadyl sulfate in DMF containing between 0.15 and 1.0% water gives three polarographic reduction waves at the D.M.E. Polarographic data for the first two waves are shown in Table I. Variations in water content had no effect on these waves.

TABLE I

POLAROGRAPHIC DATA FOR THE REDUCTION OF VANADYL SULFATE IN DMF

| *Conc. ($M \cdot 10^4$)* | *First wave* | | *Second wave* | |
|---|---|---|---|---|
| | *$i_d$ ($\mu A$)* | *$E_{\frac{1}{2}}$ ($V$)* | *$i_d$ ($\mu A$)* | *$E_{\frac{1}{2}}$ ($V$)* |
| 10.06 | 0.678 | −0.439 | | |
| 11.73 | 0.908 | −0.415 | | |
| 13.04 | | | 0.552 | −1.310 |
| 16.10 | 1.24 | −0.394 | 0.594 | −1.296 |
| 16.95 | 1.47 | −0.397 | 0.612 | −1.321 |
| 20.12 | 1.76 | −0.373 | 0.780 | −1.336 |
| 26.07 | 2.20 | −0.340 | 1.01 | −1.310 |
| 30.17 | 2.49 | −0.325 | | |
| 40.23 | | | 1.68 | −1.309 |
| Slope | 0.0853 | | 0.0424 | |
| Correlation constant | 0.908 | | 0.853 | |

Coulometric runs on the first wave determined its *n*-value to be 2. It is highly unlikely that the vanadium is reduced past its divalent state. Coulometric reduction, even at −1.8 V *vs.* cadmium amalgam reference, produces ionic vanadium, not the mercury-soluble metal.

The first wave gives a straight-line plot of concentration *vs.* limiting current. Linear variation of the square root of the mercury height with wave height indicates diffusion control. The effect of temperature variation is 0.90% per degree as calculated by the method of MEITES[5].

The final two waves must be due to a reduction other than that of vanadium(IV). The second wave was found to be one-half the height of the first. Determination of the electron change for the second wave proved difficult because the foot of the third wave was drawn out and overlapped onto the second wave. The *n*-values for the second wave were not consistent but they were always greater than two and could be as high as 3.5.

Several authors have shown that vanadium(II) will react with vanadium(IV) in acidic aqueous solutions[1,6,7]. NEWTON AND BAKER[6] have shown spectrophotometrically that the product of this reaction is often a $(VOV)^{4+}$ species which can then break down to atomic vanadium(III). Their work could not be duplicated in DMF owing to a shift in the absorbance maxima. However, when an equimolar amount of vanadium(IV) was added to electrogenerated vanadium(II), a spectral shift occurred over a period of 10 min, indicating that a chemical reaction was taking place.

When these same solutions were mixed and placed in a fast-sweep polarographic cell, it was noted that the polarograms changed with time. The height of the second wave decreased with time and a more positive wave appeared. The best explanation for these data is found in the reaction scheme of NEWTON AND BAKER[6]. If the second polarographic wave is attributed to a $(VOV)^{4+}$ species the concentration of this species would be high immediately after mixing; but with the passage of time it decreases with the formation of monomeric vanadium(III). Monomeric vanadium(III) is reduced at potentials more positive than vanadium(IV) in DMF[2] and in aqueous solution[1]. This new wave which is increasing would then be due to monomeric vanadium(III).

This same reaction scheme is also supported by fast-sweep polarographic data on vanadium(IV). In these studies a hanging mercury drop electrode was used. During the initial portion of the potential sweep, all the vanadium(IV) around the electrode is reduced to vanadium(II). However, before the potential of the second wave is reached, more vanadium(IV) from the bulk of the solution chemically reacts with the vanadium(II) yielding a larger relative concentration of the proposed $(VOV)^{4+}$ species. Under these conditions, the height of the first wave is less than the height of the second wave. If the rate of voltage scan is very rapid, very little chemical reaction takes place and the first polarographic wave is much larger than the second. The variation of the ratio of $i_p\ V^{-\frac{1}{2}}$ with scan speed for the second wave is tabulated in Table II. These data indicate that at speeds slower than about 1.74 V sec$^{-1}$, a steady-state concentration of the proposed $(VOV)^{4+}$ species is established. At fast speeds, this steady-state concentration is not attained.

TABLE II

VARIATION OF THE SECOND POLAROGRAPHIC WAVE WITH SCAN SPEED

| *Speed* (*V sec*$^{-1}$) | $i_p V^{-\frac{1}{2}}$ ($\mu A\ V^{-\frac{1}{2}}$) |
|---|---|
| 0.174 | 24.9 |
| 0.347 | 24.5 |
| 0.864 | 24.9 |
| 1.740 | 24.3 |
| 3.470 | 22.6 |
| 8.640 | 18.4 |

Similar evidence for this mechanism was obtained when electrolysis, before the scan, was carried out at 1.0 V *vs.* the cadmium amalgam reference electrode. The potential of the hanging mercury drop electrode was held at 1.0 V for 1.5 min and then the potential was scanned from 0 to −3.5 V at various periods of time after the electrolysis. With no delay, the second and third waves were very prominent and no wave was found in the 0 to −1.0 V region. With increasing time delay, a sharp single wave appeared in the potential region where the vanadium(III) wave occurs. With the fast sweep, vanadium(IV) gives two waves in the −0.4 V region. The exact potential changes with concentration and scan speed. The appearance of a single wave indicates that it is the vanadium(III) rather than vanadium(IV) diffusing back to the electrode.

All of the previous data can be explained by a mechanism where vanadium(II) is the product of the first polarographic reduction. This vanadium(II) then reacts with vanadium(IV) forming a dimer of vanadium(III). The dimer slowly breaks down to ionic vanadium(III). In classical polarography, the vanadium(IV) diffuses in and is met by the vanadium(II) diffusing out. They react a slight, but discrete, distance from the electrode surface. The dimer formed creates a sphere of maximum dimer concentration very close to, but not within, reacting range of the electrode. The dimer then diffuses in both directions away from this area of maximum concentration; therefore, only one-half of the dimer diffuses back to the electrode. It reacts to form the second polarographic wave and give the two-to-one ratio of the first-to-second wave.

This mechanism also agrees with the information obtained by constant-potential coulometry. The same two oxidation waves appear on the anodic sweep of the reduction products of either of the first two vanadium(IV) waves. These oxidation waves are of the same height and can presumably be due to vanadium(II) being oxidized to vanadium(III) and then to vanadium(IV). If the product of the coulometric reduction is coulometrically oxidized at a potential poised on the plateau of the second oxidation wave, the blue solution of vanadium(IV) appears.

The third wave is very difficult to interpret. It appears as a peak before the solvent wave. The peak height does vary linearly with vanadyl sulfate concentration. The most notable characteristic of this wave is its large height variation with temperature of 8.6% per degree. The peak height does not vary with the mercury height indicating that the wave is kinetically controlled.

When constant-potential coulometric runs are made on this wave, a thick, oily precipitate forms. During these coulometric runs the current drops to the background level and if the solution is centrifuged, the vanadium is found in the precipitate, along with some sulfate. The precipitate was separated and washed with DMF, which dissolved some of the vanadium. It was then dissolved in water containing some perchloric acid. The sulfate and vanadium were separated on a cation-exchange column and determined separately. Their relative concentrations were found to be random, indicating no stoichiometric ratio between the vanadium and the sulfate.

At a potential of −1.8 V *vs.* cadmium amalgam reference, this precipitate does not form if vanadium is absent; however, if the potential is increased to above −2.0 V, a precipitate appears, presumably formed by solvent reduction. The suggestions of ISRAEL AND MEITES[1] appear consistent with these observations. If the vanadium(II) formed a complex or a bridge between the electrode and the solvent enhancing the reducibility of the solvent, the same precipitate could form at −1.8 V and at −2.0 V. The oily precipitate could entrap some vanadium and sulfate within itself. This suggestion is supported by the fact that constant-potential coulometric studies on the wave gave no fixed *n*-value. If a stoichiometric ratio existed between vanadium atoms and reduced solvent, a consistent *n*-value would exist.

DMF, like water, has good binding sites for vanadium on the oxygen or nitrogen atoms. Therefore, the possibility of a bridging solvent molecule between vanadium(II) and the electrode is as likely in DMF as in water. A cathodic polarogram on the reduction products of the first or second wave shows that the third wave still appears when only vanadium(II) is present. The wave is, in fact, higher in a fast-sweep run in the vanadium(II) solution than in vanadium(IV). This would be due to the higher vanadium(II) concentration at the electrode surface.

Polarographically, the third wave has no set ratio of peak height with the first two vanadium(IV) waves but with fast sweep using a hanging mercury drop electrode, the third wave was exactly one-half the height of the second wave. This ratio persists up to sweep rates of 300 V $sec^{-1}$. At scan speeds above this, the third wave decreases in relation to the second wave. This indicates that the vanadium(II) produced by the second wave rearranges or combines with the solvent and, at these scan speeds, the fast-sweep reaction is competing with the chemical reaction. The 2:1 ratio of waves two and three at slower scan speeds indicates that the two vanadium atoms in the dimer combine jointly with the solvent to produce a 1-electron reduction of the solvent.

The authors are indebted to the U.S. Army Medical Research and Development Command for partial support of this work under Contract No. DADA17-67-C-7161.

## SUMMARY

The polarographic technique was applied to a solution of vanadyl sulfate in dimethylformamide with 0.1 *M* tetraethylammonium perchlorate as the supporting electrolyte. The three resulting polarographic waves were examined and a mechanism is proposed to explain the waves. The mechanism involves an intermediate vanadium-(III) dimer that is the product of a vanadium(IV)–vanadium(II) reaction. This intermediate then breaks down to the monomeric (III) state. The mechanism was studied by optical, constant-potential coulometric, and fast-sweep polarographic techniques. The final polarographic wave was attributed to a solvent bridge connecting the electrode with the vanadium(II) produced at the electrode. This bridging structure allows the solvent to be reduced at a potential more positive than when vanadium is absent.

## RÉSUMÉ

La polarographie est appliquée à une solution de sulfate de vanadyle dans la diméthylformamide, en présence de perchlorate de tétraéthylammonium 0.1 *M*, comme électrolyte de base. On a examiné les trois vagues polarographiques obtenues. Le mécanisme est étudié par des techniques optiques, coulométriques à potentiel constant et par polarographie à balayage rapide.

## ZUSAMMENFASSUNG

Das polarographische Verfahren wurde auf eine Lösung von Vanadylsulfat in Dimethylformamid mit 0.1 *M* Tetraäthylammoniumperchlorat als Trägerelektrolyt angewendet. Die drei resultierenden polarographischen Stufen wurden untersucht, und es wird ein Mechanismus zur Deutung der Stufen vorgeschlagen. In dem Mechanismus ist ein intermediäres Vanadin(III)-Dimeres enthalten, das das Produkt einer Vanadin(IV)–Vanadin(II)-Reaktion darstellt. Diese Zwischenstufe zerfällt dann in monomeres Vanadin(III). Der Mechanismus wurde durch optische und coulometrische Verfahren mit konstantem Potential sowie durch Fast-Sweep-Polarographie untersucht. Die letzte polarographische Stufe wurde einer Lösungsmittelbrücke zugeschrieben, die die Elektrode mit dem an der Elektrode erzeugten Vanadin(II) verbindet. Diese Überbrückungsstruktur ermöglicht die Reduktion des Lösungsmittels bei einem positiveren Potential als ohne Gegenwart von Vanadin.

## REFERENCES

1 Y. Israel and L. Meites, *J. Electroanal. Chem.*, 8 (1964) 99.
2 M. Michlmayr and V. Gutmann, *Inorg. Chim. Acta*, 1 (1967) 471.
3 R. Annino and K. J. Hogler, *Anal. Chem.*, 35 (1963) 1555.
4 C. W. Manning and W. C. Purdy, *Anal. Chim. Acta*, in press.
5 L. Meites, *Polarographic Techniques*, Interscience, New York, 1965, p. 140.
6 T. W. Newton and F. B. Baker, *J. Phys. Chem.*, 68 (1964) 228.
7 J. W. Olver and J. W. Ross, *J. Phys. Chem.*, 66 (1962) 1699.

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

# A STUDY OF PYRIDINIUM TERNARY MOLYBDOPHOSPHATE COMPLEXES

## COLLECTION OF TRACE AMOUNTS OF TITANIUM(IV), ZIRCONIUM(IV), AND THORIUM(IV)

KATSUO MURATA AND SHIGERO IKEDA
*Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka (Japan)*

(Received February 26th, 1970)

In a previous paper[1] trace amounts of titanium(IV), zirconium(IV) and thorium(IV) ions were determined spectrophotometrically with molybdophosphoric acid solution. The method is based on the formation of the ternary heteropoly complex by the reaction of the metal ion with molybdophosphoric acid. The ternary heteropoly complex reacts with pyridine to produce a yellow precipitate, which is sparingly soluble in water. By using this reaction it may be possible to isolate trace amounts of titanium(IV), zirconium(IV) and thorium(IV) ions from slightly acidic solution. In the present paper, the possibility of collecting trace amounts of these metal ions from aqueous solution was explored, and properties of pyridinium ternary heteropoly salts were investigated by using a infrared spectrophotometer and a Derivatograph.

## EXPERIMENTAL

### *Reagents and apparatus*

*Stock solutions of titanium(IV), zirconium(IV), and thorium(IV).* These were prepared from titanium metal, zirconium oxychloride, and thorium nitrate, respectively, and were stored as 2 *M* perchloric acid solutions to prevent hydrolysis. Each solution of titanium(IV), zirconium(IV), and thorium(IV) was standardized gravimetrically by weighing as oxides after ignition of the precipitate of titanium cupferronate, zirconium cupferronate, and thorium oxalate, respectively.

*Molybdophosphate solution.* A $2.5 \cdot 10^{-2}$ *M* solution was prepared by dissolving 3.4022 g of potassium dihydrogen phosphate and 72.5940 g of sodium molybdate (both analytical-reagent grade) in water and diluting to 1 l.

Pyridine (analytical-reagent grade) was used without further purification.

A Horiba F-5 pH meter, and a Nihonbunko 402-G infrared spectrophotometer were used. The thermogravimetric analysis (TGA), differential thermal analysis (DTA), and derivative thermogravimetric analysis (DTGA) curves were automatically (photographically) recorded with a single sample in a constant nitrogen stream with a Metrimpex Derivatograph Type-OD-102 (Metrimpex, Hungary).

### *Preparation of pyridinium ternary heteropoly salts*

The previous paper reported that titanium(IV), zirconium(IV), and thorium-

(IV) form ternary heteropoly complexes with molybdophosphoric acid. These ternary heteropoly complexes give sparingly soluble precipitates with pyridine. Pyridinium salts of molybdotitanophosphate, molybdozirconophosphate, or molybdothorophosphate, were prepared by applying the method proposed by SHKARAVSKII[2] for the preparation of pyridinium molybdoniobophosphate. Sodium molybdate (14.75 g) was dissolved, 0.3 *M* potassium dihydrogen phosphate solution (16.7 ml) was added, and the pH was adjusted to 1; then titanium, zirconium, or thorium solution was added, and the whole solution was diluted to 200 ml, and heated for 5 min. The solution was then cooled, and 20 ml of a solution containing 2 ml of pyridine adjusted to pH 1 were added dropwise. The yellow precipitate formed was filtered and washed repeatedly with a solution of pH 1.

### *Procedure in the collection of trace metal ion*

To the solution containing the trace metal ion were added 20 ml of $2.5 \cdot 10^{-2}$ *M* molybdophosphate solution, and then the mixed solution was adjusted to the required pH with perchloric acid. After 1 h, which sufficed for complete formation of the ternary heteropoly complex, 10 ml of a solution containing 1 ml of pyridine adjusted to the required pH, was added dropwise. A yellow pyridinium heteropoly salt was precipitated. The precipitate was filtered on a No. 4 glass filter, and the metal ion remaining in the mother liquor was determined spectrophotometrically. Titanium was determined as the peroxo-complex, zirconium was determined by the alizarin blue method, and thorium by the thoron method.

## RESULTS AND DISCUSSION

### *Infrared spectra of pyridinium ternary heteropoly salts*

Infrared spectra of the products of molybdotitanophosphate, molybdozirconophosphate, and molybdothorophosphate are shown in Fig. 1. Molybdophosphoric acid and pyridinium molybdophosphate are shown comparatively in Fig. 2. Most of the absorption bands caused by pyridine in the products are obvious from comparing with the spectrum of molybdophosphoric acid: at 3060, 1630, 1535, 1485, 1330, 1240, 1200, 1165, 740, and 668 $cm^{-1}$. GILL *et al.*[3] have distinguished the pyridinium ion from the pyridine coordinated to elements other than hydrogen in the infrared spectra. They reported that the intense bands of pyridinium salts occur at 3200 or 2800, 1640, 1530, 1327 and 1250 $cm^{-1}$. Therefore the compounds obtained are not pyridine complexes but pyridinium salts.

Absorption bands of C=C and C=N bonds appear between 1480 $cm^{-1}$ and 1640 $cm^{-1}$. These are shifted to higher wavenumber (*ca.* 40 $cm^{-1}$) than those of pure pyridine. Ring vibration and CH deformation bands are observed near 1200 $cm^{-1}$, but their intensities are weak. Many absorption bands below 1100 $cm^{-1}$ are indistinguishable owing to the overlap of strong absorption bands in phosphate and molybdate. Although each of the four pyridinium heteropoly salts has absorption bands owing to pyridine at the same wavenumber, the $\nu_3$ vibration of $PO_4$ near 1080 $cm^{-1}$ shows specific aspects with the kind of salt. Both pyridinium molybdophosphate and pyridinium molybdotitanophosphate give the vibration $\nu_3$ of $PO_4$ at 1060 $cm^{-1}$; in pyridinium molybdozirconophosphate the $\nu_3$ splits into 1100, 1060, and 1045 $cm^{-1}$; and in pyridinium molybdothorophosphate it splits into 1120, 1070, and 1035 $cm^{-1}$.

Free phosphate ion $PO_4^{3-}$ has $\nu_1$, $\nu_2$, $\nu_3$, and $\nu_4$ modes of vibration at 970, 358, 1080, and 500 cm$^{-1}$, respectively[4]. All the four vibrations are Raman-active, whereas only $\nu_3$ and $\nu_4$ are infrared-active and are triply degenerated. The free phosphate ion belongs to the high symmetry point group $T_d$. If an ion is coordinated to a metal,

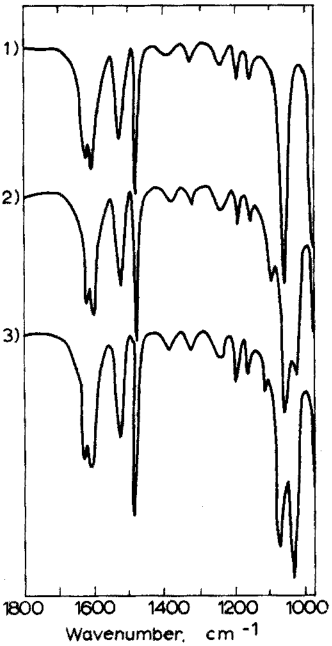


Fig. 1. Infrared spectra of pyridinium ternary heteropoly salts: (1) pyridinium molybdotitanophosphate, (2) pyridinium molybdozirconophosphate, (3) pyridinium molybdothorophosphate.

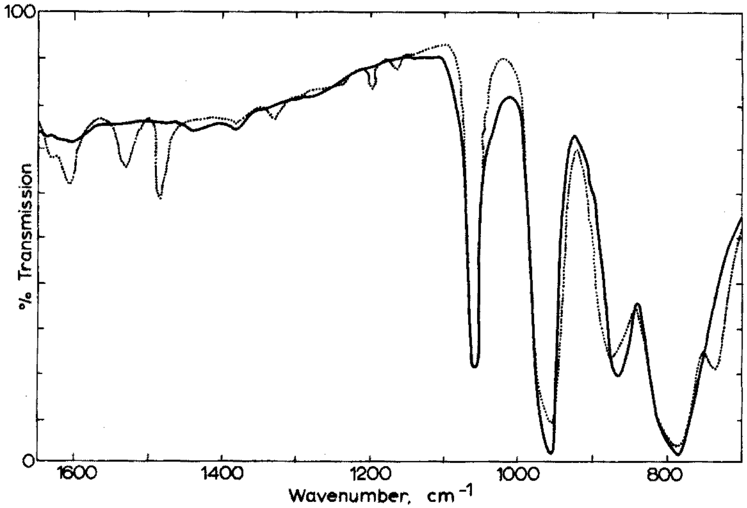


Fig. 2. Infrared spectra of molybdophosphoric acid and of pyridinium molybdophosphate salt; molybdophosphoric acid (solid line), pyridinium molybdophosphate (dotted line).

the symmetry is generally lowered and splitting of the degenerate modes occurs. NAKAMOTO *et al.*[5] have observed the splitting of the degenerate modes for sulfato complexes. They have explained the findings by assuming lowering of the symmetry from $T_d$ to $C_{3v}$ or $C_{2v}$. In the case of pyridinium molybdozirconophosphate and molybdothorophosphate, the vibration $\nu_3$ splits into three bands; in the case of molybdophosphoric acid, pyridinium molybdophosphate, and pyridinium molybdotitanophosphate, $\nu_3$ does not split. As KEGGIN AND ILLINGWORTH[6] have suggested, molybdophosphate anion is constituted of central and tetrahedral phosphate which is surrounded by twelve $MoO_6$ octahedra; every tetrahedron corner is shared by three octahedra. Therefore the phosphate remains highly symmetrical in the molybdophosphate ion as well as in the free state, and $\nu_3$ does not split. On the other hand, the symmetry of phosphate in the pyridinium ternary heteropoly salt is lowered because the $\nu_3$ mode splits into three bands. It is interesting and important to know where the component (Ti, Zr, or Th) occurs in the molybdophosphate anion. SHKARAVSKII[7,8] has considered the structure of ternary heteropoly complexes (molybdotitanophosphate and molybdoniobophosphate), and has postulated that the central group in the ternary heteropoly complex is the metal phosphate from the correspondence with the pH of the ternary complex solution giving the maximum optical density and that of the isoelectric point of $MoO_3$; he has concluded that titanium does not replace a portion of the molybdenum in the coordination sphere but does occupy, like phosphorus, the position of a central atom of the acid. It is assumed from the observation of the splitting of the $\nu_3$ band that zirconium or thorium is situated near phosphate in the pyridinium molybdozirconophosphate or molybdothorophosphate molecule. In the case of titanium, however, the situation cannot be confirmed from infrared spectra. As the atomic weight of titanium is less than that of zirconium and thorium, the presence of titanium may not so greatly contribute to the vibration of $PO_4$.

*Conversion of pyridinium ternary heteropoly salts to the acid form*

Pyridinium ternary heteropoly salts can be converted to the acidic forms by

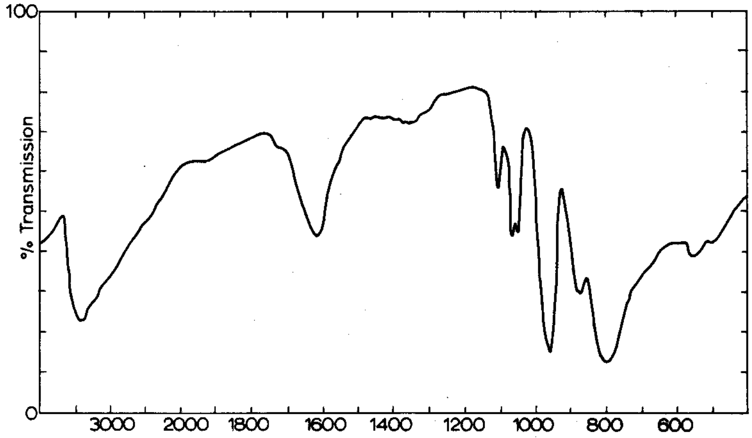


Fig. 3. Infrared spectrum in the acidic form of pyridinium molybdozirconophosphate.

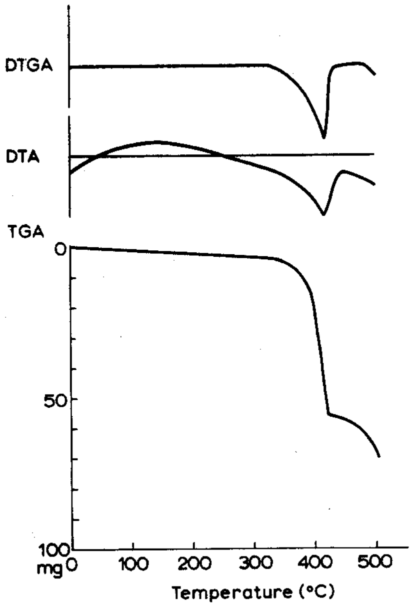
using the batch method with cation-exchange resin. About 1 g of pyridinium molybdozirconophosphate and about 100 g of Dowex 50W-X2 in the hydrogen form (100–200 mesh) were mixed in a stoppered Erlenmeyer flask containing 100 ml of water, and the mixture was shaken until the turbidity disappeared. As turbidity indicates that pyridinium ternary heteropoly salt remains, the shaking must be repeated until the solution becomes transparent. The clear solution was removed and was evaporated to dryness. The infrared spectrum of the residue is shown in Fig. 3. The absorption band of pyridine disappeared, the stretching and deformation vibration (at *ca.* 3500 $cm^{-1}$ and 1600 $cm^{-1}$) of $H_2O$ were intense, and the absorption band of $PO_4$ was still split triply. This indicates that the pyridinium molybdozirconophosphate salt is completely converted to the acidic form and that the splitting of the degenerate $PO_4$ mode is not due to the effect of pyridine but to the effect of zirconium. Other pyridinium ternary heteropoly salts could also be converted to the acidic form by the same treatment.

*Collection of trace amounts of titanium(IV), zirconium(IV), and thorium(IV)*

Titanium(IV), zirconium(IV) and thorium(IV) were each found to form with molybdophosphate a ternary heteropoly complex with absorbance in the visible[1] and infrared region, and the pyridinium salts were found to be sparingly soluble in water. This indicates the possibility of collection of these elements from slightly acidic solutions by means of precipitation of the pyridinium ternary heteropoly salts. Zirconium(IV) and thorium(IV) could be quantitatively collected from 10-p.p.m. solutions at pH 1–3, and titanium(IV) from 50-p.p.m. solutions at pH 1–3. The pyridinium heteropoly salts can thus be used as scavengers for trace amounts of titanium(IV), zirconium(IV), and thorium(IV).

*Thermal analysis of pyridinium ternary heteropoly salts*

Thermal analyses of these pyridinium ternary heteropoly salts were obtained by simultaneous measurements of TGA, DTA and DTGA curves, as shown in Figs. 4–7. Samples of 500 mg were used to obtain a derivatogram. The TGA curve of pyridinium molybdophosphate is the most normal and distinct one of the four curves; virtually no change occurs up to 400° and the weight then alters very sharply (Fig. 4), indicating possibly that pyridinium molybdophosphate has no structural strain or distortion. The TGA curves of the three pyridinium ternary heteropoly salts tend to show a gradual degradation as the temperature increases. Pyridinium molybdozirconophosphate shows no well-defined degradation steps, whereas the TGA curve of pyridinium molybdotitanophosphate is most similar to that of pyridinium molybdophosphate, the curve for pyridinium molybdothorophosphate being intermediate between these. These findings can be correlated with the results obtained in the infrared investigation, *i.e.* the splitting of $PO_4$. Zirconium and thorium are effective in splitting of $PO_4$ in pyridinium heteropoly salts, but titanium is not effective. The decomposition temperatures of the pyridinium ternary heteropoly salts are 390, *ca.* 300, and 260°, respectively. These correlate with the fact that infrared spectra of the salts after treatment at 400° showed no absorption bands of pyridine. Above 500° the sublimation of molybdenum begins and the sample tubes become dirty. No useful conclusions could be drawn from the DTA curves of the pyridinium heteropoly salts.



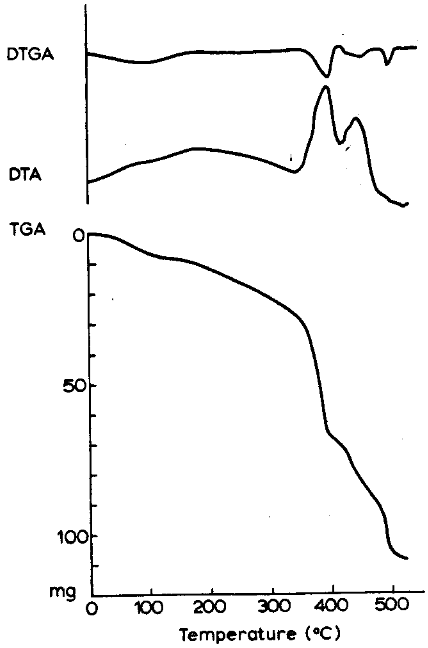
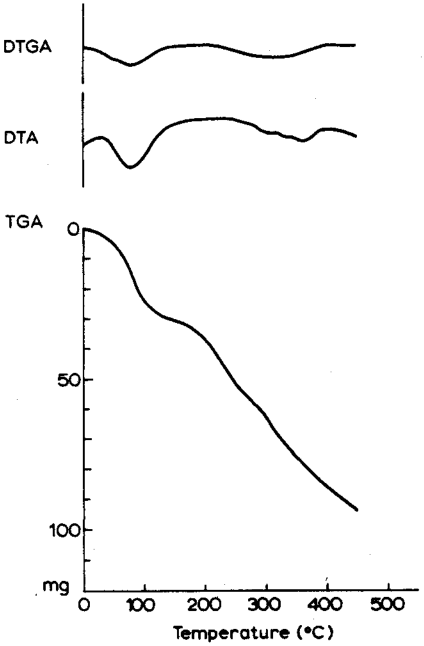


Fig. 4. Derivatogram of pyridinium molybdophosphate.

Fig. 5. Derivatogram of pyridinium molybdotitanophosphate.



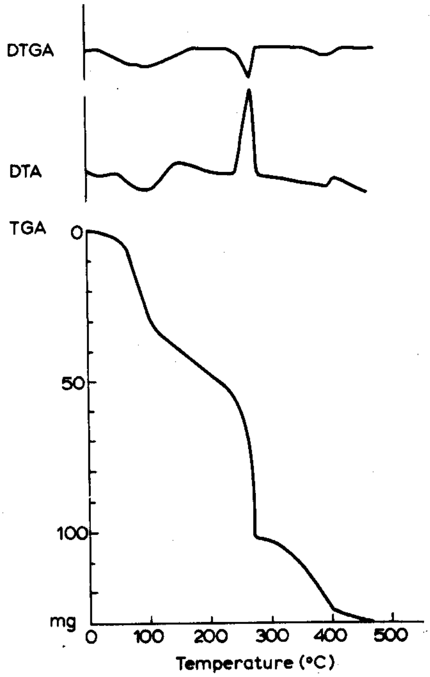


Fig. 6. Derivatogram of pyridinium molybdozirconophosphate.

Fig. 7. Derivatogram of pyridinium molybdothorophosphate.

The authors wish to thank Dr. R. TSUCHIYA for the use of a Derivatograph.

## SUMMARY

Trace amounts of titanium(IV), zirconium(IV), and thorium(IV) can be quantitatively collected from pyridinium solutions at pH 1–3 with the molybdophosphate complex. The metal ions react with molybdophosphate, and are then precipitated as the pyridinium ternary heteropoly salts. These salts were investigated by infrared spectrophotometry and thermogravimetric techniques.

## RÉSUMÉ

Des traces de titane(IV), de zirconium(IV) et de thorium(IV) peuvent être quantitativement entrainées de solutions pyridine, au pH de 1 à 3, à l'aide du complexe molybdophosphate. Ces métaux réagissent avec le molybdophosphate et sont précipités ensuite comme hétéropolysels ternaires. Ces sels sont examinés par spectrophotométrie infra-rouge et thermogravimétrie.

## ZUSAMMENFASSUNG

Spurenmengen von Titan(IV), Zirkonium(IV) und Thorium(IV) können aus Pyridinium-Lösungen quantitativ bei pH 1–3 mit dem Molybdatophosphat-Komplex gesammelt werden. Die Metallionen reagieren mit Molybdatophosphat und werden dann als ternäre Pyridinium-Heteropolysalze gefällt. Diese Salze wurden durch Infrarotspektrophotometrie und thermogravimetrische Verfahren untersucht.

## REFERENCES

1 K. MURATA, Y. YOKOYAMA AND S. IKEDA, *Anal. Chim. Acta*, 48 (1969) 349.
2 Y. F. SHKARAVSKII, *Zh. Neorgan. Khim.*, 10 (1965) 1179.
3 N. S. GILL, R. H. NUTTALL, D. E. SCAIFE AND D. W. A. SHARP, *J. Inorg. & Nucl. Chem.*, 18 (1961) 79.
4 K. NAKAMOTO, *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley, New York, 1963, p. 107.
5 K. NAKAMOTO, J. FUJITA, S. TANAKA AND M. KOBAYASHI, *J. Am. Chem. Soc.*, 79 (1957) 4904.
6 J. F. KEGGIN AND J. W. ILLINGWORTH, *J. Chem. Soc.*, (1935) 575.
7 Y. F. SHKARAVSKII, *Zh. Neorgan. Khim.*, 8 (1963) 2668.
8 A. K. BABKO AND Y. F. SHKARAVSKII, *Zh. Neorgan. Khim.*, 6 (1961) 2091.

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

# SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS IN ALUMINIUM, COPPER AND NICKEL ALLOYS, AND WHITE METALS

P. PAKALNS
*Australian Atomic Energy Commission Research Establishment, Lucas Heights, N.S.W. 2232 (Australia)*

(Received April 10th, 1970)

Previous workers have determined phosphorus in brasses and bronzes by the yellow phosphovanadomolybdate procedure directly[1,2] or after extraction of the phosphovanadomolybdate complex into isoamyl alcohol. In the ASTM method[1] more than 10% of tin produces low results, and antimony hydrolyses after the addition of hydrogen peroxide. In the British Standard method[2] more than 25% of tin and 1% of antimony give low recoveries. Silver also interferes by producing turbidity. In the extraction procedure[3] only 10% of tin and 0.25% of antimony can be tolerated.

In this paper a general method is described for the determination of phosphorus in aluminium, copper and nickel alloys, white metals, tungsten, zinc, and silver babbitts by forming a yellow phosphovanadomolybdate complex in nitric acid solutions containing fluoride, and then extracting this complex into methyl isobutyl ketone. More than 5% of silicon gives high results, and in the analysis of zirconium only 2% of silicon can be tolerated. In the analysis of aluminium the maximum sample weight is 0.25 g, and the amount of silicon is limited to 2%. Samples of these metals containing larger amounts of silicon can be analysed for phosphorus by volatilising silicon as fluoride from fuming perchloric[4] or sulphuric acid[5].

## EXPERIMENTAL

### *Apparatus and reagents*

A Unicam SP 600 spectrophotometer with 2-cm and 4-cm cells was used.

*Standard phosphorus solution.* Prepare a stock solution containing 0.1 mg P per ml by dissolving 0.4393 g of potassium dihydrogen phosphate in 1 l of water. Prepare a working solution (0.04 mg ml$^{-1}$) by diluting 100 ml of stock solution to 250 ml.

*Ammonium molybdate solution (15%).* Prepare from $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and store in a polythene bottle.

*Ammonium vanadate solution (0.25%).* Dissolve 2.5 g of ammonium metavanadate in 500 ml of water by heating. Cool and dilute to 1 l.

### *Recommended procedure*

Transfer 0.5 g of the sample to a 250-ml Teflon beaker and add 20 ml of water, 10 ml of 15 *M* nitric acid and 3 ml of 40% hydrofluoric acid. After dissolution, dilute with water to 35 ml and bring to the boil. Add 5 ml of 1% potassium permanganate solution, boil for 2 min, then add 2 ml of 5% sodium nitrite solution and boil for 3 min. Cool, add 10 ml of ammonium vanadate solution and 65 ml of ammonium molybdate solution, and then allow to stand for 15 min. Add 30 ml of water, transfer the solution to a 250-ml separating funnel and dilute to 150 ml with water.

Add 15 ml of 50% citric acid solution, mix, immediately add 40 ml of methyl isobutyl ketone (MIBK) and shake for 30 sec. Allow the two layers to separate and discard the aqueous layer. Filter the ketone layer through a double-layer rapid filter paper into a small dry beaker and measure the absorbance immediately at a wavelength of 425 nm in 2-cm cells for 50–400 $\mu$g of phosphorus, and at 400 nm in 4-cm cells for 0–50 $\mu$g of phosphorus, using water as a reference solution. Subtract the blank value.

To prepare a blank and a standard curve in the range 0–400 $\mu$g of P, add 10 ml of 15 *M* nitric acid to aliquots of the standard phosphorus solution and continue as in the recommended procedure.

## DISCUSSION AND RESULTS

### *Dissolution of sample*

Although it is recommended that samples be dissolved in (1+2) nitric acid, stronger nitric acid is sometimes required to dissolve various metals or alloys. Bismuth metal must be dissolved in 15 *M* nitric acid and nickel alloys dissolve faster in (1+1) nitric acid. Hydrofluoric acid assists in the dissolution step and complexes metals, such as antimony, bismuth, tin, niobium, and tungsten, which have a tendency to hydrolyse on dilution.

It is important that antimony and selenium be in the highest valency state, otherwise low phosphorus recoveries are obtained. When phosphorus is determined in antimony or selenium metals, add 20 ml of 1% potassium permanganate to 0.5 g of sample to obtain a permanent pink colour; use only 2 ml of 5% sodium nitrite solution to discharge the permanganate colour.

### *Sensitivity and stability of the method*

The absorbance of the phosphovanadomolybdate can be measured between 400 and 480 nm. The absorbance of the complex and blanks increases with decreasing wavelength. A wavelength of 425 nm and the 2-cm cells were selected to determine phosphorus between 0.01 and 0.08% in a 0.5-g sample. Below 0.01% phosphorus must be determined in 4-cm cells at a wavelength of 400 nm, where the sensitivity in nearly twice that obtained at 425 nm. The molar absorptivity of the complex in MIBK is 1820 and 3110 at 425 and 400 nm respectively. Beer's law is obeyed to at least 38 $\mu$g P ml$^{-1}$.

The colour of the complex in the organic phase measured against the reagent blank is stable for at least 1 h. After a 15-min standing time, an additional filtration step is necessary. The absorbance of the phosphovanadomolybdate does not change in the investigated temperature range, 19–25°.

### *Choice of acidity and effect of varying reagent concentrations*

The amount of nitric acid was varied to determine the effect of nitric acid concentration on the absorbance. Constant absorbances were obtained when 6–15 ml of 15 *M* nitric acid was used in the sample dissolution procedure. The total volume for colour development was 115 ml. An amount of 3 ml of 40% hydrofluoric acid was required to complex 0.5 g of antimony, bismuth, tin, titanium, niobium and tungsten completely, thus releasing phosphorus to form the yellow phosphovanadomolybdate. The amount of ammonium molybdate was increased to 65 ml to compensate for the added fluoride. It was necessary to add 17 ml of 15% ammonium molybdate for each ml of 40% hydrofluoric acid, in order to obtain the maximum colour development of phosphovanadomolybdate. The effect of vanadate concentration was discussed previously[5].

### *Reagent blanks and standard curve*

The absorbance of the reagent blanks is low (0.020 and 0.090 abs. units against water at 425 and 400 nm, respectively) and depends on the phosphorus content of the ammonium molybdate reagent.

It was established that all metals in the amounts mentioned below have no effect on the absorbance and therefore the standard curve may be prepared by omitting these metals from the procedure.

### *Extraction*

The volume of solution before extraction was increased to 150 ml to overcome any precipitation in the filtered organic phase caused by a high salt concentration in the aqueous layer. The filtered organic solution starts to show turbidity after a 15-min standing time, and to overcome any errors caused by formation of precipitates in the blank, water is recommended as a reference solution. Provided that the concentration of nitric acid is correct for the formation of the phosphovanadomolybdate, dilution before the extraction has no effect on the absorbance.

### *Study of interference*

No interference was observed in the determination of 200 $\mu$g of phosphorus from 1 mg of As or from 0.5 g of the following elements: Ag, Bi, Cd, Ce, Co, Cu, Fe, Hg, La, Mn, Mo, Nb, Ni, Pb, Sb, Se, Sn, Th, Ti, U, W, Zn.

This procedure is recommended for the determination of phosphorus in tungsten metal[5], because the tungsten–fluoride complex remains in solution and no interference of tungsten is observed.

*Aluminium*, up to 0.5 g, does not interfere but because the metal forms a very strong complex with fluoride, silicon is released from its fluoride complex and even submilligram amounts of silicon give high absorbance readings. Therefore only a maximum of 0.25 g of sample must be taken for analysis, and silicon must be below 2%. A positive error of 2% is given by 4% of silicon. In 0.5-g metal samples containing 20% and 50% of aluminium, the silicon level must not be higher than 5% and 2%, respectively.

*Chromium* interferes slightly when present in large amounts, producing an error of −3% for every 50 mg of chromium.

*Germanium* above 1 mg gives a positive error.

*Silicon*. The maximum permissible concentration of silicon in a 0.5-g metal sample is 5%, and 10% of silicon gives an error of 2%.

*Vanadium* interferes slightly; 0.5 g of metal produces a positive error of 12%. The error is proportional to the amount of vanadium present.

*Zirconium* up to 0.5 g does not interfere, but when together with silicon the limiting concentration of silicon is 2%. On a 0.25-g sample, the silicon level can be increased up to 20%.

### *Determination of phosphorus in silica*

When samples are dissolved in nitric–hydrofluoric acid mixture, most of the silicon remains in solution and interferes when present above 5%. Silicon can be volatilised as fluoride from fuming perchloric[4] or sulphuric acid[5]. Therefore it was expected that phosphorus could be determined in silica after volatilisation of silicon as tetrafluoride. Experimental results showed that after dissolution of silica in hydrofluoric–nitric acid mixtures, only perchloric acid could be used to remove silicon. Sulphuric acid may be used[5] when 0.5 g of a metal is present in the fuming solution, because the metal prevents the conversion of phosphates to partially insoluble pyrophosphates. Solutions containing phosphate, but no metal ions, showed varying degrees of phosphate recoveries depending on the time taken to fume with sulphuric acid.

TABLE I

SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS IN VARIOUS MATERIALS

| *Sample* | | *P found (%)* | *Other values P (%)* | |
|---|---|---|---|---|
| Manganese brass | BCS 179 | 0.0574 | 0.06[b] | 0.0575[c] |
| Bronze | BCS 207/1 | 0.0005 | $<$0.001[b] | 0.0005[d] |
| Cupro-nickel | BCS 180 | 0.0018 | 0.0014[c] | 0.0018[d] |
| Aluminium alloy | BCS 181 | 0.0010 | 0.0012[c] | 0.0010[d] |
| 11 Si–Al | BCS 182/1 | 0.0008[e] | 0.0009[d,f] | |
| Zircaloy | V379[a] | 0.0005 | 0.0006[d] | |
| Zircaloy | V380[a] | 0.0046 | 0.0045[d] | |
| Zircaloy | V381[a] | 0.0353 | 0.0346[d] | |
| Zircaloy | V382[a] | 0.0162 | 0.0158[d] | |
| Zircaloy | V647[a] | 0.0007 | 0.0007[d] | |
| 2.5 Nb–Zr | | 0.0010 | 0.0009[d] | |
| White metal (Sn-based) | NBS 54d | 0.0008 | — | |
| White metal (Sn-based) | BCS 178 | 0.0005 | — | |
| White metal (Pb-based) | BCS 177/1 | 0.0002 | — | |
| Lead powder (A.R.) | | 0.0003 | — | |
| Tin powder (A.R.) | | 0.0002 | — | |
| Devarda's alloy | | 0.0115 | 0.0116[d] | |
| Nb metal (Comm.) | | $<$0.0001 | — | |
| $Zr(NO_3)_4$ (Comm.) | | 0.0063[g] | — | |
| $Na_2WO_4$ (A.R.) | | 0.0030[g] | — | |
| $Fe(NO_3)_3 \cdot 9H_2O$ (A.R.) | | 0.0004[g] | — | |
| $Th(NO_3)_4 \cdot 4H_2O$ (A.R.) | | 0.0016[g] | 0.0014[c] | |

[a] Samples prepared by Venthon Research Laboratories (France).
[b] Certified value.
[c] Ref. 6.
[d] In $H_2SO_4$ system as in Ref. 5.
[e] Sample size 0.12 g.
[f] Dissolved in 3 ml of 40% HF.
[g] Sample analysed contained 0.5 g of the metal.

### *Reproducibility and sensitivity of the method*

Readings on a series of 10 standards showed that the relative standard deviation at the 5 μg P ml$^{-1}$ level (in MIBK) is ±0.5%. Similar results for the 1.25 μg P ml$^{-1}$ level gave a relative standard deviation of ±1%, which leads to a limit of detection at the 95% confidence level of 1.5 μg of phosphorus.

### *Results*

The results obtained for a variety of materials are shown in Table I, and are in good agreement with other values.

It is a pleasure to acknowledge the assistance given by Mrs. B. McAllister with the experimental work.

## SUMMARY

A method is described for the spectrophotometric determination of up to 0.08% of phosphorus in aluminium, copper and nickel alloys, white metals, tungsten, zinc, and silver babbitts based on the extraction of the phosphovanadomolybdate complex by methyl isobutyl ketone. The matrix metals are complexed by fluoride ion and do not interfere in the procedure. The molar absorptivity is 1820 and 3110 at 425 and 400 nm respectively, with a standard deviation of ±0.5%.

## REFERENCES

1 ASTM, Part 32, E62, para 14 and 22, 1965.
2 BRITISH STANDARD: 1748: Part 8: 1960.
3 W. T. Elwell and H. N. Wilson, *Analyst*, 81 (1956) 136.
4 P. Pakalns, *Anal. Chim. Acta*, 49 (1970) 511.
5 P. Pakalns, *Anal. Chim. Acta*, 50 (1970) 103.
6 P. Pakalns, *Anal. Chim. Acta*, 40 (1968) 1.

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

# THE USE OF 2-NITROSO-1-NAPHTHOL AS AN EXTRACTION AND SPECTROPHOTOMETRIC REAGENT FOR COBALT IN PLANT MATERIALS

H. SSEKAALO
*Animal Health Research Centre, P.O. Box 24, Entebbe (Uganda)*

(Received April 15th, 1970)

2-Nitroso-1-naphthol has been widely used for the separation and spectrophotometric determination of trace quantities of cobalt[1,2]. In general, this reagent should be preferred to others as it possesses several advantages: (*a*) it is more selective than other available reagents for cobalt; (*b*) it forms a complex with cobalt that is readily extractable into chloroform, and the excess reagent extracted along with the complex into the chloroform is easily removed[3] from the organic into the aqueous layer by shaking it with dilute sodium hydroxide at about 20°. Moreover, when the absorbance is measured in the range 360–370 nm, 2-nitroso-1-naphthol is one of the most sensitive spectrophotometric reagents available for cobalt.

The separation and determination of cobalt as proposed in this paper is done in a citrate-buffered medium essentially as described by SANDELL[1]. However, certain modifications were needed because of the high concentration of sulphate ion arising from the use of sulphuric acid mixtures for the wet oxidation of plant materials, and because of the greater sensitivity provided by the use of the absorbance maximum at 367 nm. Sulphuric acid in the presence of perchloric acid and nitric acid or hydrogen peroxide is the most useful medium for the decomposition of biological materials.

## EXPERIMENTAL

### *Reagents*

All reagents were of analytical grade. However, some of these needed further purification: (*a*) nitric acid was redistilled; (*b*) aqueous 50% (w/v) sodium citrate was purified along the lines suggested by SANDELL[1]; (*c*) 1% (w/v) 2-nitroso-1-naphthol in glacial acetic acid was mixed with activated charcoal in an amount four times the weight of the reagent and then filtered through Whatman No. 1 filter paper. A standard cobalt solution was prepared from $CoCl_2 \cdot 6H_2O$.

### *Apparatus*

A Unicam SP 500 spectrophotometer was used for measuring absorbances in 1-cm fused silica cells.

### *Procedures*

Cobalt 2-nitroso-1-naphtholate complex was prepared from a standard cobalt solution for plotting the absorbance spectrum and for construction of calibration curves, as follows. To a standard cobalt solution in a 50-ml beaker add 0.3 ml of concentrated sulphuric acid and then heat the solution until white fumes form. Cool the solution and dilute to about 10 ml. Add 50% (w/v) sodium citrate (0.5 ml) and adjust the pH of the solution to 3–4 (using Johnson's universal indicator paper) with 2 *M* sodium hydroxide and 1 *M* sulphuric acid. Add 2 ml of 1% 2-nitroso-1-naphthol solution and leave the solution to stand for 45 min. Extract the complex into 5.0 ml of chloroform by vigorous shaking for 1 min, and then remove the excess of reagent from the organic layer by shaking with 20 ml of 2 *M* sodium hydroxide. The reagent-free chloroform solution is pinkish red.

*Preparation of sample material.* Oxidize 5–10 g of oven-dried plant material in a 250-ml conical flask with 5 ml of concentrated sulphuric acid and concentrated nitric and perchloric acids as required. Cool the digest, dilute and filter through a sintered glass funnel. Adjust the pH of the filtrate (now about 100 ml) to 3–4 after the addition of 5 ml of 50% sodium citrate; use a strong (10 *M*) sodium hydroxide solution initially in order to keep the volume low, and make the final pH adjustment with 2 *M* sodium hydroxide and 1 *M* sulphuric acid. Add 2 ml of 30% hydrogen peroxide and 4 ml of 1% 2-nitroso-1-naphthol to the buffered solution. Extract the complex into two portions (20 and 10 ml) of chloroform, combine the extracts and shake with 20 ml of 1 *M* sulphuric acid to destroy the extracted complexes of certain metals such as copper. In order to concentrate the solution, evaporate off all the chloroform and wet-oxidize the residue with 0.3 ml of concentrated sulphuric acid, 2–4 ml of concentrated nitric acid and 1 ml of 60% perchloric acid. Treat the resulting sulphuric acid digest as outlined above for the standard cobalt solution. Prepare a reagent blank in the same way as the samples.

*Note.* For most plant materials the washing of the chloroform extract with 1 *M* sulphuric acid may be omitted since the quantities of ions forming extractable complexes are too small to interfere. Iron(II), which would interfere by forming an extractable complex, is oxidized by hydrogen peroxide to iron(III) which is then complexed by the citrate. Copper(II) which forms a dark brown extractable complex does not interfere even if present in amounts as high as 25 mg[1].

Cobalt can be extracted with 2-nitroso-1-naphthol from the same sample solution from which molybdenum has been previously extracted at pH 0–0.5 with cupferron. Cupferron also extracts iron(III) quantitatively and copper(II) nearly so under these conditions, hence addition of hydrogen peroxide and washing of the chloroform extract with 1 *M* sulphuric acid become unnecessary when molybdenum is simultaneously determined. This method has been applied satisfactorily for several hundred samples.

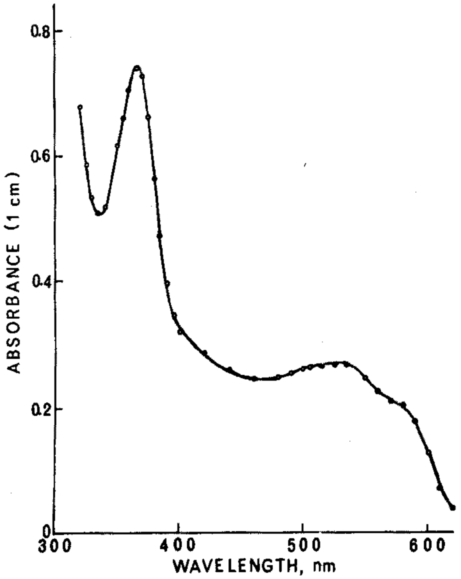
## RESULTS

### *Absorbance spectrum of cobalt 2-nitroso-1-naphtholate complex*

The absorbance spectrum of the cobalt 2-nitroso-1-naphtholate complex has two well-defined maxima, at 367 nm and at 530 nm (Fig. 1). The absorbance at 367 nm is about three times that at 530 nm (*cf.* the wavelength of maximum absorbance is at 362 nm for the complex in amyl acetate[4]).

### *Standard curves*

As shown in Fig. 2, Beer's law was obeyed strictly within the concentration range 0.05–0.6 p.p.m. Co when the absorbances were measured at 367 nm. Good linearity of the curve could be extended up to 1.0 p.p.m. Co. Corresponding absorbances and concentrations at 530 nm were plotted for comparison purposes. The calculated molar absorptivities at 367 nm and 530 nm are $4.4 \cdot 10^4$ and $1.6 \cdot 10^4$, respectively.



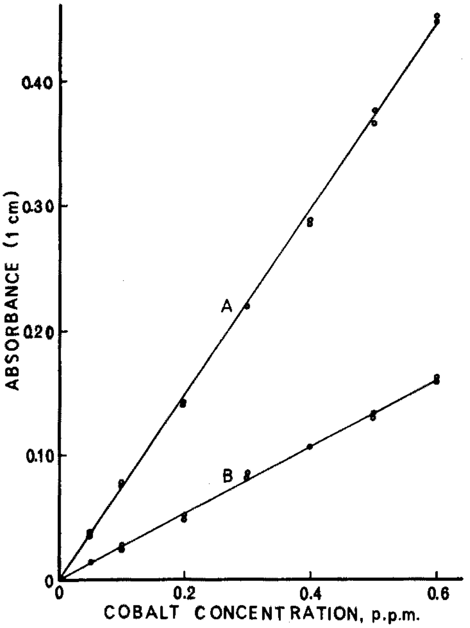


Fig. 1. Absorbance spectrum of cobalt 2-nitroso-1-naphtholate complex in chloroform; 1.0 p.p.m. Co concentration.

Fig. 2. Standard curves for cobalt determination with 2-nitroso-1-naphthol; (A) at 367 nm; (B) at 530 nm.

### *Excess of reagent in the separation stage*

Two sets of twelve reagent blanks each were prepared for the determination of their cobalt content. In one set the excess of reagent was not destroyed in the separation stage, and in the other the excess of reagent was removed from the chloroform extract by shaking it with 2 *M* sodium hydroxide as outlined in the procedure. The cobalt concentrations in both sets were found to be of the same magnitude. It is therefore proposed that there is no need to remove the excess of reagent from the chloroform extract at the separation stage.

### *Stability of cobalt 2-nitroso-1-naphtholate complex*

After extraction of the cobalt–reagent complex into chloroform and after destruction of the excess of reagent, the red solutions were placed in glass-stoppered tubes in a closed cupboard. The absorbances of the solutions were read every 6 h, and were found to remain stable for at least 6 days. This stability was maintained both for the complex formed from a standard cobalt solution and from 5-g samples of grass, six replicates being used.

### *Reagent purification*

As has been established by other workers[3,5] it is necessary to purify the reagent. Activated charcoal was satisfactory for this purpose as shown by Claassen and Daamen[3]. It is of interest to note that the reagent blanks can vary greatly from batch to batch of reagent, and it is advisable to test for each batch the optimal amount of charcoal needed to reduce the blanks to the region of a few hundredths p.p.m. of cobalt; some batches may require 3–4 times the amount of charcoal as that needed by relatively pure samples.

### *Precision and accuracy tests*

The precision of the method when absorbances were measured at 367 nm or 530 nm was tested on twenty determinations for each of two pasture plants, *Chloris gayana* and *Panicum maximum*. The results of the precision test are shown in Table I.

TABLE I

PRECISION TEST

| *Plant* | *No. of detns.* | *Average Co concn. at 367 nm (p.p.m.)* | *Coefficient of variation at 367 nm* | *Average Co concn. at 530 nm (p.p.m.)* | *Coefficient of variation at 530 nm* |
|---|---|---|---|---|---|
| *Chloris gayana* | 20 | 0.42 | 2.4 | 0.42 | 4.5 |
| *Panicum maximum* | 20 | 0.18 | 5 | 0.18 | 10 |

TABLE II

ACCURACY TEST

| *Co added (µg)* | *Total Co found (µg)* | *% Recovery* | *Co added (µg)* | *Total Co found (µg)* | *% Recovery* |
|---|---|---|---|---|---|
| *Panicum maximum I at 367 nm*[a] | | | *Panicum maximum II at 530 nm*[b] | | |
| Nil | 0.45 | — | Nil | 1.00 | — |
| 0.125 | 0.58 | 104 | 0.25 | 1.25 | 100 |
| 0.25 | 0.70 | 100 | 0.50 | 1.52 | 104 |
| 0.50 | 0.95 | 100 | 0.75 | 1.72 | 96 |
| 0.75 | 1.25 | 104 | 1.00 | 1.92 | 92 |
| 1.00 | 1.40 | 95 | 1.25 | 2.17 | 94 |
| 1.25 | 1.60 | 95 | 1.50 | 2.45 | 97 |
| Nil | 0.90 | — | 1.75 | 2.70 | 97 |
| 0.25 | 1.15 | 100 | 2.00 | 3.00 | 100 |
| 0.50 | 1.37 | 94 | 2.25 | 3.18 | 97 |
| 1.00 | 1.90 | 100 | 2.50 | 3.45 | 98 |
| 1.50 | 2.40 | 100 | 2.75 | 3.73 | 99 |
| 2.00 | 2.85 | 97 | 3.00 | 4.02 | 101 |

[a] 2.5-g samples were taken for the first 7 determinations and 5.0-g samples for the last 6.
[b] 5.0-g samples were used throughout.

The accuracy test was carried out on two sets of samples of the pasture plant, *Panicum maximum* from two different localities. Standard cobalt solutions were added to the samples before wet oxidation of the plant material. The results are shown in Table II.

## DISCUSSION AND CONCLUSION

The results of the precision test (Table I) and of the accuracy test (Table II) show that the use of 2-nitroso-1-naphthol as a separating and spectrophotometric reagent for trace quantities of cobalt in plant materials is both reliable and accurate. Owing to the greater sensitivity at 367 nm ($\varepsilon = 4.4 \cdot 10^4$), the precision at this wavelength is better than that at 530 nm ($\varepsilon = 1.6 \cdot 10^4$). For this reason the greater sensitivity of the reagent at 367 nm makes it very useful for cobalt determination in the majority of plant materials where the level of this element is very low. There is no reason why measurements at 367 nm should not be preferred for trace amounts of cobalt, provided that a spectrophotometer with a narrow slitwidth is used, as the absorbance peak is wide enough.

The concentration of the sulphate ion when maintained at 0.50–0.75 *M* did not cause interference. This concentration is about the amount that remains from the quantity of sulphuric acid used in the wet oxidation of the amounts of sample which are usually necessary to yield a sufficient amount of cobalt for accurate determinations.

The use of this reagent as presented in this work should offer a competitive method among the other spectrophotometric reagents. If the absorbance is measured at 367 nm, the method is one of the most sensitive spectrophotometric procedures so far available for cobalt. The procedure is straightforward and comparatively rapid.

The author is very grateful to Mr. A. OKUMU of this Centre for his assistance in many of the analyses. This article is published by permission of the Permanent Secretary, Ministry of Animal Industry, Game and Fisheries, Uganda.

## SUMMARY

The separation and spectrophotometric determination of trace amounts of cobalt in plant materials with 2-nitroso-1-naphthol is described. The cobalt complex is formed in citrate-buffered medium in the presence of 0.5–0.75 *M* sulphate ion which arises from the sulphuric acid used for wet oxidation of sample materials. The absorbance is measured at 367 nm ($\varepsilon = 4.4 \cdot 10^4$) which provides greater sensitivity and precision than the usual measurement at 530 nm ($\varepsilon = 1.6 \cdot 10^4$). The method is suitable for samples containing as little as 0.05–0.25 p.p.m. Co, the error being ±5% in oxidized plant materials.

## RÉSUMÉ

On décrit une méthode de séparation et de dosage spectrophotométrique de traces de cobalt dans les plantes, au moyen de nitroso-2-naphtol-1. Le complexe de cobalt est formé en milieu tampon citrate, en présence de sulfate 0.5–0.75 *M*, provenant de l'acide sulfurique utilisé pour l'oxydation par voie humide de l'échantillon. Les mesures se font à 367 nm ($\varepsilon = 4.4 \cdot 10^4$) permettant d'obtenir une meilleure sensibilité et précision que les mesures usuelles à 530 nm ($\varepsilon = 1.6 \cdot 10^4$). Cette méthode peut s'appliquer à des échantillons contenant 0.05 à 0.25 p.p.m. Co (erreur ±5%).

## ZUSAMMENFASSUNG

Es wird die Abtrennung und spektrophotometrische Bestimmung von Kobaltspuren in Pflanzen mit Hilfe von 2-Nitroso-1-naphthol beschrieben. Der Kobaltkomplex wird in citratgepuffertem Medium in Gegenwart von 0.5–0.75 *M* Sulfat gebildet, welches von der für die nasse Oxidation der Proben benutzten Schwefelsäure stammt. Die Extinktion wird bei 367 nm ($\varepsilon = 4.4 \cdot 10^4$) gemessen; Empfindlichkeit und Genauigkeit sind hier besser als bei der sonst benutzten Wellenlänge 530 nm ($\varepsilon = 1.6 \cdot 10^4$). Die Methode ist für Proben mit so geringen Gehalten wie 0.05–0.25 p.p.m. Co geeignet, wobei der Fehler bei oxidierten pflanzlichen Proben ±5% ist.

## REFERENCES

1 E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Edn., Interscience, New York, 1959.
2 J. A. W. Dalziel and A. K. Slawinski, *Talanta*, 15 (1968) 367.
3 A. Claassen and A. Daamen, *Anal. Chim. Acta*, 12 (1955) 547.
4 A. Baron, *Z. Anal. Chem.*, 140 (1953) 184.
5 M. Needham, *Anal. Chem.*, 38 (1966) 915.

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

# STUDIES ON THE CATION-EXCHANGE BEHAVIOUR OF AMMONIUM 12-MOLYBDOPHOSPHATE

## PART I. SEPARATION OF RUBIDIUM, THALLIUM AND CAESIUM

S. DUTTA ROY AND M. SANKAR DAS
*Analytical Division, Bhabha Atomic Research Centre, Modular Laboratories, Trombay, Bombay-85 (India)*

(Received April 29th, 1970)

The separation of alkali metal ions from each other with ammonium 12-molybdophosphate (AMP) columns has been reported by a number of workers in recent years[1-4]. Various studies[5-7] have shown that in acidic medium, in addition to the alkali metal ions, other monovalent cations such as thallium(I), silver and mercury(I) form insoluble 12-molybdophosphates, which have been proved by X-ray studies to be isomorphous with those of alkali metal ions[8]. The distribution coefficient values ($K_d$) for silver, thallium(I) and the alkali metal ions reported by SMIT *et al.*[9] are in accordance with the above observations. However, no method for the separation of thallium from alkali metal ions, particularly rubidium and caesium, on AMP columns has been reported in the literature. The present paper presents such a study.

## EXPERIMENTAL

### *Ion-exchanger*

Ammonium 12-molybdophosphate (AMP), prepared by the "direct method"[9], was of the microcrystalline variety, usually substantially smaller than 200 mesh.

### *Reagents*

All reagents used were B.D.H. AnalaR grade.

*Thallium carrier solution.* Dissolve thallium(I) nitrate in dilute nitric acid to give 20 mg Tl per ml.

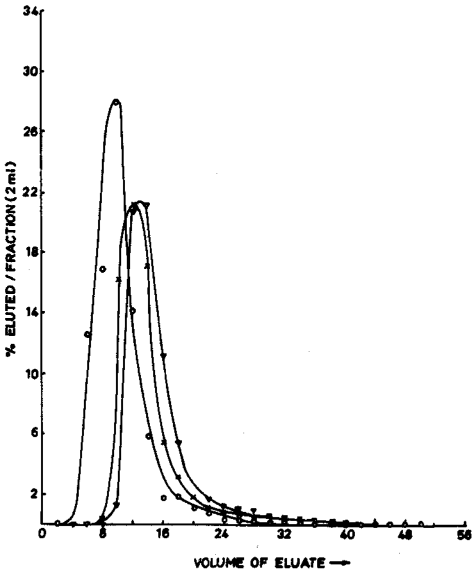
*Caesium or rubidium carrier solution.* Dissolve caesium or rubidium chloride in distilled water to give 15 mg Cs or Rb per ml.

*Bromine solution.* Prepare 0.05 *M* bromine in 5% potassium bromide and standardise by titration with standard sodium thiosulphate solution.

### *Tracers*

The following tracers (Isotope Division, B.A.R.C.) were used and their purity was checked by standard methods[10].

| *Tracer* | *Half-life* | *Mode of decay*[11] |
|---|---|---|
| $^{204}$Tl | 4.1 yr | $\beta^-$, $E_{max}=0.765$ MeV (100%) |



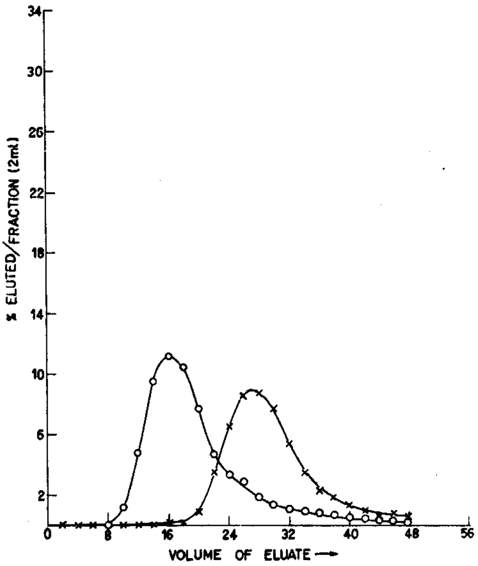
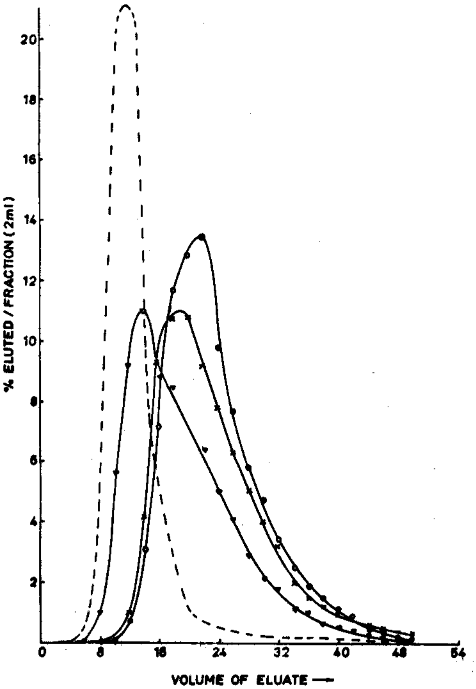


Fig. 1. Influence of flow rate on the elution of thallium(I); AMP on column 1.5 g + 0.75 g asbestos; Tl(I) loaded, 0.09 meq; eluant, 12 *M* $NH_4NO_3$; rate of elution: (○) 1 ml $min^{-1}$, (×) 0.5 ml $min^{-1}$, (▽) 0.2 ml $min^{-1}$.

Fig. 2. Influence of flow rate on the elution of caesium; AMP on column 1.5 g + 0.75 g asbestos; Cs loaded = carrier-free $^{137}Cs$; eluant, 7 *M* $NH_4NO_3$; rate of elution: (○) 1 ml $min^{-1}$, (×) 0.25 ml $min^{-1}$.



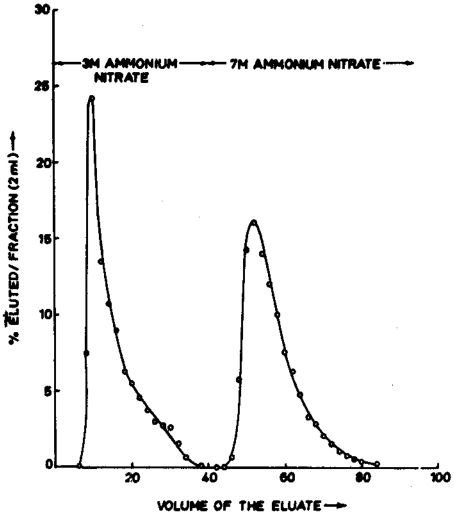


Fig. 3. Influence of column load with respect to caesium on the separation of thallium from caesium on AMP column: 1.5 g AMP + 0.75 g asbestos; rate of elution, 0.33 ml $min^{-1}$; eluant, 12 *M* $NH_4NO_3$; (----) Tl(I), 0.049 meq; (○) Cs = carrier-free $^{137}Cs$; (×) Cs, 0.083 meq; (▽) Cs, 0.195 meq.

Fig. 4. Separation of rubidium and thallium(I); AMP on column 1.5 g + 0.75 g asbestos; rate of elution: 0.8 ml $min^{-1}$.

| | | |
|---|---|---|
| $^{86}$Rb | 18.7 d | $\beta^-$, $E_{max}(\beta_1^-)=1.78$ MeV (84%)<br>$E_{max}(\beta_2^-)=0.71$ MeV (15%)<br>$E_\gamma=1.08$ MeV |
| $^{137}$Cs | 30 yr | $\beta^-$, $E_{max}(\beta_1^-)=1.176$ MeV (6.5%)<br>$E_{max}(\beta_2^-)=0.514$ MeV (93.5%)<br>$E_\gamma=0.662$ MeV |

### *Counters and counting*

$\gamma$-Activities from $^{86}$Rb and $^{137}$Cs were recorded with a single-channel spectrometer coupled to a 3×3″ NaI (Tl) crystal. For confirmation of the radiochemical purity, the $\gamma$-spectra were measured with a 400-channel analyser (Electronics Division, B.A.R.C.).

The activities of thallium eluate fractions were counted by means of bremsstrahlung radiation for convenience, while the activities caused by $^{86}$Rb and $^{137}$Cs in the eluate fractions were determined in their respective photopeaks.

### *Preparation of the AMP columns*

Glass columns of dimension 30 cm × 1.0 cm with stopcocks to regulate the flow and containing a wad of glass-wool and asbestos as the support were used. AMP and analytical-grade asbestos were mixed in the weight ratio 2:1, slurried with 5 *M* nitric acid and transferred to the column. Before use, the columns were washed with five column-volumes of 5 *M* nitric acid to remove any excess ammonium ions. Column I contained 4.5 g of the AMP–asbestos mixture in a 14-cm high bed with a free column-volume of 8 ml, whereas column II contained 2.25 g of the mixture in a 7-cm high bed with a free column-volume of 4 ml.

### *Column studies*

*Determination of loading conditions for thallium(I).* Thallium-204 tracer along with 0.09 meq of thallium(I) carrier was evaporated to dryness, taken up in 4 ml of 5 *M* nitric acid and loaded on column II. Washing the column with 50 ml of nitric acid of any concentration upto 8 *M* did not show the presence of any thallium activity in the effluent. Hence for quantitative loading of thallium(I) on the AMP column, 5 *M* nitric acid was selected.

*Elution of thallium(I) from the column.* 0.09 meq of thallium(I) after loading on column II as described above could not be eluted with 3 *M* ammonium nitrate, an eluant used for the desorption of rubidium[4], whereas, like caesium, it could be eluted with 7 or 12 *M* ammonium nitrate. However, at a constant elution rate a sharper quantitative elution could be obtained with 12 *M* ammonium nitrate than with 7 *M*.

*The influence of flow rates and concentration on the elution.* Preliminary studies on the elution of thallium(I) and caesium taken individually, indicated that the elution peaks were separated by about two column-volumes, hence the effect of flow rate was studied. The results are shown in Figs. 1 and 2 for the elution of thallium (0.09 meq) with 12 *M* ammonium nitrate, and the elution of carrier-free caesium with 7 *M* ammonium nitrate, respectively. The influence of the caesium concentration on the extent of contamination of the thallium fraction eluted with 12 *M* ammonium nitrate is shown in Fig. 3.

### *Separation of rubidium from thallium(I)*

The separation of 0.17 meq of rubidium from 0.09 meq of thallium(I) on column II was possible by means of the scheme represented in Fig. 4.

### *Separation between rubidium, thallium(I) and caesium*

In view of the difficulty in achieving the differential elution of thallium(I) and caesium on AMP columns with ammonium nitrate of any concentration, this separation was studied on the basis of oxidation of thallium(I) to thallium(III)[12], the latter having a negligible $K_d$ value on AMP under the loading conditions mentioned above.

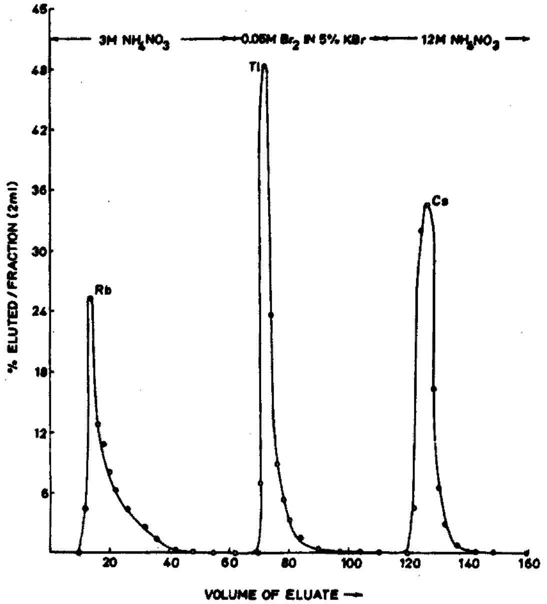


Fig. 5. Separation of rubidium, thallium and caesium; AMP on column 3.0 g + 1.5 g asbestos; rate of elution: 0.8 ml min$^{-1}$.

TABLE I

SEPARATION OF RUBIDIUM, THALLIUM AND CAESIUM

| *Element* | *Amount of carrier taken (meq)* | *Activity of tracer added (counts/min)* | *Activity recovered in the specified eluant (counts/min)* | *Recovery %* | *Eluant* |
|---|---|---|---|---|---|
| Rb | 0.17 | 16770 | 15896 (40)[a]<br>16399 (60) | 94.8<br>97.8 | 3 *M* $NH_4NO_3$ |
| Tl | 0.09 | 17730 | 16912 (30)<br>17497 (40) | 95.4<br>98.7 | 0.05 *M* $Br_2$ in 5% KBr |
| Cs | 0.11 | 35690 | 33621 (30)<br>34113 (50) | 94.2<br>95.5 | 12 *M* $NH_4NO_3$ |

[a] Values in brackets refer to the volumes of the eluant collected.

With the 3-g AMP column (column I), the separation of rubidium, thallium and caesium from one another was found to be possible by means of the scheme shown in Fig. 5. Elution of thallium(I) by oxidation to thallium(III) was carried out with 0.05 *M* bromine in 5% potassium bromide which was about 5 *M* in nitric acid. With this eluant there was no observable swelling of the ion-exchange bed. The results obtained in the separation are given in Table I.

## RESULTS AND DISCUSSION

The absence of cross-contamination of the isolated elements was established as follows: the purities of the rubidium and caesium fractions were checked by $\gamma$-spectrometry with a 400-channel analyser. In the case of the thallium fraction, the purity was checked as follows: the absence of contamination by rubidium was verified by counting the activity through an aluminium absorber with a thickness of 340 mg cm$^{-2}$, which is sufficient to cut off the $\beta$-radiation from $^{204}$Tl but is insufficient to stop the $\beta$-radiation from $^{86}$Rb. It was also checked by comparing the $\beta$-absorption curve with that from a pure $^{204}$Tl standard. Contamination from caesium was found to be absent from the $\gamma$-ray spectrum.

The available data on the distribution coefficients of monovalent cations on AMP in the presence of 0.1 *M* ammonium nitrate[9], as well as the quantitative loading conditions reported for rubidium and caesium[2,4], suggested that thallium(I) could be quantitatively loaded on the AMP column from 5 *M* nitric acid. This acidity for loading was chosen because under such conditions, the multivalent metal ions and also the smaller monovalent cations sodium and potassium have negligible exchange with AMP[13], thus permitting the gross separation of rubidium, thallium and caesium from other cations.

SMIT *et al.*[13] have shown that exchange equilibria between ammonium and other cations is rapidly established on AMP so that high flow rates of the order of 1 ml min$^{-1}$ can be used in column separations. While this seems to be so, the results shown in Figs. 1 and 2 for the effect of flow rate on the elution of thallium and caesium, respectively, show increased tailing with decrease of flow rate, which seems to indicate that the exchange inside the AMP–crystal lattice becomes more significant compared to the surface exchange at slower flow rates, as reported by MEIER AND TREADWELL[14].

The study of COETZEE AND ROHWER[3] has shown that in the case of two ions like sodium and potassium with a similar range of $K_d$ values, their separability is very much influenced by the ratio of the concentrations of the two ions, the concentration of the ion with the higher $K_d$ value influencing the extent of separation. It was therefore considered necessary to study the influence of the caesium concentration on its separation from thallium(I). The effect of the caesium concentration on the degree of overlap between thallium and caesium is shown in Fig. 3, which reveals the difficulty of separation between these ions when present at carrier levels of concentration. To improve the separation between thallium(I) and caesium, the use of longer AMP columns might be suggested, but this was not tried because of the practical difficulty in achieving satisfactory flow rates.

The theoretical capacity of AMP is reported to be 1.57 meq g$^{-1}$, but the actual capacity for the larger cations seems to be significantly lower. For example, when attempts were made to load about 0.37 meq of a mixture of rubidium, thallium(I) and caesium on column II containing 1.5 g of AMP, all the ions were detected in the effluent. Hence the separations reported here were carried out with the 3-g AMP column.

The use of oxidative or reductive elution has the advantage of being highly specific for particular elements. EHMANN AND HUYZENGA[15] reported a reductive elution of thallium(III) from a Dowex 1-X10 column for its separation from bismuth and mercury. A quantitative separation of thallium(I) from caesium being impossible with any concentration of ammonium nitrate as eluant, the use of oxidative elution was found necessary. The results showed that 95–98% of the element could be recovered in the specified volume of the eluant. These recoveries can be made quantitative by collecting a larger volume of the same eluant, before changing the eluant composition.

## SUMMARY

The cation-exchange behaviour of ammonium 12-molybdophosphate (AMP) for thallium(I) is discussed. Conditions are described for the separation of rubidium, thallium and caesium from one another on a column of AMP suitably mixed with asbestos. The three elements are adsorbed from 5 *M* nitric acid. Rubidium is first eluted with 3 *M* ammonium nitrate. Thallium is separated by oxidative elution using bromide–bromine mixture. Caesium is finally removed by 12 *M* ammonium nitrate.

## RÉSUMÉ

On examine le comportement "échangeur-cations" du molybdophosphate d'ammonium (AMP) pour le thallium(I). Les conditions sont décrites pour la séparation de rubidium, thallium, et césium les uns des autres à l'aide d'une colonne AMP mélangée à de l'amiante. Les trois éléments sont adsorbés en milieu acide nitrique 5 *M*. Le rubidium est d'abord élué avec nitrate d'ammonium 3 *M*. Le thallium est séparé par élution oxydante, en utilisant le mélange bromure–brome. Le césium est finalement éliminé par le nitrate d'ammonium 12 *M*.

## ZUSAMMENFASSUNG

Das Kationenaustausch-Verhalten von Ammonium-12-molybdatophosphat (AMP) gegenüber Thallium(I) wird diskutiert. Die Bedingungen für die Trennung von Rubidium, Thallium und Caesium voneinander mittels einer AMP–Asbest-Kolonne werden beschrieben. Die drei Elemente werden aus 5 *M* Salpetersäure adsorbiert. Zuerst wird Rubidium mit 3 *M* Ammoniumnitrat eluiert. Thallium wird durch oxydative Elution unter Verwendung eines Bromid–Brom-Gemisches abgetrennt. Schliesslich wird Caesium durch 12 *M* Ammoniumnitrat entfernt.

## REFERENCES

1 J. VAN R. SMIT, *Nature*, 181 (1958) 1530.
2 J. VAN R. SMIT, W. ROBB AND J. J. JACOBS, *J. Inorg. & Nucl. Chem.*, 12 (1959) 104.

3 C. J. Coetzee and E. F. C. G. Rohwer, *Anal. Chim. Acta*, 44 (1969) 293.
4 E. V. Gangadharam and G. R. Reddy, *Radiochim. Acta*, 11 (1969) 90.
5 J. W. Illingworth and J. A. Santos, *Nature*, 134 (1934) 971.
6 R. Belcher and J. W. Robinson, *Anal. Chim. Acta*, 8 (1953) 239.
7 H. Buchwald and W. P. Thistlethwaite, *J. Inorg. & Nucl. Chem.*, 5 (1958) 341.
8 J. W. Illingworth and J. F. Keggin, *J. Chem. Soc.*, (1935) 575.
9 J. van R. Smit, J. J. Jacobs and W. Robb, *J. Inorg. & Nucl. Chem.*, 12 (1959) 95.
10 R. T. Overman and H. M. Clark, *Radioisotope Techniques*, McGraw Hill, New York, 1960.
11 C. M. Lederer, J. M. Hollander and I. Perlman, *Table of Isotopes*, 6th Edn., John Wiley, New York.
12 I. M. Korenman, *Analytical Chemistry of Thallium*, Israel Program for Scientific Translation, Jerusalem, 1963.
13 J. van R. Smit and W. Robb, *J. Inorg. & Nucl. Chem.*, 26 (1964) 509.
14 D. Meier and W. D. Treadwell, *Helv. Chim. Acta*, 34 (1951) 155.
15 W. D. Ehmann and J. R. Huyzenga, *Geochim. Cosmochim. Acta*, 17 (1959) 125.

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

# SHORT COMMUNICATIONS

## Thorium hydroxide as a collector of molybdenum from sea water*

In a recent paper the behavior of commonly used iron(III) hydroxide was described in order to clarify its role as a collector of the trace element molybdenum in sea water[1]. It was shown that the hydroxide which is formed in sea water possesses a pH-dependent charge. At pH 4.0 the iron(III) hydroxide has an apparent maximum positive charge density and is capable of adsorbing molybdenum quantitatively as the molybdate anion. Procedures were worked out for the determination of molybdenum concentrated by iron(III) hydroxide and evaluated spectrophotometrically as the thiocyanate complex. The investigation indicated that a second condition besides that of charge may be necessary for the collection of a trace species. The PANETH–FAJANS–HAHN rule[2] requires that the collector contain an ion which forms a compound of low solubility with the counter ion adsorbed. This together with the charge of the particle are probably the dominant factors in the trace ion adsorption on a solid particle. The requirement is met satisfactorily in the case of iron(III) hydroxide at low pH since iron(III) molybdate is relatively insoluble but not with aluminum hydroxide despite the fact that the latter forms a positively charged colloid at pH 5.5. The work suggested that thorium hydroxide should be equally if not more effective as a collector of molybdenum from sea water because of the insolubility of thorium molybdate.

This paper is concerned with the study and use of thorium hydroxide as a collector of the trace element molybdenum from sea water before its spectrophotometric determination as the thiocyanate complex. This new collector offers advantages over iron(III) hydroxide. These include enhanced sensitivity and accuracy, and elimination of the need for masking iron(III) since thorium ion does not react with thiocyanate. The thorium hydroxide coprecipitate, also, is less bulky than iron(III) hydroxide and easier to handle and filter. The use of aluminum hydroxide as a collector was also investigated for comparative purposes.

### *Apparatus and reagents*

A Beckman DU spectrophotometer with matched quartz 1.0-cm cells, a Beckman Zeromatic pH meter, and Millipore HA filters (47 mm diameter) were used. Separatory funnels used for extraction were equipped with teflon stopcocks.

All chemicals employed were of analytical grade, and aqueous reagents were prepared in doubly distilled deionized water.

*Standard molybdenum solution.* Pure ammonium molybdate, $(NH_4)_2Mo_7O_{24} \cdot 4H_2O$, was used to prepare the standard solution as described previously. Appropriate aliquots when added to filtered sea water furnished concentrations of molybdenum ranging from 0 to 6 $\mu$g per 500 ml, not including that originally present in sea water.

### *Preliminary studies*

*Effect of pH.* The working procedure adopted to study the effect of pH was

---

* Hawaii Institute of Geophysics Contribution No. 343.

essentially similar to that described by KIM AND ZEITLIN[1]. The filtered pool of sea water was analyzed for molybdenum and found to contain 6.0 μg per 500 ml. To 500 ml samples were added sulfuric acid, 3–4 ml of 0.1 *M* thorium nitrate and 6.0 μg of molybdenum providing samples containing a total of 12.0 μg of molybdenum. The samples in duplicate were adjusted with dilute ammonia to pH 6.0, 7.5, 8.5, and 9.5 (±0.1), and one drop of 0.5 *M* iron(III) chloride was added in order to enhance the color of the complex[3]. Additional pairs of samples adjusted to each pH to which no molybdenum was added, acted as sea-water blanks. The coprecipitates containing the molybdenum were collected, dissolved in hydrochloric acid, and analyzed for molybdenum as described previously except that EDTA solution was omitted. For assessment of recovery the absorbances measured were compared with those obtained from the analysis of replicate standards containing exactly 12.0 μg of molyb-

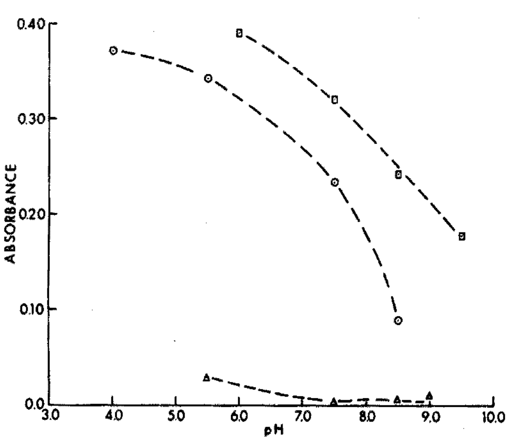


Fig. 1. Effect of pH on recovery of molybdenum. (⊡) With thorium hydroxide, (⊙) with iron(III) hydroxide, (◬) with aluminum hydroxide.

TABLE I

RECOVERY DATA FOR MOLYBDENUM IN SEA WATER

(6 μg Mo added to 500 ml of sea water)

| pH (± 0.1) | 6.0 | 7.5 | 8.5 | 9.5 |
|---|---|---|---|---|
| Recovery (%) | 99.5 | 81.5 | 61.6 | 46.4 |

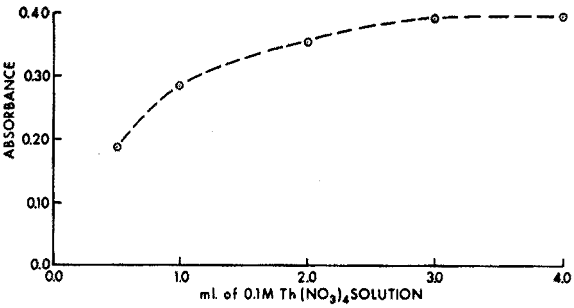


Fig. 2. Optimal amount of thorium nitrate for maximal recovery of molybdenum.

denum in which the coprecipitation step was omitted. The results are given in Fig. 1 and Table I.

*Optimal volume.* In order to find the proper amount of thorium for maximum recovery of molybdenum, various amounts of 0.1 *M* thorium nitrate solution were used at pH 6.0 (Fig. 2).

*Solubility of molybdate compounds.* Confirmation of the validity of the PANETH–FAJANS–HAHN rule in the collection of trace amounts of molybdate by various metal hydroxides requires information on the relative solubilities of the metal molybdates. Since solubility data on iron(III) and thorium molybdates are apparently not available, these compounds were prepared[4] and the solubilities measured[5] (Table II).

TABLE II

SOLUBILITY OF METALLIC MOLYBDATES

| *Compounds* | *Solubility at 25° (g/100 ml)* |
|---|---|
| $Th(MoO_4)_2$ | $2 \cdot 10^{-4}$ |
| $Fe_2(MoO_4)_3$ | $3 \cdot 10^{-3}$ |
| $Al_2(MoO_4)_3$ | Soluble (< pH 5.5) |

### *Determination of molybdenum in sea water*

Since maximal recovery of molybdenum from sea water was obtained by thorium hydroxide at pH 6.0, this pH is incorporated in the determination of molybdenum. To duplicate samples of 500 ml of sea water were added 2.0, 4.0, and 6.0 μg of molybdenum. One pair of samples receiving no molybdenum was included as sea-water blanks. Sulfuric acid (1 ml of 18 *N*) and 3.0 ml of thorium nitrate solution (0.1 *M*) were added to each sample. The pH was adjusted to 6.0 with dilute ammonia. The coprecipitate was allowed to settle for 30 min, collected on an 8-μm millipore filter, and dissolved in 2–3 ml of concentrated hydrochloric acid. The solution was evaporated to dryness on a low-temperature hot-plate and allowed to cool. The residue was dissolved in 5 ml of 6 *N* hydrochloric acid and the solution was analyzed for molybdenum by the thiocyanate method[3] as follows. The cooled solution was transferred to a separatory funnel, and diluted with water to 40 ml. One drop of 0.5 *M* iron(III) chloride solution, 1 ml of aqueous 40% (w/v) potassium thiocyanate solution and 1 ml of 40% (w/v) tin(II) chloride solution in 1.5 *N* hydrochloric acid were added and the solution was mixed thoroughly. Organic solvent (5 ml of 1:1 chloroform:carbon tetrachloride) was added and the mixture shaken manually for 1 min in order to extract the molybdenum complex. After separation, the bottom phase was drawn into a 1.0-cm absorption cell and absorbance measured at 470 nm against the blank. A straight line in conformity with Beer's law was obtained when absorbance was plotted *versus* molybdenum concentration. When the absorbance obtained from the sea-water blank (0.192) was subtracted, the line passed through the origin. The absorbance obtained by the analysis of sea water to which no molybdenum was added was practically identical with the absorbance from a sea-water sample containing 6.0 μg of molybdenum.

### *Discussion*

Previous work had shown that the recovery of molybdenum from sea water by iron(III) hydroxide was pH dependent and was 96.5% at the optimum pH 4.0. This constituted an improvement over that reported by ISHIBASHI AND FUJINAGA[6]. The work with thorium hydroxide showed that the effectiveness of this collector was also pH dependent. At the optimal pH an increased recovery of 99.5% was obtained. Thorium hydroxide precipitation is complete[7] near pH 6. At this pH, the colloid probably possesses maximum positive charge density and is capable of collecting quantitatively an anionic species such as molybdate. However, the results demonstrate that the requirement stipulated by the PANETH–FAJANS–HAHN rule is equally significant in the coprecipitation mechanism. Aluminum hydroxide which was examined similarly by use of 0.1 *M* aluminum sulfate is virtually ineffective (7.8% recovery) as a collector of molybdenum although at pH 5.5 it is positively charged and should be capable of coprecipitating molybdate if charge were the sole criterion. The failure is attributed to the relatively high solubility of aluminum molybdate at low pH. The adsorption of ions on the oppositely charged colloid depends upon both the charge density of the collector and the solubility of the compound produced by combination of ions being collected in solution with the lattice ions in the collector. This view is supported by comparison of the recoveries of the three collectors studied with the solubilities of the metal molybdates. At the optimal pH for collection maximum recovery is obtained with thorium hydroxide, recovery with iron(III) hydroxide is slightly less, and that from aluminum hydroxide is below 10%. The solubility data are consistent with the recoveries since thorium and iron(III) molybdate are both relatively insoluble whereas aluminum molybdate is soluble. From the analytical viewpoint the use of thorium hydroxide in place of iron(III) hydroxide results in increased sensitivity and accuracy in the spectrophotometric determination of molybdenum in sea water.

The results of this study point to the conclusion that additional metallic trace anionic species may be coprecipitated along with molybdenum by thorium hydroxide from sea water. Efforts are underway to identify and develop appropriate procedures for their separation and determination.

*Department of Chemistry and*
*Hawaii Institute of Geophysics,*
*University of Hawaii,*
*Honolulu, Hawaii 96822 (U.S.A.)*

YOUNG S. KIM
HARRY ZEITLIN

1 Y. S. KIM AND H. ZEITLIN, *Anal. Chim. Acta*, 46 (1969) 118.
2 O. HAHN, *Applied Radiochemistry*, Cornell Univ. Press, Ithaca, N.Y., 1936; H. A. LAITINEN, *Chemical Analysis*, McGraw-Hill, 1960, p. 167.
3 E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, Interscience, New York, 1965, p. 644.
4 R. S. SAXENA AND M. L. MITAL, *J. Sci. Ind. Res. (India)*, 21B, No. 2 (1962) 92; *C. A.*, 57 (1962) 4272b.
J. W. MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. XI, Longmans, London, 1931, p. 565–573.
5 G. J. PAPAIELLO AND W. J. MADER, in I. M. KOLTHOFF AND P. J. ELVING, *Treatise on Analytical Chemistry*, Part 1, Vol. 7, Interscience, New York, 1967, p. 4807.
6 M. ISHIBASHI AND T. FUJINAGA, *J. Chem. Soc. Japan*, 79 (1958) 1496.
7 G. CHARLOT, *Qualitative Inorganic Analysis*, Wiley, New York, 1957, p. 180.

(Received March 15th, 1970)

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

# Lanthanum as a releasing agent in atomic absorption spectroscopy in organic solvents

The use of lanthanum as a chemical interference suppressor has been widely reported in the literature, for both flame emission spectroscopy[1,2] and atomic absorption spectroscopy[3-5], and numerous references to specific analytical applications are given in standard texts[6,7]. Lanthanum is particularly effective as a releasing agent in the determination of calcium, where many species, *e.g.* aluminium, phosphate, sulphate, etc., suppress the calcium absorption signal, the severity of the suppression depending largely upon the flame system employed. FASSEL AND BECKER[8] have shown that such interferences can be eliminated at moderate interferent concentrations by arranging optimum conditions for aerosol particle size distribution, flame temperature and flame residence time, but the requisite experimental facilities will not necessarily be available to analysts working with commercial spectrophotometers.

To date, the reported applications of lanthanum as a releasing agent have been confined to analysis in aqueous solutions. The present paper shows that the same technique may be used in atomic absorption analysis in purely organic media. The compound lanthanum caprate is proposed as the source of lanthanum for this purpose. Lanthanum caprate is a stable, solid material which, solubilized with naphthenic acid, is miscible with a wide range of organic solvents at the lanthanum concentration (2000 p.p.m.) recommended.

*Preparation of lanthanum caprate*

Weigh 86 g of capric acid (decanoic acid) into a 4-l beaker, add 500 ml of distilled water and warm on a water bath until the acid liquefies. Add, with stirring, a slight excess of ammonia solution to neutralize the acid and continue stirring until dissolved. Dilute to 2.5 l with distilled water, and add, with vigorous stirring, a solution of 72 g of lanthanum nitrate hexahydrate in 500 ml of distilled water.

Separate the precipitate of lanthanum caprate by suction filtration, wash with five successive 500-ml portions of distilled water, followed by three successive 150-ml portions of acetone. Allow the product to air-dry and, finally, dry in vacuum over phosphorus pentoxide.

For lanthanum caprate, $[CH_3(CH_2)_8COO]_3La$, La (theoretical) = 21.3% and La (found) = 20.8%.

*Preparation of stock lanthanum solution*

To 10 g of lanthanum caprate add 15 ml of a solubilizing mixture consisting of equal parts, by volume, of naphthenic acid and white spirit. Warm gently until the organic salt gels and slowly dissolves. Care is necessary to avoid depositing gel-forming salt on the sides of the beaker, when dissolution may become very slow. Make up to a final volume of 100 ml with white spirit, to give a nominal "2%" lanthanum stock solution. Since equal additions are made to both sample and standard solutions, the precise lanthanum concentration is immaterial.

*Purity checks*

The original lanthanum nitrate contained 5.8 p.p.m. calcium and 0.7 p.p.m.

magnesium. The lanthanum caprate prepared from it contained 0.5 p.p.m. calcium and 0.16 p.p.m. magnesium. Thus, in a 1% solution of lanthanum caprate (equivalent to 2000 p.p.m. La), the respective calcium and magnesium concentrations from this source are 0.005 p.p.m. and 0.0016 p.p.m. These levels are generally negligible.

### *Miscibility*

At ten-fold dilution, corresponding to an addition of 2000 p.p.m. lanthanum, the 2% lanthanum stock solution has been found to be freely miscible with the following organic solvents commonly employed as diluents in atomic absorption spectroscopy: iso-octane, *n*-heptane, methyl isobutyl ketone, white spirit and aviation gasolines.

### *Apparatus*

A Perkin-Elmer Model 303 atomic absorption spectrophotometer was used throughout, with the experimental conditions as shown in Table I, set for the determination of calcium.

### *Results*

With white spirit as the base solvent, standard solutions were prepared for aluminium, barium, calcium, phosphorus, sodium and vanadium, from commercial naphthenates or lube oil additives, chemically analysed for metal content. For both flame types (Table I), the absorbance given by 2.0 p.p.m. calcium was measured, with and without additions of the other metals, and the same series of readings was repeated with a standard addition of 2000 p.p.m. lanthanum to all solutions. This lanthanum concentration was selected as the result of trials on the strongly-suppressing vanadium addition; for a vanadium/calcium ratio of 100:1, the calcium absorbance increased with increasing lanthanum up to 1500–2000 p.p.m., but greater lanthanum additions produced no further improvement. The results of the four series of measurements are given in Table II, and show that in both flames the lanthanum addition gives an enhanced and essentially stable calcium response.

TABLE I

EXPERIMENTAL CONDITIONS—PERKIN-ELMER MODEL 303

| | *Flame type* | |
|---|---|---|
| | *Air/acetylene* | *Nitrous oxide/acetylene* |
| Wavelength (nm) | 422.6 | 422.6 |
| Slit bandpass (Å) | 13 | 13 |
| Scale expansion (×) | 1 | 1 |
| Lamp current (mA) | 10 | 10 |
| Burner slot (cm) | 10 | 5 |
| Air—Supply (p.s.i.) | 25 | — |
| Flowmeter (divs.) | 9 | — |
| Acetylene—Supply (p.s.i.) | 8 | 8 |
| Flowmeter (divs.) | 7 | 6.5 |
| Nitrous oxide—Supply (p.s.i.) | — | 30 |
| Flowmeter (divs.) | — | 7.5 |
| Beam height (mm) | 10 | 12 |

TABLE II

EFFECT OF INTERFERING ELEMENTS ON CALCIUM ABSORBANCE, WITH AND WITHOUT ADDITION OF LANTHANUM

| *Added element*[a] *(p.p.m.)* | *Absorbance* | | | |
|---|---|---|---|---|
| | *Air/acetylene* | | *Nitrous oxide/acetylene* | |
| | *No La* | *with 2000 p.p.m. La* | *No La* | *with 2000 p.p.m. La* |
| Nil | 0.138 | 0.148 | 0.099 | 0.188 |
| Al 100 | 0.120 | 0.147 | 0.088 | 0.193 |
| Ba 200 | 0.105 | 0.144 | 0.139 | 0.191 |
| Na 200 | 0.141 | 0.148 | 0.195 | 0.192 |
| P 200 | 0.118 | 0.147 | 0.098 | 0.193 |
| V 200 | 0.013 | 0.147 | 0.137 | 0.188 |

[a] All solutions contained 2.0 p.p.m. Ca.

In a further series of experiments, at a calcium concentration of 1.0 p.p.m. in all solutions, it was found that a standard addition of 2000 p.p.m. lanthanum produced a consistent calcium absorbance in the presence of up to 100 p.p.m. aluminium, 200 p.p.m. sodium, or 500 p.p.m. barium, phosphorus or vanadium. The same addition was effective in the presence of combined dopings of (*a*) 500 p.p.m. each of barium and phosphorus, and (*b*) 100 p.p.m. aluminium with 200 p.p.m. each of sodium, barium, phosphorus and vanadium.

## *Conclusion*

Lanthanum is shown to be an effective releasing agent for atomic absorption analysis in organic solvents, as in previously reported work in aqueous solutions. Lanthanum caprate is a convenient, stable source of lanthanum for this purpose. The technique should find application in such analytical situations as (*a*) determination of calcium in crude oils and fuel oils, where a high vanadium or sodium concentration may be present, and (*b*) determination of calcium in lubricating oils, where high barium and phosphorus levels occur.

*Chemical Inspectorate,*
*Royal Arsenal,*
*London, S.E. 18 (England)*

R. A. Mostyn
B. T. N. Newland
W. E. Hearn

1 C. H. Williams, *Anal. Chim. Acta*, 22 (1960) 163.
2 J. Yofe, R. Avni and M. Stiller, *Anal. Chim. Acta*, 28 (1963) 331.
3 D. J. David, *Analyst*, 85 (1960) 495.
4 J. B. Willis, *Spectrochim. Acta*, 16 (1960) 259; *Anal. Chem.*, 38 (1961) 556.
5 D. J. Trent and W. Slavin, *Atomic Absorption Newsletter*, 3 (1964) 118.
6 W. Slavin, *Atomic Absorption Spectroscopy*, 1st Edn., Interscience, New York, 1968.
7 J. Ramirez-Muñoz, *Atomic-Absorption Spectroscopy*, 1st Edn., Elsevier, Amsterdam, 1968.
8 V. A. Fassel and D. A. Becker, *Anal. Chem.*, 41 (1969) 1522.

(Received April 20th, 1970)

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

# Neuer Automat zur Sauerstoffbestimmung in organischen Substanzen mit kolorimetrischer Endpunktsindikation

In einem Beitrag zur Mikrobestimmung des Sauerstoffs berichteten wir kürzlich über eine neue Variante der Endbestimmung durch vollautomatische Titration der gebildeten Kohlensäure mittels kolorimetrischer Endpunktsindikation[1]. Diese automatisierte Titrieranordnung war auch der erste Schritt zur Entwicklung einer weitgehend vollautomatisch arbeitenden Apparatur zur Bestimmung des Sauerstoffgehaltes in organischen Substanzen. Ein Zeitgewinn durch Verkrackung der Substanz in einem senkrecht angeordneten Quarzrohr, wie es sich bei der von uns entwickelten Stickstoff-[2] und CH-Bestimmung[3] sehr bewährt hat, schied für die Sauerstoffbestimmung allerdings aus.

Eine Verunreinigung der Kohleschicht durch störende Elemente ist hierbei unvermeidbar, was zu unkontrollierbaren Fehlwerten führen kann. Auch sollte die Strömungsgeschwindigkeit bei senkrechter Anordnung entsprechend hoch sein, was bei Russ als Füllmaterial nicht möglich ist. Der Widerstand der Kohleschicht ist sehr gross und die Verweilzeit des gebildeten Kohlenmonoxids durch Adsorptions-, Desorptionsvorgänge relativ lang. Die konventionelle Verkrackung der Substanz in einem waagrecht angeordneten Rohr blieb somit die Methode der Wahl. Wir verwenden dabei im Prinzip die von EHRENBERGER *et al.*[4] beschriebene Apparatur mit Einschleusgabel. Eine nachgeschaltete, erhitzte Kupferschicht verhindert Störungen bei schwefel- und phosphorhaltigen Substanzen. Eine Verkürzung der Analysenzeit durch Erhöhung der Strömungsgeschwindigkeit oder eine geringere Ausspülzeit ist mit dieser Anordnung aber nicht möglich. Da andererseits ein Automat nur bei einer entsprechenden Anzahl von Analysen pro Zeiteinheit sinnvoll ist, versuchten wir die andere Möglichkeit, durch Kombination zweier Apparaturen eine automatisierte Einheit zu schaffen, die einen entsprechend hohen Analysendurchsatz ermöglicht.

Der entwickelte Automat zur Sauerstoffbestimmung* setzt sich aus folgenden Teilen zusammen.

1. Aus zwei Apparaturen zur Verkrackung der Substanz. Jede der beiden Apparaturen besteht dabei aus einem Quarzrohr mit Einschleusgabel, einem Kurz- und einem Langbrenner, einer nachgeschalteten, auf 850° erhitzten Kupferschicht sowie einer Gasquelle für vorgereinigten Stickstoff. Die Kohleschicht wird durch den Langbrenner auf 1120° erhitzt. Bei Verwendung einer Proportionalregelung kann diese Temperatur auf ±1° eingehalten werden. Als Messfühler wird dabei die Thermospannung eines Platin–Platin/Rhodium-Elementes verwendet und Regelabweichungen über Triacs durch Phasenanschnittsteuerung kompensiert.
2. Zwei Titrierstände mit Motorkolbenbüretten und zentralen Vorratsgefässen für Absorptions- und Titrierlösung.
3. Den Steuerteilen zur automatischen Titration.
4. Dem Programmschaltwerk für den gesamten Analysencyclus.

Der Aufbau der beiden Sauerstoffapparaturen ist dabei von untergeordneter Bedeutung. Wir wählten eine Anordnung, bei der die beiden Krackapparaturen rechts

---

* Kann komplett von der Fa. W. C. Heraeus, Hanau, bezogen werden.

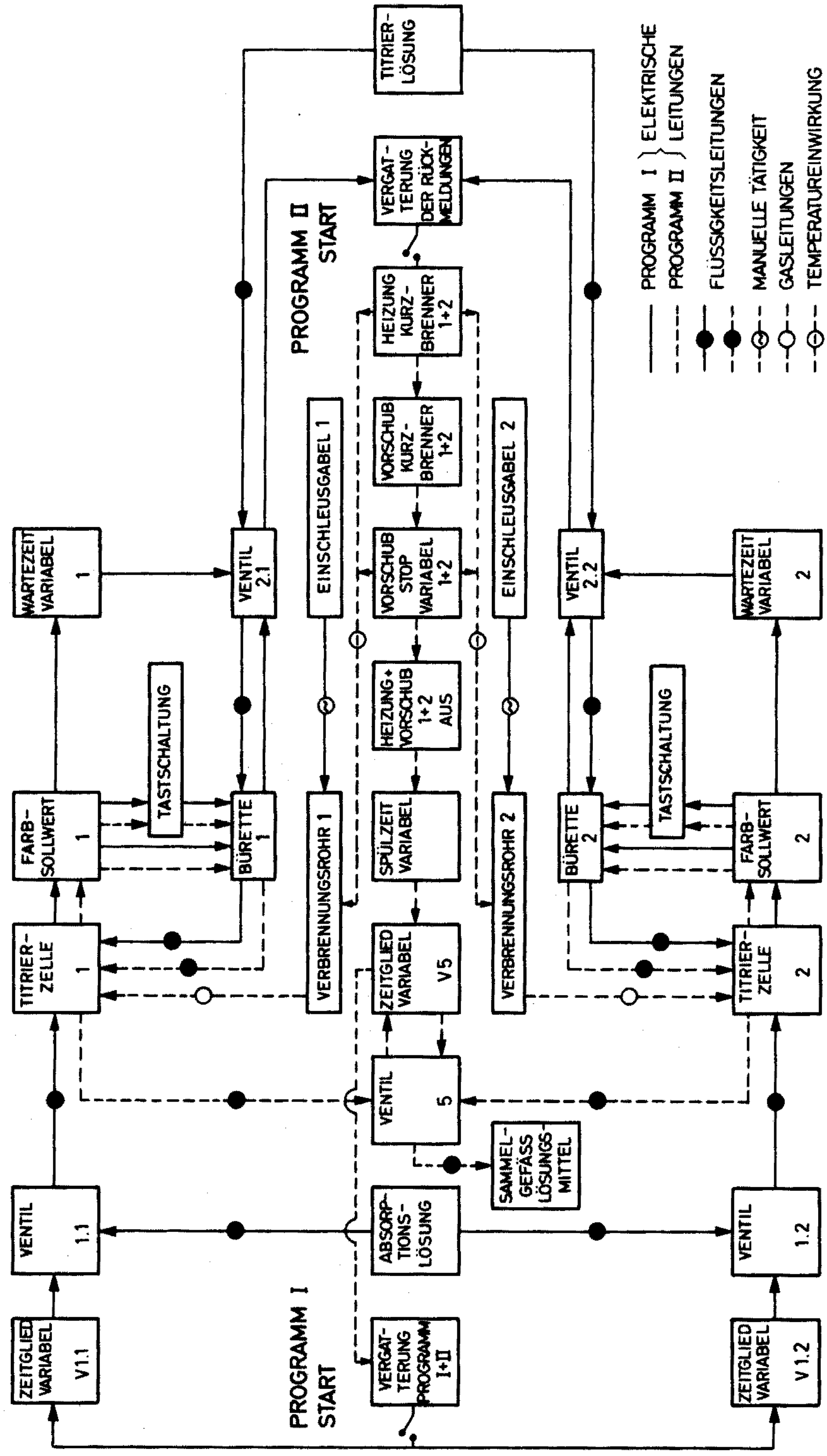


Abb. 1. Blockschaltbild des Analysenprogrammes.

und links der Steuer- und Titriereinheit aufgestellt sind, da hierbei die optimalsten Bedienungsmöglichkeiten beim Einschleusen der Proben gegeben sind. Es ist aber auch jederzeit möglich, die beiden Apparaturen hintereinander aufzustellen oder die von MONAR[5] vorgeschlagene Doppelrohrapparatur zu verwenden.

Nähere Einzelheiten über das Prinzip der Titration sowie die Titriereinrichtung selbst, sind den früheren Arbeiten[1,3] zu entnehmen. Sämtliche Zeitvorgänge werden über ein Programmschaltwerk gesteuert. Im Programm 1 erfolgt die Vorbereitung der Titrierzellen einschliesslich dem Vorabgleich der Absorptionslösung auf den gewünschten Sollwert. In dieser Zeit erfolgt auch die Einschleusung der eingewogenen Proben in die beiden Verbrennungsrohre. Das eigentliche Analysenprogramm ist das Programm 2. Da beide Verbrennungsapparaturen parallel laufen, muss eine Vergatterung für einen störungsfreien Programmablauf sorgen. Erst nach erfolgter Rückmeldung des Ablaufes von Programm 1 aus beiden Apparaturen kann Programm 2 gestartet werden. Die anfallende Kohlensäure wird fortlaufend titriert. Die Endabschaltung und gleichzeitige Entleerung der Titrierzellen erfolgt nach vorgegebener Zeit. Auf Grund der Abhängigkeit der zu analysierenden Substanz von Pyrolyse- und Ausspülzeit, sind diese entsprechend variabel gehalten.

## *Programmablauf*

Der gesamte Programmablauf der Analyse einschliesslich der automatischen Titration ist aus dem abgebildeten Blockschaltbild zu ersehen. Nach Betätigung des Startknopfes von Programm 1 werden die beiden Titrierzellen 1 und 2 über die Ventile 1.1 und 1.2 mit jeweils 20 ml Absorptionslösung[1] gefüllt. Die Öffnungszeiten der Ventile sind über variable Zeitglieder der jeweiligen Zulaufgeschwindigkeit (maximal 20 Sek) anzupassen. Nach Umschalten der Zulaufventile erfolgt automatisch die Titration auf den vorgegebenen Sollwert. Ein Übertitrieren wird durch Tastschaltung verhindert. Nach beendeter Titration wird aus Sicherheitsgründen ein programmierbares Zeitglied angesteuert. Nach Ablauf dieser Zeit werden die Ventile 2.1 und 2.2 über Impulse geschaltet, wodurch bei gleichzeitiger Ingangsetzung der Motorkolbenbüretten diese mit Titrierlösung aufgefüllt werden. Über Endabschalter an den Büretten werden schliesslich, ebenfalls impulsgesteuert, die Ventile 2.1 und 2.2 auf Titration geschaltet. Impulsgesteuerte Ventile haben gegenüber den normalen Magnetventilen den Vorteil, dass der Haltestrom entfällt, wodurch eine Erwärmung des Ventils und damit der Titrierlösung entfällt. Eine Änderung des Faktors der Lösung durch Temperaturänderung ist somit ausgeschlossen. Da die beiden Titriereinheiten auf Grund des unterschiedlichen Bürettenstandes nach der vorangegangenen Analyse verschieden lange Zeiten für das Auffüllen benötigen, ist hier eine Rückmeldung notwendig. Erst wenn die Rückmeldungen beider Büretten vorliegen, gibt die Vergatterung den Start für Programm 2 frei. Die Gesamtzeit von Programm 1 liegt bei etwa 2 Min. Diese Zeit ist ausreichend, die nächsten Proben in die Verbrennungsrohre einzubringen und zwei weitere Einwaagen in die beiden Schleusen einzusetzen. Mit Hilfe einer automatischen Probeneinführung ist dieser Zeitaufwand noch zu verkürzen.

Der Start von Programm 2 löst in beiden Verbrennungsautomaten die gleichen Vorgänge aus. Über das zentrale Programmschaltwerk werden die Kurzbrenner eingeschaltet und mit einer Verzögerung von 30 Sek in Bewegung gesetzt. Nach zwei Min wird der Vorschub der Brenner für 30 Sek unterbrochen. Diese Zeit ist variabel und so gewählt, dass der Brenner vor dem Probeschiffchen zu stehen kommt. Dadurch ist ein langsames Verkracken der Substanz ohne Rückschlagen der Krackgase gewährleistet. Anschliessend werden die Kurzbrenner direkt unter die Probeschiffchen gefahren und je nach Art der Substanz eine entsprechende Zeit gestoppt. Die Verweilzeit ist bis 2 Min programmierbar, was selbst bei schwer verkrackbaren Proben ausreichend ist. In weiteren 2 Min sind die Kurzbrenner an den Langbrennern angelangt und werden 30 Sek später automatisch ausgeschaltet. Dieser Verbrennungszeit folgt nun eine von 0 bis 8 Min programmierbare Spülzeit, nach deren Ablauf über ein variables Zeitglied das Ventil 5 betätigt wird. Durch Anlegen von Unterdruck werden die beiden Titrierzellen entleert. Die anschliessende Rückstellung des Ventils ist mit der Startfreigabe von Programm 1 verbunden. Die Apparatur ist damit für die nächste Analysenserie bereit.

Die Gesamtanalysendauer für eine Doppelanalyse beträgt je nach Wahl der variablen Zeitglieder 14 bis 18 Min. Im Routinbetrieb ergibt sich somit ein Analysendurchsatz von 40 Bestimmungen pro Arbeitstag. Diese Zahl beinhaltet keinerlei Testanalysen und kann durch Anwendung elektronischer Wägeeinheiten und entsprechender Rechner weiter erhöht werden, ohne dass dadurch grössere Anforderungen an den Analytiker zu stellen sind. Die codiert bei der Elektrowaage wie auch den Büretten anstehenden Werte werden in diesem Falle direkt der Datenverarbeitung zugeführt. An einer solchen vollautomatisierten Lösung wird gearbeitet.

## *Zusammenfassung*

Es wird über einen neuen Automat zur Sauerstoffbestimmung in organischen Substanzen berichtet. Die Endbestimmung erfolgt über vollautomatische Titration der Kohlensäure mittels kolorimetrischer Endpunktsindikation. Ein ensprechend hoher Analysendurchsatz wurde durch Kombination von zwei Krackapparaturen und automatischer Steuerung sämtlicher Zeitabläufe mittels Programmschaltwerk erreicht. Der gesamte Analysencyclus einschliesslich der Titration läuft automatisch ab.

Herrn Dipl. Ing. SCHERER danke ich für die Unterstützung bei allen elektronischen Problemen. Für den Aufbau der Steuereinheit sei auch an dieser Stelle Herrn Ing. BONN, für die gewissenhafte Ausführung der Versuche Herrn NICKLAS gedankt.

*Untersuchungslabor der Badischen Anilin-und-SodaFabrik, A.G.,* WOLFGANG MERZ
*Ludwigshafen/Rhein (Deutschland)*

1 W. MERZ, *Anal. Chim. Acta,* 50 (1970) 305.
2 W. MERZ, *Z. Anal. Chem.,* 237 (1968) 272.
3 W. MERZ, *Anal. Chim. Acta,* 48 (1969) 381.
4 F. EHRENBERGER, S. GORBACH UND W. MANN, *Mikrochim. Acta,* (1958) 778.
5 J. MONAR, *Mikrochim. Acta,* (1966) 934.

(Eingegangen den 14. April, 1970)

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

# The application of ultrasonics to the collection of traces of antimony(V) ions on alumina powder

Adsorption of traces of inorganic ions on various solids from aqueous solutions is sometimes useful as a separation technique in trace element analysis and radiochemistry. Sufficient yields and rapid collection rates of the desired trace ions are generally required in these cases. The authors reported previously that the application of an ultrasonic field accelerates the collection of traces of silver ions on finely powdered dithizone[1]. This communication describes the same effect on the collection of traces of antimony(V) ions on alumina powder.

## *Procedure*

Place 50 ml of 0.1–0.7 *M* nitric acid containing 0.01–1 μg of antimony(V) labeled with antimony-124 in a 100-ml beaker, and add 20 mg of alumina powder (Aluminum Oxide Woelm neutral, 100 mesh, obtained from M. Woelm, Eschwege, West Germany). Immerse the beaker in a 500-ml ultrasonic cleaning tank containing water (20±2°), and apply ultrasonics (45 kHz, 45 W) with stirring at *ca.* 200 r.p.m. After the prescribed time, collect the powder on a 3-cm filter paper, and wash with three 5-ml portions of 0.1 *M* nitric acid. Rinse the powder into a 50-ml beaker with acetone, and evaporate the solvent at room temperature. Add *ca.* 5 ml of hot 7 *M* nitric acid to the beaker, stir for 10 min to extract antimony, filter off the powder on a sintered-glass disc, and wash with three 5-ml portions of water. Evaporate the combined filtrate and washings to 2–10 ml, and measure the γ-activity of an aliquot with a well-type NaI(Tl) scintillation counter.

## *Results and discussion*

Figure 1 shows the effectiveness of ultrasonics in the collection of antimony

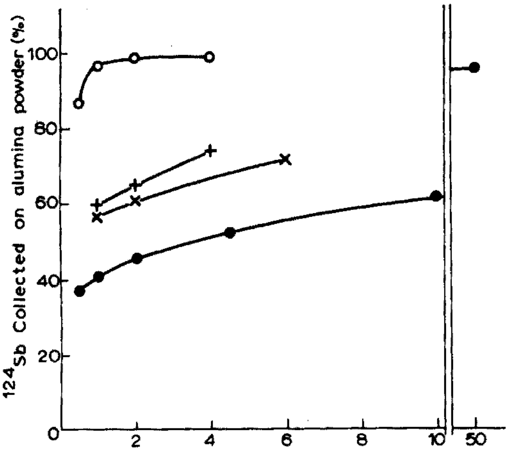


Fig. 1. Effect of ultrasonics on the collection of 0.1 μg of antimony on 20 mg of alumina powder from 50 ml of 0.5 *M* nitric acid. (○) With sound field, ~20°; (●) no sound field, ~20°; (×) no sound field, ~60°; (+) no sound field, ~80°.

on alumina powder from 0.5 *M* nitric acid. Antimony, 0.01–1 μg, was collected in 95–98% yields from 0.1–0.7 *M* nitric acid within 1.5 h. Even after 4 h of ultrasonic irradiation, no change in size and shape of alumina powder was observed under an optical microscope (90 ×). The antimony collected on alumina powder was readily extracted with hot 7 *M* nitric acid without appreciable dissolution of alumina.By the proposed technique, 0.1 μg of antimony was separated in greater than 95% yields from 0.5 *M* nitric acid solutions containing 1.0 g of copper or lead within 2 h. Copper or lead accompanying antimony was determined by EDTA titration, and found to be *ca.* 0.1 mg. Therefore, the concentration factors were *ca.* $1 \cdot 10^4$.

*Faculty of Engineering,*
*Nagoya University,*
*Chikusa-ku, Nagoya (Japan)*

KATSUAKI FUKUDA
ATSUSHI MIZUIKE

1 K. FUKUDA AND A. MIZUIKE, *Anal. Chim. Acta*, in press.

(Received March 23rd, 1970)

---

# Radiochemical investigation of the extraction of copper(II) by some Schiff's bases

A recent publication from this laboratory[1] was concerned with extraction of copper(II) by Schiff's bases. In this work the distribution of copper(II) was followed by atomic absorption spectrophotometry. Although this technique is generally very useful and convenient for analysis of low cation concentrations its application in any particular case is limited by the detection limit for the cation concerned. In the case of copper(II) this is about 0.1 p.p.m. ($1.8 \cdot 10^{-6}$ *M*) in an air–propane flame and the useful analytical range is somewhat higher than this figure. Several of the reagents examined extracted copper(II) quantitatively as measured by atomic absorption spectrophotometry and it was not possible to make accurate measurements on the aqueous phases when extraction was $\geqq 99\%$. Therefore, in order to examine the influence of structure on the extracting ability of these reagents more carefully some of these systems were re-investigated with copper-64 as tracer. With this technique it is possible to measure higher distribution ratios with much greater accuracy than with atomic absorption spectrophotometry. Although the latter technique is widely used in analysis, the emphasis in its use and development has been concerned with detection limits and not with its usefulness in quantitative studies. Hence the comparison between the atomic absorption data and the radiochemical data has added significance.

The radiochemical data were obtained in the same manner as the atomic absorption data[1]. The copper-64 was obtained from the Australian Atomic Energy Commission as copper sulphate and was used in this form. Table I contains the values of pH$_{1/2}$ and maximum distribution ratio ($q$ max) as measured by the radiochemical technique as well as pH$_{1/2}$ data obtained by atomic absorption spectrophotometry[1].

TABLE I

EXTRACTION OF COPPER(II) INTO MIBK BY SCHIFF'S BASES

| *Reagent ($10^{-2}$ M)* | *Radiochemical data* | | *A.a.s. data* |
|---|---|---|---|
| | *pH$_{1/2}$* | *$q_{max}$* | *pH$_{1/2}$* |
| Bis(acetylacetone)-ethylenediimine | 4.39 | 55 | 4.36 |
| Bis(salicylaldehyde)-ethylenediimine | 2.86 | 49 | 2.61 |
| Bis(5-bromosalicylaldehyde)-ethylenediimine | 1.93 | 916 | 2.00 |
| Bis(salicylaldehyde)-*o*-phenylenediimine | 1.10 | 845 | 1.00 |
| Bis(5-bromosalicylaldehyde)-*o*-phenylenediimine | 0.96 | 2460 | 0.98 |

In the salicylaldehyde series it can be seen that replacement of salicyaldehyde by 5-bromosalicylaldehyde results in a marked improvement in extraction; a similar improvement is caused by the introduction of *o*-phenylenediamine in place of ethylenediamine. And as might be expected the condensation of 5-bromosalicylaldehyde and *o*-phenylenediamine results in the most powerful extractant of this series. This increase in extracting ability is accompanied by a decrease in pH$_{1/2}$.

Comparison of bis(salicylaldehyde)-ethylenediimine and bis(acetylacetone)-ethylenediimine shows that there is no significant difference in the extracting ability of these ligands as measured by the maximum $q$ values of the systems although the pH$_{1/2}$ values differ by about 1.5 units. The difference in pH$_{1/2}$ is most probably caused by a difference in the formation constants of the copper(II) complexes but this cannot be confirmed since these are not known at present. The copper(II) extracts in these two systems also differ in another respect: bis(acetylacetone)-ethylenediiminecopper(II) in MIBK is purple ($\lambda_{max}$ 544 nm, $\varepsilon$ 197) while bis(salicylaldehyde)-ethylenediiminecopper(II) is yellow-green. The difference in the colour of crystalline copper(II) complexes of this type has been attributed to the presence of a fifth bond perpendicular to the plane of the molecule[2]. Although no comparable studies appear to have been made on these complexes in organic solvents, if this conclusion is correct, then it would appear that bis(acetylacetone)-ethylenediiminecopper(II) is 4-coordinate in methyl isobutyl ketone and bis(salicylaldehyde)-ethylenediiminecopper(II) is 5-coordinate, the fifth position being occupied by methyl isobutyl ketone or water.

In conclusion, apart from a small discrepancy in the bis(salicylaldehyde)-ethylenediimine system, the atomic absorption spectrophotometric and radiochemical data are in excellent agreement.

*Chemistry Department,*
*University of Auckland,*
*Auckland (New Zealand)*

J. AGGETT
R. A. RICHARDSON

1 J. AGGETT AND R. A. RICHARDSON, *Anal. Chim. Acta*, in press.
2 E. N. BAKER, D. HALL AND T. N. WATERS, *J. Chem. Soc., A* (1970) 406.

(Received April 11th, 1970)

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

# Multi-element atomic fluorescence spectroscopy
## Part III. A new type of dual-element microwave-excited electrodeless discharge tube

It has recently been shown that multi-element electrodeless discharge tubes made by introducing several elements simultaneously into a single discharge tube are satisfactory as spectral line sources for atomic spectroscopy when the elements present exert similar vapour pressures at the working temperature of the tube[1-3]. When the elements or salts required to be present in the tube have widely different volatilities, however, either one constituent would tend to predominate in the discharge, or the tube would be unstable. Several workers have investigated the effect of surrounding discharge tubes with low-pressure jackets[4-6], and have noted appreciable improvements in the stabilities of the resulting discharges, and in some cases the occurrence of a discharge within the outer jacket[4,6]. The jacketing method[6] can be applied to the manufacture of dual-element electrodeless tubes which contain elements of quite widely differing volatility, by placing the volatile compound or metal in the outer jacket and the less volatile one in the inner jacket which is then protected from cooling effects. A preliminary investigation of the stability, intensity and applicability of the resultant sources has been made.

### *Experimental*

Blank tubes are prepared as shown in Fig. 1a. These are degassed by strong heating of the outer tube in the normal way. The internal diameters of the tubes used were 2 mm and 8 mm for the inner and outer tubes respectively. Unless the constituent to be introduced to the outer tube is extremely volatile, *e.g.* iodine, mercury, the elements or halides used are introduced simultaneously to the inner and outer tubes, and the elements are sublimed and the tube is sealed as usual[7]. If the element in the outer tube is highly volatile, it is advisable to seal off the outer tube before introducing the sample to the inner tube. The final appearance of a tube of this type is shown in Fig. 1b.

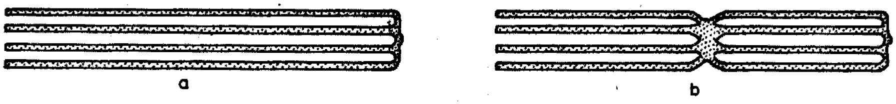


Fig. 1. Blank tube prepared for filling (section) (a) and sealed dual-cavity electrodeless discharge tube (section) (b).

The stabilities of a number of tubes of this type are shown in Table I. The tubes were excited at 2450 MHz with a "Microtron 200" high-frequency generator, and operated in a three-quarter wave cavity (Electro-Medical Supplies Limited); all stability and fluorescence measurements were made on a modified Southern Instruments A1740 grating flame photometer[2] in conjunction with a Servoscribe chart recorder. It can be seen from Table I that the element in the inner tube tends to give a more stable discharge than the element in the outer tube. Another interesting point is that for certain elements, such as tellurium, lead and thallium, stable and intense

TABLE I

SOURCE STABILITY

| *Tube* | *Components* | | *Stability*[a] | | *Power (W)* |
|---|---|---|---|---|---|
| | *Inner* | *Outer* | *Inner* | *Outer* | |
| Te/Se | Te | Se | 1.7 | 3.8 | 60 |
| As/Se | As/I$_2$ | Se | 1.9 | 2.5 | 50 |
| Ag/Zn | Ag/AgCl | Zn | 1.9 | 3.2 | 65 |
| Ag/Cd | Ag/AgCl | Cd | 1.8 | 1.9 | 65 |
| Ag/Hg | Ag/AgCl | Hg | 3.2 | 5.2 | 60 |
| Zn/Hg | Zn | Hg | 1.7 | 3.8 | 60 |
| Pb/Cd | Pb | Cd | 0.7 | 4.5 | 60 |
| Pb/Cd | Pb/PbI$_2$ | Cd | 4.8 | 3.5 | 65 |
| Cr/Cd | CrCl$_3$[b] | Cd | 3.0 | 4.8 | 50 |
| Ni/Cr | NiCl$_2$ | CrCl$_3$[b] | 3.2 | 4.8 | 60 |
| Mn/Cr | MnCl$_2$ | CrCl$_3$[b] | 2.7 | 7.9 | 60 |
| Sb/Bi | Sb/I$_2$ | I$_2$ | 2.2 | 2.2 | 50 |

[a] Expressed as ± % h$^{-1}$ after an initial running-in period of 1 h.
[b] Obtained by vacuum dehydration of the hydrated salt.

TABLE II

ATOMIC FLUORESCENCE DETECTION LIMITS WITH DUAL-ELEMENT SOURCES

| *Tube* | *Element* | *Line (nm)* | *Detection limit*[a] | *Flame height (cm)* |
|---|---|---|---|---|
| Te/Se | Te | 214.3 | 1.5 | 7 |
| Te/Se | Se | 196.0 | 0.8 | 7 |
| As/Se | As | 193.7 | 25. | 7 |
| As/Se | Se | 196.0 | 0.6 | 7 |
| Ag/Zn | Ag | 328.1 | 0.002 | 10 |
| Ag/Zn | Zn | 213.9 | 0.0001 | 10 |
| Ag/Cd | Ag | 321.8 | 0.0008 | 10 |
| Ag/Cd | Cd | 228.8 | 0.00004 | 10 |
| Ag/Hg | Ag | 328.1 | 0.004 | 10 |
| Ag/Hg | Hg | 253.7 | 12. | 10 |
| Zn/Hg | Zn | 213.9 | 0.001 | 10 |
| Zn/Hg | Hg | 253.7 | 16. | 8 |
| Pb/Cd | Pb | 405.7 | 12. | 10 |
| Pb/Cd | Cd | 228.8 | 0.00006 | 10 |
| Pb/Cd[b] | Pb | 405.7 | 10. | 10 |
| Pb/Cd[b] | Cd | 228.8 | 0.00001 | 10 |
| Cr/Cd | Cr | 359.3 | 30. | 5 |
| Cr/Cd | Cd | 228.8 | 0.00008 | 10 |
| Ni/Cr | Ni | 232.0 | 0.8 | 5 |
| Ni/Cr | Cr | 359.3 | 20. | 5 |
| Mn/Cr | Mn | 279.4 | 0.1 | 5 |
| Mn/Cr | Cr | 359.3 | 20. | 5 |
| Sb/Bi | Sb | 231.1 | 6. | 6 |
| Sb/Bi[c] | Bi | 302.5 | 10. | 6 |

[a] p.p.m. corresponding to twice standard deviation at specified wavelength.
[b] Lead present as lead iodide.
[c] Detection limit obtained with strong cooling of discharge tube.

discharges can be obtained from the element, instead of the halide normally used, without running the tubes at high power.

To evaluate the usefulness of these sources as atomic spectral line sources, a series of detection limits was determined in a slightly fuel-rich oxy–hydrogen flame burning on a Beckman total-consumption burner (Table II). Although these results are of the expected order of magnitude, some of the results obtained for the elements in the inner tube are slightly lower than expected; it was therefore decided to investigate the properties of the mercury-jacketed zinc tube in greater detail. Figure 2 shows the effect of operating power on the intensity of (*a*) a normal zinc discharge tube, (*b*) a mercury-jacketed zinc discharge tube, (*c*) the fluorescence signal obtained for 0.1 p.p.m. zinc with a normal zinc tube, and (*d*) the fluorescence signal obtained for 0.1 p.p.m. zinc with a mercury-jacketed zinc tube. These results indicate that self-reversal is taking place, and this conclusion was supported by a brief investigation of these tubes interferometrically[8]. The temperature of the inner tube was estimated with an optical pyrometer, by taking measurements on the inner tube immediately after extinction, and the results obtained indicate that the inner tube can reach a temperature of about 600° at 60 W. It may, therefore, be concluded that the element or compound introduced to the inner tube should have a vapour pressure of about not more than 1 Torr at 600° to prevent self-absorption. Alternatively, the amount of element introduced should be insufficient to provide a saturated vapour at the working temperature of the tube.

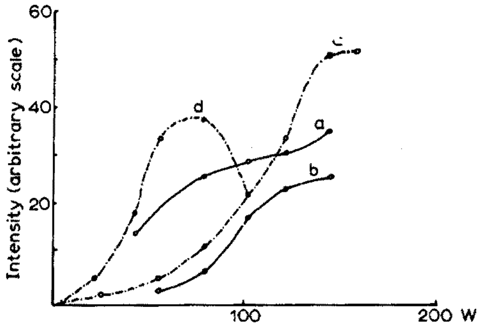


Fig. 2. Effect of power on 213.9-nm Zn line from discharge tube sources and effect on fluorescence signal. (a) Zn source, (b) Zn/Hg source, (c) 213.9-nm fluorescence of 0.1 p.p.m. Zn using (a), (d) 213.9-nm fluorescence of 0.1 p.p.m. Zn using (b).

Although these dual-element electrodeless discharge tubes have been used for atomic fluorescence studies, they are equally applicable to atomic absorption measurements provided that conditions are chosen to minimise line broadening and self-reversal. They may prove, therefore, to be of more practical value than multi-element hollow-cathode lamps for the latter technique.

*Chemistry Department,*
*Imperial College,*
*South Kensington,*
*London S.W.7 (England)*

M. S. Cresser
T. S. West

1 G. B. Marshall and T. S. West, in G. B. Marshall, *Ph.D. Thesis*, Imperial College, London, 1968.
2 G. B. Marshall and T. S. West, *Anal. Chim. Acta*, (1970) in press.
3 H. A. Fulton, K. C. Thompson and T. S. West, *Anal. Chim. Acta*, 51 (1970) 373.

4 K. E. ZACHA, M. P. BRATZEL, JR., J. D. WINEFORDNER AND J. M. MANSFIELD, JR., *Anal. Chem.*, 40 (1968) 1733.
5 H. C. HOARE, R. A. MOSTYN AND B. T. N. NEWLAND, *International Atomic Absorption Spectroscopy Conference, Sheffield, England, 1969.*
6 K. M. ALDOUS, R. M. DAGNALL AND T. S. WEST, *Lab. Pract.*, 19 (1970) 587.
7 R. M. DAGNALL AND T. S. WEST, *Appl. Opt.*, 7 (1968) 1287.
8 G. F. KIRKBRIGHT, M. SARGENT AND T. S. WEST, unpublished results.

(Received March 1st, 1970)

# Spectrophotometric determination of boron in steel with methlyene blue

The solvent extraction technique described by DUCRET[1] and modified by PASZTOR *et al.*[2], for the determination of micro quantities of boron in steel has been examined. The disadvantages of the method as described[2] are: (*a*) the limited range over which Beer's law is obeyed; (*b*) the high absorbance of the blank; and (*c*) the use of hydrofluoric acid. In this communication, a modified method is described which has been in routine use in an industrial laboratory for the past year. Results on several British Standard steels and on a selection of austenitic steels are given, together with their boron contents determined by the dianthrimide[3] and curcumin[4] methods.

## *Equipment*

Spectra were obtained with a Unicam S.P. 800 Spectrophotometer; precise absorbance measurements at 660 nm were obtained with a Unicam S.P.500 spectrophotometer in 4-cm cells. Sample dissolutions were carried out in polythene bottles, and polythene laboratory ware was used throughout.

## *Reagents*

*Methylene blue.* Dissolve 5.98 g in 1 l of water and dilute 10 ml to 100 ml to give a 0.0016 *M* solution.

*1,2-Dichloroethane.* Commercial purified grade was redistilled.

## *Procedure*

Weigh accurately about 0.25 g of steel sample into a flask and dissolve in 2.8 ml of 50% (v/v) sulphuric acid under reflux. Cool and add 2.2 ml of water through the condenser. Transfer the contents of the flask quantitatively to a 100-ml polythene bottle with 5 ml of water. Add 5 ml of aqueous 5%(w/v) sodium fluoride solution, mix and allow to stand for 2 h. Add 0.1 *M* potassium permanganate (A.R.) solution dropwise until a permanent pink colour appears and then add 2 ml of ammonium iron(II) sulphate solution (7%(w/v) in 0.05 *M* sulphuric acid). Dilute to 50 ml with water. Add 10 ml of methylene blue solution and 25 ml of 1,2-dichloroethane, stopper the bottle and shake for 1 min. Allow the layers to separate, pipette 10 ml of the organic layer into a small beaker, add 15 ml of 1,2-dichloroethane, mix and measure the absorbance at 660 nm against a solvent blank. The total boron content of the steel is determined from a calibration curve obtained by taking aliquots of a standard boron solution (10 $\mu$g B ml$^{-1}$) through the procedure described above.

### *Results and discussion*

According to DUCRET[1], the methylene blue concentration has to be present in at least a 4:1 molar excess over boron. However, the method of PASZTOR *et al.*[2] has an upper limit of around 15 $\mu$g of boron determined by the use of 0.001 *M* methylene blue. When the methylene blue concentration was increased to 0.0016 *M*, it was found that Beer's law was obeyed in the range 0–25 $\mu$g of boron.

With the extraction method of PASZTOR *et al.*, the reagent blank (against pure solvent) was found to be 0.280 absorbance units. If this is due to the partitioning of "methylene blue fluoride" between aqueous and organic phases, one would expect the blank to increase as the hydrofluoric acid concentration used increased. It was found, however, that the blank value is virtually independent of fluoride concentration but is influenced by sulphuric acid concentration. Blanks obtained on various solutions were determined (Table I); it can be seen from the figures that low blanks can be obtained by substituting phosphoric for sulphuric acid. However, difficulty with the steel dissolution stage prevents this from being a practical proposition. The substitution of sodium fluoride for hydrofluoric acid gives satisfactory results and is a great improvement as far as the safety aspects of routine analytical procedures are concerned. Variation of absorbance with fluoride concentration was, in fact, found to be negligible

TABLE I

PARTITIONING OF METHYLENE BLUE BETWEEN 1,2-DICHLOROETHANE AND VARIOUS AQUEOUS MIXTURES

| *Components of aqueous phase* | *Absorbance at 660 nm* |
|---|---|
| 10 ml of methylene blue and | |
| 1. 10 ml 14% $H_2SO_4$: 5 ml 5% NaF: 35 ml $H_2O$ | 0.260 |
| 2. 10 ml 14% $H_2SO_4$: 40 ml $H_2O$ | 0.260 |
| 3. 50 ml $H_2O$ | 0.205 |
| 4. 10 ml 14% $H_3PO_4$: 5 ml 5% NaF; 35 ml $H_2O$ | 0.160 |
| 5. 10 ml 14% $H_3PO_4$: 40 ml $H_2O$ | 0.140 |
| 6. 5 ml 5% NaF: 45 ml $H_2O$ | 0.140 |
| 7. 10 ml 14% $HNO_3$: 40 ml $H_2O$ | >1.0 |

TABLE II

BORON CONTENTS OF BRITISH STANDARD STEELS

| *Steel* | *Boron content (% w/w)* | |
|---|---|---|
| | *Proposed method* | *Standard figure* |
| B.S. 326 | 0.0007<br>0.0008 | 0.001 |
| 328 | 0.0036<br>0.0037 | 0.004 |
| 329 | 0.0078<br>0.0080 | 0.008 |
| 330 | 0.0068<br>0.0072 | 0.007 |

down to 5 ml of 1% sodium fluoride used. At a concentration of 0.6% sodium fluoride, there was a noticeable decrease in absorbance, presumably because of incomplete conversion of boron to fluoroborate.

The dissolution technique described is satisfactory for austenitic and high-alloy steels. Low-alloy steels may be dissolved by refluxing with 2.8 ml of 50%(v/v) sulphuric acid and 2.2 ml of water.

Table II shows duplicate results on four British Standard (mild) steels, whilst Table III gives a comparison, for six austenitic steels, of the boron content by the proposed method and the averages of the results obtained by the dianthrimide and quinalizarin methods previously used.

TABLE III

COMPARISON OF BORON RESULTS ON AUSTENITIC STEELS

| *Steel* | *Boron content (% w/w)* | |
|---|---|---|
| | *Proposed method* | *Dianthrimide/quinalizarin methods* |
| 1 | 0.0006 | 0.0008 |
| 2 | 0.0012 | 0.0010 |
| 3 | 0.0015 | 0.0014 |
| 4 | 0.0037 | 0.0038 |
| 5 | 0.0042 | 0.0042 |
| 6 | 0.0055 | 0.0053 |

Analysis of results obtained over the past year show that a boron containing steel (of the order of 0.004% w/w boron) can be analysed with an accuracy of ±3%.

*Department of Chemistry,*
*Sheffield Polytechnic,*
*Pond Street,*
*Sheffield S1 1WB (England)*

F. VERNON
J. M. WILLIAMS

1 L. DUCRET, *Anal. Chim. Acta*, 17 (1957) 213.
2 L. PASZTOR, J. D. BODE AND Q. FERNANDO, *Anal. Chem.*, 32 (1960) 277.
3 E. GORFINKEL AND A. G. POLLARD, *J. Sci. Food Agr.*, 3 (1952) 622.
4 M. R. HAYES AND J. METCALFE, *Analyst*, 87 (1962) 956.

(Received April 6th, 1970)

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

# Determination of small amounts of aminecarboxylic acid complexing agents in the presence of excess trivalent lanthanides and actinides

Frequently, small amounts of aminecarboxylic acid complexing agents such as ethylenediaminetetraacetic acid (EDTA), hydroxyethylethylenediaminetriacetic acid (HEDTA), or diethylenetriaminepentaacetic acid (DTPA) must be determined in solutions containing excess amounts of ions that form strong complexes, such as trivalent lanthanide or actinide cations. A relatively rapid and accurate method that is applicable to such solutions is presented here.

The method consists of adding an excess of iron(III) to a sample of the solution containing the complexing agent. Since iron(III) is complexed by most chelating agents much more strongly than the trivalent lanthanides or actinides, the complexing agent is quantitatively converted to the iron(III) complex. The solution is then passed through a cation-exchange column containing resin in the sodium form; this resin retains the lanthanides, actinides, and uncomplexed iron, but not the complexed iron, which is present as an anionic or neutral species. Since iron forms a 1:1 chelate with aminecarboxylic acid complexing agents, the amount of chelate in the eluate from the column can be determined easily by determining the amount of iron present.

Any method for the determination of iron in the presence of the chelating agents will be satisfactory. However, we have used the following photometric methods. The first method[1] involves the formation of colored thiocyanatoiron(III) complex in 0.5 *M* nitric acid. The iron(III) chelates dissociate at high acidity, but the thiocyanate complex still forms because thiocyanic acid is a fairly strong acid. The second method[1] consists of reducing the iron(III) to iron(II) with hydroxylamine hydrochloride, and forming the colored complex of the iron(II) ion with 1,10-phenanthroline, which forms a more stable complex with iron(II) than does the chelate.

### *Reagents and apparatus*

The complexing agents used were EDTA (Fisher Scientific), HEDTA (Chemical Procurement Laboratories), and DTPA (J. T. Baker). Solutions of these complexing agents were standardized by titration with a standard lanthanum nitrate solution and xylenol orange as indicator[2]. The lanthanum nitrate solution was prepared by dissolving a weighed quantity of pure $La_2O_3$ in dilute nitric acid. A standard iron(III) nitrate solution was prepared by dissolving a weighed amount of iron wire in nitric acid. Dowex 50W-X8 (50–100 mesh) cation-exchange resin in the sodium form was used in the ion-exchange columns.

The ion-exchange columns were *ca.* 10 cm long and 0.5 cm in diameter. Each had a stopcock at one end and a reservoir at the other, and each was loaded with about 1 ml of resin. A Beckman DU Model spectrophotometer was used for the determinations of iron.

### *Procedure*

Test solutions containing either lanthanum(III) or samarium(III) and 0.4–2.0 $\mu$mole of a complexing agent were taken. Iron(III) nitrate (10–40 $\mu$mole) was mixed

*Anal. Chim. Acta*, 51 (1970) 536–538

with the sample, and the mixture was passed through the ion-exchange column. The effluent and the rinses from the column were collected in a 25-ml volumetric flask.

*Thiocyanate method.* To determine iron by this method, ammonium thiocyanate and nitric acid were added to the above eluate, and this solution was diluted to a final concentration of 0.5 *M* in hydrogen ion and 1 *M* in thiocyanate. The absorbance of the solution was measured at 380 nm. The iron concentration was then calculated from a standard curve. After the addition of reagents, samples were read as rapidly as possible to minimize the effect of fading of the color.

*1,10-Phenanthroline method.* To determine iron by this method, 1 ml of a 10% solution of hydroxylamine hydrochloride was added to the above eluate; 10 ml of 0.1% 1,10-phenanthroline was then added, followed by three drops of concentrated ammonia solution. In the absence of complexing agents, the tris(1,10-phenanthroline) iron(II) color developed immediately. When HEDTA was the complexing agent, color development was fairly rapid even at room temperature. However, when either EDTA or DTPA was used, color development was much slower. The reaction with DTPA was so slow that it was necessary to heat the solution for 2 h at 70–80° to assure completion. After complete color development, the solutions were diluted to volume, and the absorbance was measured at 510 nm. The iron concentration was determined from a standard curve.

### *Results and discussion*

Table I shows data from typical analyses of the aminecarboxylic acids and indicates which method is applicable to HEDTA, EDTA, and DTPA. Errors ranged from less than 1% in most cases to a maximum of 2%. Satisfactory results were obtained in the presence of lanthanum and samarium. The method was also tested with other light rare-earth elements, and on EDTA and DTPA in solutions containing small amounts of the trivalent actinide elements ($Am^{3+}$, $Cm^{3+}$, $Bk^{3+}$, $Cf^{3+}$, and $Es^{3+}$)

TABLE I

TYPICAL ANALYSES OF AMINECARBOXYLIC ACIDS BY IRON–ION-EXCHANGE METHOD

| *Iron determination method* | *Sample composition* | | | | *$Fe^{3+}$ added (μmoles)* | *$Fe^{3+}$ in eluate (μmoles)* |
|---|---|---|---|---|---|---|
| | *Lanthanide* | | *Complexing agent* | | | |
| | *Ion* | *Amount (μmoles)* | *Agent* | *Amount (μmoles)* | | |
| Thiocyanate | $La^{3+}$ | 0.50 | HEDTA | 0.504 | 30 | 0.500 |
| | | 1.50 | | 1.500 | 30 | 1.495 |
| | $Sm^{3+}$ | 10 | HEDTA | 0.504 | 30 | 0.508 |
| | | 6 | | 0.504 | 30 | 0.500 |
| | | 6 | | 0.504 | 40 | 0.505 |
| 1,10-Phenanthroline | $Sm^{3+}$ | 6 | HEDTA | 0.420 | 30 | 0.410 |
| | | 6 | | 0.840 | 30 | 0.845 |
| | | 6 | | 1.260 | 30 | 1.250 |
| | $Sm^{3+}$ | 6 | EDTA | 0.999 | 10 | 1.008 |
| | | 6 | | 2.000 | 10 | 1.988 |
| | $Sm^{3+}$ | 15 | DTPA | 0.996 | 10 | 1.008 |
| | | 6.0 | | 0.996 | 10 | 1.013 |
| | | 7.0 | | 1.008 | 10 | 1.001 ± 0.005[a] |

[a] Standard deviation of six measurements.

with satisfactory results. In this technique, the complexing agents were so thoroughly converted to the iron(III) form that all radioactivity was removed when the solution was subsequently passed through an ion-exchange column, and the effluents then could be treated as "cold" solutions.

The amount of iron(III) added does not affect the results if this amount is kept within the range shown in Table I. When large amounts of iron (200–300 $\mu$moles) were used with HEDTA, or when a column was used several times with HEDTA, the results were low. When large amounts of iron are adsorbed, perhaps some HEDTA is also adsorbed. However, this effect was not observed with EDTA. In routine work, fresh resin was normally used in the columns for all complexing agents.

The pH of all the solutions analyzed was between 2 and 5 before addition of iron, and about 2 after addition. The acidity did not appear to be critical unless it was high enough to interfere with the formation of the iron(III) complex, and then the results were low and erratic. Similar behavior was found when hydrogen-form cation-exchange resin was used.

Both analytical techniques for the determination of iron in the presence of complexing agents were satisfactory. However, the 1,10-phenanthroline method was more sensitive (because of a higher extinction coefficient) and more convenient (because of less tendency of the color to fade) than the thiocyanate method.

The present method for HEDTA, EDTA, and DTPA has been thoroughly tested, and is now being used routinely for these compounds. Preliminary tests have also been made with *trans*-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (DCTA) and ethylenebis(oxyethylenenitrilo)tetraacetic acid. These tests indicate that this method will be satisfactory for these and perhaps other aminecarboxylic acids.

The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

*Savannah River Laboratory,*
*E.I. du Pont de Nemours and Company,*
*Aiken, S.C. 29801 (U.S.A.)*

R. M. WALLACE
J. F. HINTON*

1 F. D. SNELL AND C. T. SNELL, *Colorimetric Methods of Analyses*, 3rd Edn., D. Van Nostrand, New York, 1951, pp. 307, 314.
2 J. KÖRBL AND R. PRIBIL, *Chemist-Analyst*, 45 (1956) 102.

(Received March 15th, 1970)

---

* Department of Chemistry, University of Arkansas, Fayetteville, Ark. This work was done while J. F. H. was an Oak Ridge Associated Universities Research Participant at the Savannah River Laboratory.

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

# An anode film obtained during constant-current coulometric oxidation of manganese(II)

In a recent study of the constant-current coulometric generation of manganese(III) at a platinum anode in phosphoric acid and in phosphoric–sulfuric acid mixtures, a gradual decrease in current generation efficiency in solutions containing less than 20 (v/v) % acid was reported[1]. This decrease was associated with the formation of a grey film on the anode. The nature of the anode film is discussed in this communication.

The electrolyses during which film formed were typically carried out at 8.63 mA on a shiny platinum electrode of area 24.6 cm$^2$ at a temperature of 23±1° and a starting concentration of manganese(II) of *ca.* 0.1 *M*. The results quoted below are for electrolytes without sulfuric acid.

The films were effectively stripped by immersing the platinum anode in dilute hydrogen peroxide for 5 min. Most of the deposit dissolved during the first minute. The appearance of the platinum electrode was unchanged by repeated cycles of deposition and stripping, and its tare weight remained constant within 0.02 mg. The weights of the films analysed, determined by difference, ranged from 0.3 to 0.5 mg.

After destruction of the hydrogen peroxide by boiling in a 100-ml Kjeldahl flask, the solution was analysed for manganese by periodate oxidation and spectrophotometric measurement as permanganate[2]. Five films obtained from various electrolyses showed 42, 37, 28, 20 and 17% of manganese. The accuracy of the procedure is conservatively estimated to be ±5%. A separate determination of phosphate by the molybdenum blue method[3] gave *ca.* 45%. For comparison, the following calculated results are given, the first number in each parenthesis being percent manganese, and the second if given being percent phosphate: MnO (77), $Mn_2O_3$ (70), $MnO_2$ (63), $Mn_3O_4$ (72), $MnPO_4$ (37, 63), $Mn_3(PO_4)_2$ (47, 53), $Mn_3(PO_4)_4$ (30, 70).

The films are believed to be of variable composition like those recently reported in a similar pyrophosphate medium by HARRAR AND RIGDON[4], who found upon examination by ion microprobe mass spectrometry that the concentration of manganese decreased from the film surface toward the metal electrode. The prompt reaction with hydrogen peroxide indicates that the manganese present has been oxidized from the divalent state, and the low manganese content together with the presence of substantial amounts of phosphate rules out a mixture of manganese oxides. The phosphate of manganese(III) is soluble. It is not likely that in the film, manganese(IV) is present.

This work was part of a project supported by the National Research Council of Canada. One of the authors (G.A.B.) was the holder of a Province of Ontario Graduate Fellowship.

*Department of Chemistry,*
*University of Waterloo,*
*Waterloo, Ontario (Canada)*

G. A. BRYDON
G. F. ATKINSON

1 G. F. Atkinson and G. A. Brydon, *Anal. Chim. Acta*, 46 (1969) 309.
2 E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Edn., Interscience, New York, 1959, p. 608.
3 D. F. Boltz and M. G. Mellon, *Anal. Chem.*, 19 (1947) 873.
4 J. P. Harrar and L. P. Rigdon, *Anal. Chem.*, 41 (1969) 758.

(Received January 22nd, 1970)

*Anal. Chim. Acta*, 51 (1970) 539–540

---

# Inexpensive near-infrared and infrared cell holders for disposable liquid infrared cells

In the near-infrared region, where the operating ranges of some ultraviolet–visible and some infrared spectrophotometers overlap, the source-detector system of tungsten lamp and photoconductive cell yields, under the appropriate conditions, more definitive spectra than a Globar or Nernst glower–thermocouple combination. In the course of work conducted in these laboratories, a holder for disposable silver chloride infrared cells (Beckman #195476, Beckman Instruments, Inc., Fullerton, Calif.) was constructed to permit their use in the near-infrared region, in the double-beam Beckman DK-2 Ratio Recording Spectrophotometer. Since these disposable cells are uncalibrated, a cell holder for use with the Perkin-Elmer Model 21 Infrared Spectrophotometer (Perkin-Elmer Corp., Norwalk, Conn.) was fabricated, and the interference fringe pattern method was used to calculate the pathlength of each cell.

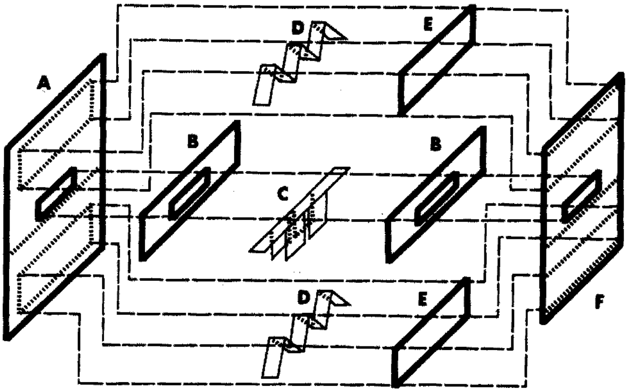


Fig. 1. Exploded view of infrared cell holder.

The cell holder for use with the infrared instrument is shown in Fig. 1, and the components are shown with their dimensions in Fig. 2. Components A and F in Fig. 2, G in Fig. 4, and M and O in Fig. 5, *vide infra*, were cut from cardboard stock that was *ca.* 1 mm thick, whereas the remaining cardboard parts were fabricated from a thinner (0.1–0.4 mm) cardboard stock, which had a smooth white surface on one side.

*Infrared cell holder*

The individual components and the rectangular holes in parts A, B, and F were cut to the given specifications. B was glued (Elmers Glue All, Borden Chemical Co., New York, N.Y.) to A, and a second B to F (later trimming off the excess width of B). The four side pieces of C were folded down so that each formed a 90° angle with C5. C1 and C2 were glued to A, aligning C5 with line A1, while the surfaces of C5 and A were kept perpendicular. Glue was applied to the long edge of a fan folded D, which was then placed on A within area A2, and a second D within area A3. F was gently placed over A, and if slight spaces remained, then spacers, such

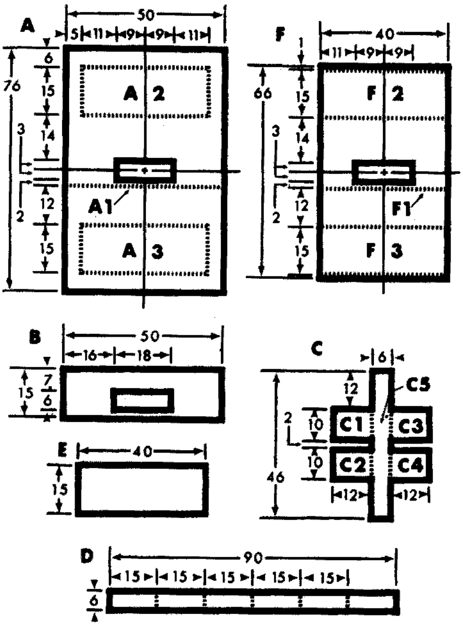


Fig. 2. Infrared cell holder components. Dimensions are in mm. Two B, D, and E components are needed.

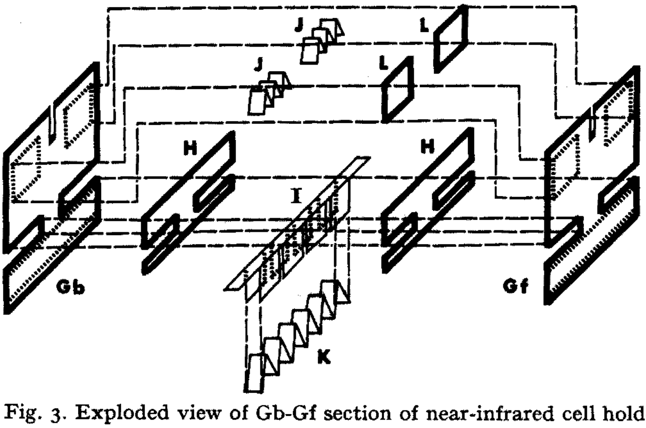


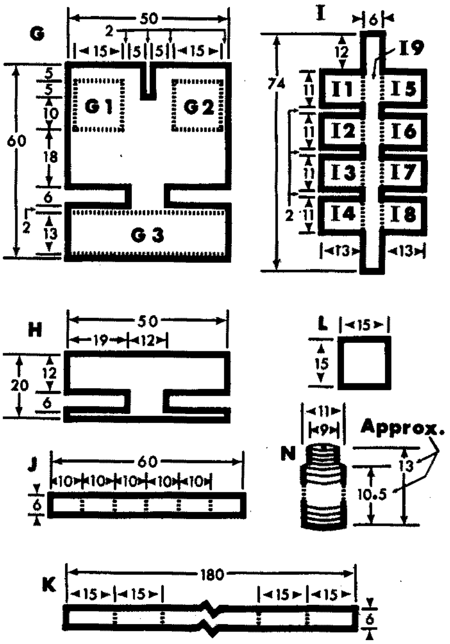
Fig. 3. Exploded view of Gb-Gf section of near-infrared cell holder.

as E, of the appropriate size and thickness, were glued to the edge of D. Before the glue applied to F set, precise alignment of the rectangular cut-outs in A and F, and the edge of C5 with line F1 was necessary. Since the design of D permitted the holder to withstand a compressional force of over one pound, a perpendicular pressure could be applied to F to force it closer to A.

*Near-infrared cell holder*

Part of the cell holder for use with the DK-2 (the section in which the cells are held during the recording of spectra) is shown in Fig. 3. Figure 4 shows these components and the metal cylinder, N. The base, M, the vertical divider, O, the completely assembled cell holder, P, and the accessory ties, Q, are shown in Fig. 5.

The components of Figs. 3 and 4 were assembled in a manner similar to that described for the infrared instrument cell holder. After removing the indicated rectangular cut-outs from G and H, H was glued to G, and two such units, Gf and Gb, were made. The eight side pieces of I were folded down, as shown in Fig. 3. I1 to I4 were glued to area G3 of Gb, with alignment of I9 and the bottom of H, while the surfaces of I9 and Gb were kept perpendicular. Two J parts were fan-folded and glued to Gb, in areas G1 and G2, as was K onto I1 to I4. I5 to I8 were then glued onto K.



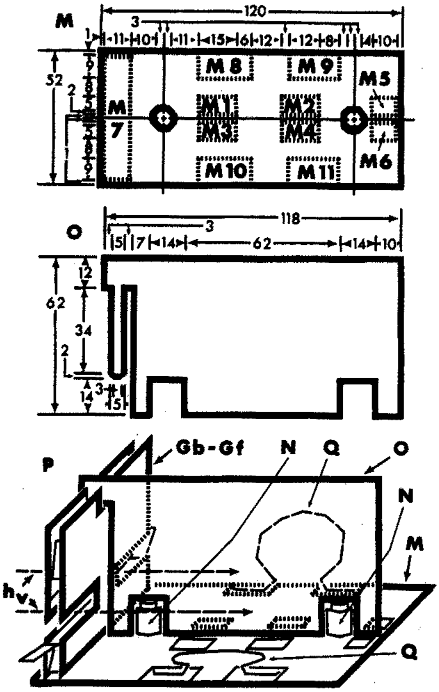


Fig. 4. Near-infrared cell holder components. Dimensions are in mm. Two G, H, J, L, and N components are needed.

Fig. 5. Near-infrared cell holder base, vertical divider, and completely assembled unit. Dimensions are in mm. Two Q parts are needed.

When the glue had set sufficiently to retain I, J, and K in place, Gf was gently placed over the Gb unit, and if necessary, spacers of the appropriate size (and thickness), for example L, were prepared and glued to J and/or I. When Gf was glued to the Gb unit, and after the rectangular cut-outs were properly aligned, pressure was applied to force Gb and Gf closer together. Again, the structural strength was sufficient to withstand over one pound of compressional force.

The two holes for the base, M, may be circles (conveniently cut with the appropriate size cork borer) or octagons, as shown in Fig. 5, whose midpoints of the linear segments are each 3 mm from the center. Fifteen size-10 nickel-plated steel washers (No. KMW-404, Waldom Electronics Inc., Chicago, Ill.) were glued together so that a cylinder about a common vertical axis was formed. As the glue is squeezed out from between the washers, a sheath may be formed to encase the cylinder. Similarly, three size-8 washers (No. KMW-403) were glued together, and this second cylinder was centered and glued to the top of the first, as seen as N. Two N cylinders were made, centered over the two M holes, and glued to M as shown in P. Rectangles, of the dimensions indicated by areas M1 to M6 in Fig. 5, were cut from the 1-mm thick cardboard stock, and glued to the appropriate areas. Glue was applied to the bottom edges of Gb and Gf, and to area M7, to which Gb–Gf was then glued.

If desired, to permit convenient handling of the cell holder, two ties, Q (in this case, vinyl-covered wires), may be glued to M, as shown as part of P, by the insertion of the ends of the ties into pools of the glue, placed approximately in areas M8 through M11.

*Recording of spectra*

Before the recording of spectra is begun and after sliding the disposable infrared cells into place in the Gb–Gf part of the holder, O is positioned as shown in P. P then is placed into the DK-2 cell compartment, with the two posts inserted into the two holes in the base, M, and encased by the metal cylinders, N.

At the conclusion of the spectral recording, P may be removed from the cell compartment by grasping both ties, Q, and the Gb–Gf part of P, and pulling straight up. Once O is lifted up and removed from P, the cells may be more easily removed from their places in Gb–Gf.

The DK-2 cell holder is designed for double-beam operation, and is not commercially available at the present time. Although a Model 21 holder is commercially available, it was deemed to be too expensive. These infrared and near-infrared cell holders are inexpensive and can be rapidly fabricated.

The author wishes to thank Professor THOMAS MEDWICK for his advice and continued interest in this work. The author is grateful to Merck and Co., Inc. for the awarding of a Merck Company Foundation Fellowship.

HERMAN J. HINITZ

*College of Pharmacy,*
*Rutgers-The State University,*
*Newark, N. J. 07104 (U.S.A.)*

(Received March 5th, 1970)

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

# The purity of commercial diphenylcarbazide

Diphenylcarbazide (DPCI) and diphenylcarbazone (DPCO) are frequently used in analytical chemistry for spot tests, metal complexing and other routine procedures. KRUMHOLZ AND KRUMHOLZ[1], however, have shown that commercially available DPCO is an equimolar mixture of DPCI and DPCO. They described a method for separating the components based upon a greater solubility of DPCO in sodium hydroxide.

Earlier, the DPCI reagent, prepared by heating urea with an excess of phenylhydrazine, was found[2] to be an addition compound of DPCI and phenylsemicarbazide (PSCI). However, according to the method of CAZENEUVE AND MOREAU[3], no PSCI is formed on reacting phenylhydrazine with either diphenyl or guaiacol carbonate instead of urea. Therefore, dissimilar reagents have been used in studies of Cr–DPCI complexes[4–12], which probably explains the controversial results published so far. It is also known that the purity of the DPCI reagent seems to be a major factor governing the colour intensity of these complexes[13]. On the other hand, the results obtained by extracting with isopentanol these complexes formed by either the pure or the double compound appeared to be quite similar[14].

The purpose of the present work was therefore to investigate the composition of commercial DPCI obtained from several sources, and where the reagents were impure, to separate the components by column chromatography.

## *Experimental*

*Apparatus.* Glass plates were used for thin-layer chromatography. The analytical separations were performed with a column of 20 cm length and 4 cm diameter. A 1-l separatory funnel provided with a pressure-regulation tube was placed at the top of the column. The lower portion, fitted with a porous disk of sintered glass (P1), was closed by a glass stopcock. The fractions were collected with a Serva Model 63 fraction collector (Heidelberg). Preparative-scale separations were performed with columns of 60 cm length and 7 cm diameter, equipped with a 2-l separatory funnel and a pressure-regulation tube. The eluents were nitrogen-pressurized. A 2-way stopcock at the bottom of the column permitted either sampling or collection of the effluents. The collectors were placed in a glove bag (model X-17-17 I$^2$R, Cheltenham, Pa.) which was also nitrogen-pressurized. The column and accessories were placed in a dark room.

Melting points were determined with a Mettler FP1 Melting and Boiling Point Apparatus (Zürich, Switzerland). The ultraviolet spectra (methanol) were obtained with a Beckman DK 2A Spectrophotometer. The infrared spectra (KBr disks) were recorded on a Perkin-Elmer Model 225 Spectrophotometer.

*Materials.* The following DPCI samples were investigated: (A) DPCI, prepared in the laboratory by reaction of diphenyl carbonate and phenylhydrazine; (B) BDH Analar, Poole, G.B.; (C) Matheson, Coleman and Bell, Norwood, U.S.A.; (D) Fluka purum (reagent grade), Buchs, Switzerland; (E) Schuchardt F: ~163°, München, W. Germany; (F) BDH, Spot Test Reagent; (G) UCB (reagent grade), Brussels, Belgium; (H) Merck (reagent grade), Darmstadt, W. Germany; (I) Baker

Analyzed Reagent, Baker Chemicals, Deventer, The Netherlands; (J) Carlo Erba RP, Milano, Italy; and (K) as (A) but with *urea* instead of diphenyl carbonate.

The following adsorbents were used: (I) polyamide powder TLC 6 (Perlon); (II) polyamide powder TLC 11 (Nylon 11); and (III) TLC 66 (Nylon 66). All were obtained from Macherey-Nagel GmbH., W. Germany.

The t.l.c. plates were either hand-made from one part of polyamide powder (I–III) and five parts of methanol, or commercial (DC-Alufolien Polyamid 11, F254, Merck, Darmstadt). The column adsorbent was M & N polyamide powder (column chromatography grade).

*Chromatographic procedures.* A solvent system *A* (water–methanol–acetic acid 1:3:0.04) was used for thin-layer and chromatographic separations. Thin-layer chromatography was performed by the classical ascending technique. The spots were detected by irradiation with light at 366 nm for several hours. However, instant detection was also possible when commercial t.l.c. plates were used by means of light at about 254 nm.

The column adsorbent was washed several times with methanol before use. The column was charged with about 8 mg of DPCI and eluted at a rate of one drop per 7–8 sec. The effluents were collected at intervals of 100 sec and monitored with the spectrophotometer at a wavelength of 280 nm. The first component was eluted with a 5-fold aqueous dilution of solvent system *A* whereas the second component was eluted with undiluted *A*.

The experiments were repeated on a preparative scale to permit identification of the first component by other techniques. The column was charged with about 1.5 g of DPCI sample, and again nitrogen-pressurized. The effluents were collected with the use of a glove bag, and evaporated to dryness with a Büchi Rotavapor at 28°. The precipitate was dissolved in water and allowed to crystallize in the cold. A second crystallization in methanol was performed on a steam bath. Carbon tetrachloride was added slowly to start crystallization.

Since the components appeared to be both air- and light-sensitive, particularly when in solution, it was necessary to chromatograph in the dark and in an atmosphere of nitrogen. Samples which were kept in the dark and under nitrogen did not lose colour for several months.

## *Results and discussions*

The t.l.c. results (Fig. 1) confirm that most DPCI samples were a mixture of two components. All elution patterns (Fig. 2) obtained with small columns were quite similar for samples D–K. The first component was identified as PSCI by infrared spectroscopy (Fig. 3). The $R_F$-values for different adsorbents were as shown in Table I.

The amount of PSCI (about 40%) present in some commercial samples was estimated by spot colorimetry according to the fluorescence quenching technique. However, the ultraviolet spectra (Fig. 4) of both components are quite similar, as may be expected for hydrazide derivatives. Both compounds display an "aniline-spectrum" with maxima around 232 and 280 nm. The strong absorbance band of PSCI ($\lambda_{max}$ 230.5 nm) does not coincide with the corresponding band of DPCI ($\lambda_{max}$ 234.0 nm). On the other hand, both molecules absorb at 280 nm. This band may be attributed to the phenylhydrazo chromophore, so that an $\varepsilon$-value twice that

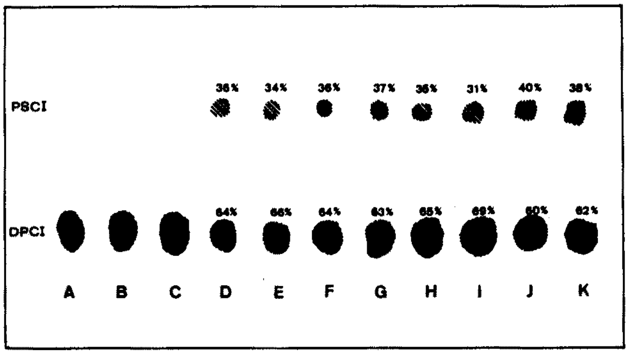


Fig. 1. Thin layer chromatograms (plate b) of samples A–K on Polyamide 11.

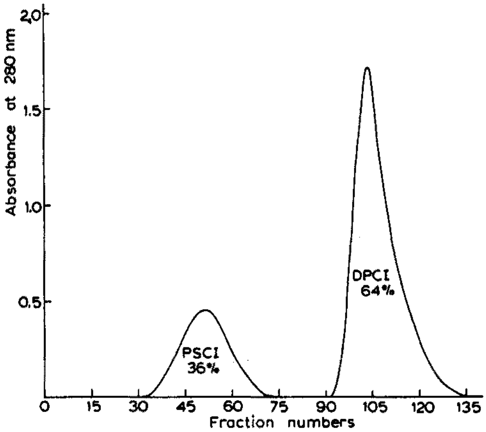


Fig. 2. Elution pattern of sample D with an analytical column (Polyamide 6).

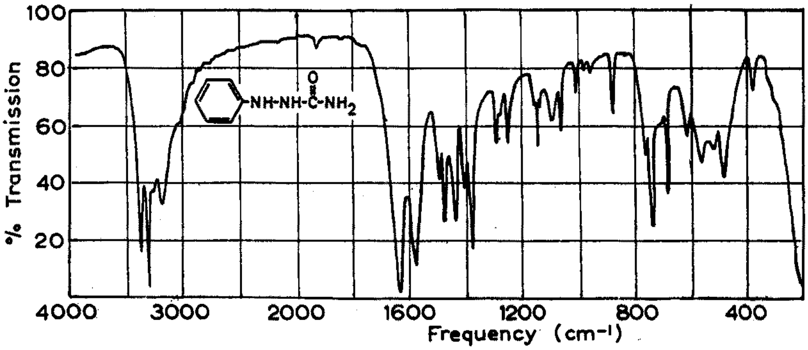


Fig. 3. The infrared spectrum of phenylsemicarbazide (KBr).

of PSCI may be expected for DPCI. The reference $\varepsilon$-values for DPCI and PSCI were determined from commercial samples which were purified as described above. The percentages of DPCI and PSCI were calculated by linear interpolation between these values. The results are given in Table II.

TABLE I

$R_F$ VALUES FOR DPCI AND PSCI ON DIFFERENT ADSORBENTS

| *Adsorbent* | *I* | *II* | *III* |
|---|---|---|---|
| Diphenylcarbazide (DPCI) | 70 | 63 | 73 |
| Phenylsemicarbazide (PSCI) | 81 | 87 | 83 |

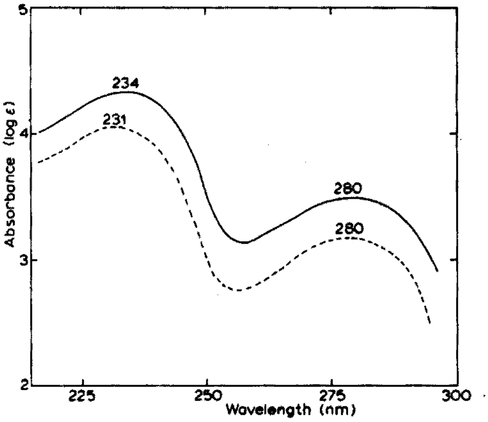


Fig. 4. The ultraviolet spectra (methanol) of diphenylcarbazide (solid line) and phenylsemicarbazide (dotted line).

TABLE II

MELTING POINTS, %DPCI AND PSCI, $\lambda_{max}$ AND LOG ε-VALUES OF SOME COMMERCIAL DPCI SAMPLES

| *Samples* | *M.p.* | *% DPCI* | *% PSCI* | $\lambda_{max}$ | *Log ε* |
|---|---|---|---|---|---|
| A | 171.9 | 100 | 0 | 234<br>280 | 4.351<br>3.497 |
| B | 172.0 | 100 | 0 | | |
| C | 171.2 | 100 | 0 | | |
| D | 164.9 | 64 | 36 | | |
| E | 164.5 | 66 | 34 | | |
| F | 164.7 | 64 | 36 | | |
| G | 163.9 | 63 | 37 | | |
| H | 163.2 | 65 | 35 | | |
| I | 162.1 | 69 | 31 | | |
| J | 163.7 | 60 | 40 | | |
| K | 164.1 | 62 | 38 | | |
| PSCI[a] | 170.5 | 0 | 100 | 231<br>280 | 4.066<br>3.173 |

[a] Commercial phenylsemicarbazide (Merck) purified as described in the text.

## *Conclusion*

Most commercial DPCI reagents are approximately equimolar mixtures of DPCI (61%) and PSCI (39%), when prepared by heating urea with phenylhydrazine. By reaction of diphenyl carbonate, instead of urea, with phenylhydrazine, no PSCI is formed.

We thank Dr. A. E. F. Chandler for his help in preparing this manuscript. We are also grateful to Mrs. J. Vermylen-De Winter for recording the u.v. spectra.

*Laboratory of Analytical Chemistry,*
*Pharmaceutical Institute,*
*Katholieke Universiteit,*
*Louvain (Belgium)*
G. J. Willems
R. A. Lontie*

*Janssen Pharmaceutica, Research*
*Laboratories, Beerse (Belgium)*
W. A. Seth-Paul

1 P. Krumholz and E. Krumholz, *Monatsh. Chem.*, 70 (1937) 431.
2 C. R. Noller, *J. Am. Chem. Soc.*, 51 (1930) 1132.
3 P. Cazeneuve and Moreau, *Bull. Soc. Chim. France*, (1900) 51.
4 P. Cazeneuve, *Bull. Soc. Chim. France*, (1900) 701.
5 A. Moulin, *Bull. Soc. Chim. France*, (1904) 295.
6 A. K. Babko and L. A. Palii, *Zh. Analit. Khim.*, 5 (1950) 272.
7 M. Bose, *Anal. Chim. Acta*, 10 (1954) 209.
8 R. T. Pflaum and L. C. Howick, *J. Am. Chem. Soc.*, 78 (1956) 4862.
9 A. K. Babko and T. E. Getman, *Zh. Obshch. Khim.*, 29 (1959) 2416.
10 J. Minczewski and W. Zmijewska, *Roczniki Chem.*, 34 (1960) 1559.
11 I. E. Lichtenstein and Th. L. Allen, *Phys. Chem.*, 65 (1961) 1238.
12 H. Marchart, *Anal. Chim. Acta*, 30 (1964) 11.
13 Th. L. Allen, *Anal. Chem.*, 30 (1958) 447.
14 I. E. Lichtenstein and Th. L. Allen, *J. Am. Chem. Soc.*, 81 (1959) 1040.

(Received April 20th, 1970)

---

* Present address: Laboratorium voor Biochemie, Katholieke Universiteit, Louvain, Belgium.

---

# Preparation and use of electrodeless discharge tubes for the atomic absorption spectrophotometry of some alkali metals

Most atomic absorption methods for the determination of alkali metals have used spectral-discharge lamps as light sources although hollow-cathode lamps are commercially available. Aldous *et al.*[1] recently described the preparation of electrodeless discharge tubes for these elements; the metals were used as the lamp charge for the sodium and potassium tubes and for magnesium, whereas the chloride was preferred for lithium. Attack on the tube walls by the metallic vapours was minimised by using a two-ply glass for the tube envelopes, the inner layer being a sodium vapour-resistant glass, but the preparation of the tubes then required considerable care. The applicability of these tubes to atomic absorption spectroscopy was not discussed.

This communication describes the preparation of electrodeless discharge tubes for lithium, sodium and potassium by a straightforward method in silica tubing with various compounds as the lamp charges. Over 80 tubes were prepared and tested for atomic absorption spectrophotometry. In addition to single element tubes, analytically useful tubes were prepared for combinations of the alkali metals; these were designed for the determination of elements consecutively without alteration of the operating conditions of the tube, the only adjustment required being the monochromator wavelength setting.

*Preparation of electrodeless discharge tubes*

The discharge tubes for the alkali metals were prepared by the method described by DAGNALL AND WEST[2], which has been previously applied to a number of other elements[3]. An exhaustive study of the optimum conditions of preparation was not undertaken. The tube length (*ca.* 4 cm) and argon fill pressure (3 Torr) first selected proved satisfactory and no variations were made.

Alkali metal discharge tubes were first prepared from the metal silicates after RAINS had reported that satisfactory sodium electrodeless discharge tubes could be prepared from sodium silicate[4]. The silicates used in the present work were prepared by fusion of the appropriate carbonate with a large excess of silica in a platinum dish, followed by aqueous extraction and evaporation to dryness. X-Ray fluorescence determination of the silica contents indicated that the compositions of the sodium and potassium compounds prepared were $Na_2O \cdot 9SiO_2$ and $K_2O \cdot 2SiO_2$. Satisfactory sodium tubes were also prepared from silicate of composition $Na_2O \cdot 4SiO_2$ so it would appear that the $M_2O:SiO_2$ ratio is not critical.

Commercially available anhydrous metal borates, *viz.* sodium tetraborate, potassium tetraborate, and lithium tetraborate, (B.D.H. Chemicals Ltd., Poole, England) were also used to prepare analytically useful tubes. In general, the greater volatility of borates compared to silicates was beneficial because the tubes could be operated at lower input powers. The tubes prepared from both silicates and borates tended to form a coating of the compound on the inner wall of the silica envelope, hence the preparation of electrodeless discharge tubes from metal phosphates was attempted. Several discharge tubes were therefore prepared from commercial sodium orthophosphate dodecahydrate, or lithium orthophosphate, and from copper(II),

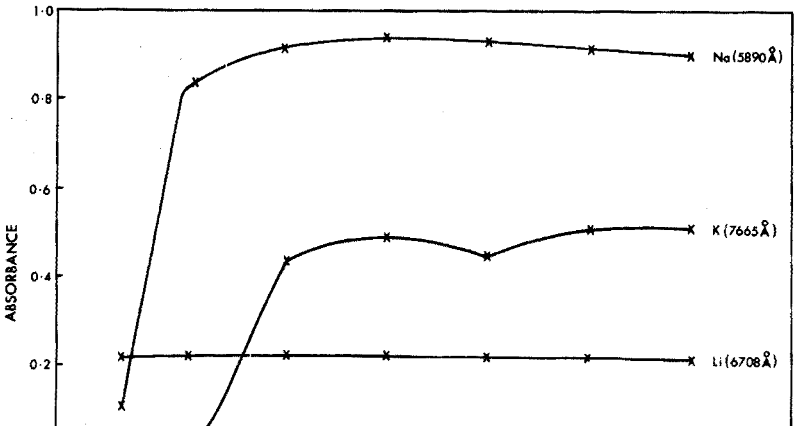


Fig. 1. Variation of absorbance with input power for multi-element tube prepared from borates. Metal concentrations (aqueous solution) 6 p.p.m.; air–propane flame; slit 3; gain as necessary in range 0–5.5.

iron(III), lead and magnesium phosphates prepared by precipitation. Table I describes the tubes prepared during this study.

The charge weight used in the single-element tubes was not critical within a reasonable range. Thus, analytically useful tubes were prepared from weights of sodium tetraborate varying between 15 and 30 mg. The weights listed in Table I should be regarded only as a guide to the quantities required. For the multi-element tubes, the relative amounts of the different silicates and borates used were more important if the tubes were to be used for more than one element with constant operating conditions; satisfactory weights are listed in Table I.

TABLE I

CHARACTERISTICS OF ELECTRODELESS DISCHARGE TUBES PREPARED

| *Element(s)* | *Compounds used* | *Weight used (mg)* | *Input power − reflected power (W)* | *Sensitivity (p.p.m./1% abs)* |
|---|---|---|---|---|
| Li | Silicate | 15 | 140 − 2 | 0.07 |
| | Tetraborate | 15 | 100 − 8 | 0.09 |
| | Phosphate | 15 | 120 − 25 | 0.09 |
| Na | Silicate | 20 | 100 − < 1 | 0.02 |
| | Tetraborate | 25 | 100 − 1 | 0.02 |
| | Phosphate | 15 | 100 − 30 | 0.02 |
| K | Silicate | 15 | 140 − 45 | 0.036 |
| | Tetraborate | 15 | 70 − 7 | 0.021 |
| Li + Na | Silicates | 19 + 2 | 90 − 2 | 0.15, 0.02 |
| Li + K | Silicates | 13 + 13 | 100 − 7 | 0.18, 0.05 |
| Na + K | Silicates | 1.2 + 25 | 130 − 20 | 0.02, 0.05 |
| Li + Na + K | Silicates | 12 + 2 + 12 | 100 − 2 | 0.13, 0.02, 0.05 |
| Li + Na + K | Tetraborates | 8 + 8 + 8 | 100 − 9 | 0.10, 0.025, 0.05 |
| Mg | Phosphate | 15 | 110 − 4 | 0.017 |
| Fe(III) | Phosphate | 15 | 150 − 7 | 0.54 |
| Cu | Phosphate | 15 | 110 − 11 | 0.18 |
| Pb | Phosphate | 15 | 105 − 5 | 0.85 |

The discharge tubes for lithium, sodium and potassium were also prepared with borosilicate (Pyrex) glass envelopes; it was hoped that this material would be more resistant than silica to attack by the enclosed vapours. However, the borosilicate tubes proved unsatisfactory because the input powers needed to produce adequate metallic vapour concentrations inside the envelope ( > 100 W for the tubes prepared from silicates) were also sufficient to cause softening, distortion and, in some instances, implosion of the envelopes themselves. Metal borates would probably be more satisfactory.

*Operation of electrodeless discharge tubes*

The tubes were operated in a Broida-type ¾-wave cavity, No. 210L, linked with a Microtron 200 generator (Electro-Medical Supplies Limited, London). Discharges were initiated with a "Tesla coil". Initiation was invariably obtained at input powers below 50 W, but under these conditions the emission was essentially an argon spectrum.

Higher input powers were needed to obtain the required alkali metal spectra but it was found that, after "running-in" for about 3–5 h, tubes operated under the conditions listed in Table I had stability and reproducibility such that no adjustment to the "Gain" control was needed during a set of readings taking 30–60 min. Cooling of the cavity and/or the discharge tube was not used. The tubes were used in conjunction with a Perkin-Elmer 303 atomic absorption spectrophotometer as previously described[3].

## *Results*

*Operating characteristics of electrodeless discharge tubes.* Alkali metal tubes containing either silicates or borates were simple to prepare and easy to operate. The multi-element tubes (Table I) were suitable for use in the determination of all the elements included, usually without alteration of the input power used. In some instances, *e.g.* sodium silicate–potassium silicate tubes, resonance lines of effectively equal emission intensity, after allowance for monochromator transmission, photomultiplier response, etc., were obtained, so that it was also unnecessary to adjust the spectrophotometer "Gain" setting. Similar equality could probably have been achieved for all element mixtures by appropriate choice of the charge weights, but this was not investigated fully because of the simplicity of the "Gain" adjustment needed if the emission intensities differed.

After several hours of operation at an input power around 100 W, the inside of the envelopes of the alkali metal tubes assumed a "frosted" appearance. This effect did not occur with quartz tubes containing 3 torr of argon only, which strongly suggested that the charge material participated in the change. The tube then emitted a spectrum containing only the major resonance lines of the alkali metal(s) included. For example, Table II lists the relative intensities of all of the lines emitted in the range 2000–8000 Å by a tube prepared from lithium, sodium and potassium silicates operated at an input power of 140 W. Little change in the performance of the tubes was then found during many hours of operation although it appeared that attack of the inner surface of the envelope by the enclosed vapour was continuing. This eventually (after *ca.* 3 kWh of operation in most instances) resulted in cracking of the envelope and failure of the tube. The effect could be minimised, but not eliminated, by taking care not to operate the tubes at powers higher than were necessary to obtain satisfactory analytical performance.

TABLE II

RELATIVE LINE INTENSITIES IN MULTI-ELEMENT ELECTRODELESS DISCHARGE TUBE[a]

| *Wavelength (Å)* | *Element* | *Relative intensity* |
|---|---|---|
| 4044.1 | K | 25 |
| 4047.2 | K | 15 |
| 5890.0 | Na | 100 |
| 5895.9 | Na | 60 |
| 6707.8 | Li | 5 |
| 7664.9 | K | 20 |
| 7699.0 | K | 15 |

[a] Intensities were measured by exposure of an Ilford "long range spectrum" photographic plate followed by measurement with a Jarrell-Ash microdensitometer. No corrections were applied for variation in response with wavelength.

Of the discharge tubes prepared from metal phosphates, several appeared satisfactory for analytical use (Table I) but were not studied in detail.

*Analytical applications.* The analytical applicability of the prepared tubes was tested by measurement of the absorption produced by known concentrations of metals under standard instrumental conditions. Sensitivities obtained varied with variations in the operating conditions of the tubes. With an air–propane flame, the sensitivity for sodium and potassium approached a maximum and then decreased as the input power to the microwave cavity was increased, the decrease being due to line-broadening and self-reversal; for lithium, little variation in the sensitivity was observed over a wide range of input power (Fig. 1). Curves obtained from multi-element tubes prepared from silicates behaved similarly but usually showed more pronounced absorption maxima with reduced sensitivities at higher input powers. The sensitivities observed for all of the tubes prepared are shown in Table I. The sensitivities for the alkali metals are of the same order as those obtained with hollow-cathode lamps with air–acetylene flames[5].

In order to demonstrate the absence of mutual interferences between the alkali metals when a multi-element discharge tube was used, six calibration graphs were constructed without variation of the operating conditions. One curve was prepared over the range 1–5 p.p.m. for each alkali metal and an additional curve was prepared for each metal in which the other two alkali metals were present in large excess (500 p.p.m. each). With an air–propane flame (flow rates, air 11 l $\mathrm{min}^{-1}$, propane 1.5 l $\mathrm{min}^{-1}$), calibration graphs passing through the origin were obtained with analytical sensitivities similar to the figures quoted in Table I. Large excesses of the other alkali metals reduced the observed absorptions by *ca.* 10% relative in all instances. This effect was probably caused by reduced efficiency of the atomisation process for solutions containing *ca.* 0.2% salt. No spectral interferences were observed. The multi-element tubes were suitable for the determination of each alkali metal in the presence of large excesses of other alkali metals provided that the overall salt concentration did not decrease the atomising efficiency of the flame.

## *Discussion*

These studies have shown that analytically useful electrodeless discharge tubes can be prepared from oxygen-containing salts of alkali metals and other elements; previously the metals themselves or their halides have been used almost exclusively. High emission intensity, spectral purity and good analytical sensitivity were obtained. It was therefore possible to use the discharge tubes to exploit the advantages of atomic absorption spectrophotometry compared to thermal emission spectrophotometry, principally freedom from interference, for the determination of sodium and potassium in complex matrices. The relative ease of preparation of the multi-element discharge tubes is advantageous for the sequential determination of sodium and potassium. It should be feasible to prepare a wider range of useful multi-element tubes provided that the volatilities of the compounds selected are similar and that the emission spectra obtained are relatively simple.

The major disadvantage of these alkali metal discharge tubes, whether prepared from silicates or borates, is their limited lifetime caused by attack on the tube envelope by the enclosed vapours. This problem has not been solved, but the analytical usefulness of the tubes prepared as described is such that they have been used for about 1000 determinations of, *e.g.* potassium in condensates and sodium in catalysts and effluents.

The author is most grateful to Miss J. M. HALL and Mr. T. H. CUSHLEY who carried out the bulk of the experimental work discussed herein.

*Imperial Chemical Industries Limited,*
*Agricultural Division,*
*Billingham, Teesside (England)*

COLIN WOODWARD

1 K M. ALDOUS, R. M. DAGNALL AND T. S. WEST, *Anal. Chim. Acta*, 44 (1969) 457.
2 R. M. DAGNALL AND T. S. WEST, *Appl. Opt.*, 7 (1968) 1287.
3 C. WOODWARD, *At. Abs. Newsletter*, 8 (1969) 121.
4 T. C. RAINS, National Bureau of Standards, Washington, D.C., U.S.A., private communication.
5 W. SLAVIN, *Atomic Absorption Spectroscopy*, Interscience, 1968, p. 60.

(Received February 20th, 1970)

---

## Titrimetric determination of vanadium(IV) with potassium permanganate or cerium(IV) sulphate at room temperature

Vanadium(IV) can be determined by titration with potassium permanganate or cerium(IV) sulphate. The reaction between vanadium(IV) and permanganate is slow at room temperature, hence potentiometric titration[1] at 70–80° or visual titration at 50° with ferroin indicator[2] have been recommended. Vanadium(IV) can be titrated with permanganate at room temperature in presence of orthophosphoric acid, which catalyses the reaction[3], and the colour of permanganate itself and ferroin have been used to indicate end-points in titrations involving 0.05 $N$ and 0.01 $N$ solutions, respectively.

The titration of vanadium(IV) with cerium(IV) also requires higher temperatures and potentiometric titrations at 60° [4] and 70–75° [5] have been studied. From a kinetic study of the vanadium(IV)–cerium(IV) reaction, RECHNITZ AND RAO[6] have established that the reaction is not slow as suggested by earlier workers, but is fast even at room temperature, although temperatures of about 70° [4,5] are required for immediate attainment of equilibrium. Recently, it has been reported[7,8] that vanadium(IV) can be titrated with cerium(IV) sulphate at room temperature in a mixed medium of acetic and sulphuric acids (7.0–8.5 $N$+0.2–0.6 $N$[7] and 8–9 $N$+0.1–0.2 $N$[8], respectively).

In a continuation of this work, it has been observed that the titration of vanadium(IV) with permanganate or cerium(IV) is possible at room temperature in presence of ferroin and the triphenylmethane dyes, Erioglaucine A, Eriogreen B, Xylenecyanol FF, Setoglaucine O, and Setocyanine Supra (Colour Index Nos. 42090, 44025, 42135, 42025, and 42140, respectively) as redox indicators, provided that a small amount of potassium hexacyanoferrate(III) is present. The method developed is more convenient than the earlier methods because it does not require higher temperatures or high concentrations of acetic acid.

## *Experimental*

*Reagents. Ca.* 0.05 *N* solutions of vanadium(IV) sulphate, cerium(IV) sulphate (both in 0.5 *N* sulphuric acid) and potassium permanganate were prepared. The vanadium(IV) and cerium(IV) solutions were standardised as described by Gopala Rao and Dikshitulu[9] and the permanganate by potentiometric titration against standard sodium oxalate. B.D.H. AnalaR potassium hexacyanoferrate(III) was used.

All the other chemicals were of reagent grade quality.

*Procedure.* Treat 5–20 ml of vanadium(IV) solution with sulphuric acid, to give an overall acidity of 0.2–0.5 *N* when diluted to 50 ml (the acidity must not exceed 0.5 *N*), and add 0.1 ml of 0.01 *M* ferroin or 0.5 ml of aqueous 0.1% Erioglaucine A, Eriogreen B, Xylenecyanol FF, Setoglaucine O, or Setocyanine Supra, and 0.5–1 ml of aqueous 1% potassium hexacyanoferrate(III) solutions. Titrate with 0.05 *N* potassium permanganate or cerium(IV) sulphate. (In titrations with permanganate, add the triphenylmethane dye near the end-point because of the partial destruction of these indicators). Near the end-point, add the oxidant dropwise, waiting for about 10 sec after each addition; the colour changes are shown in Table I.

TABLE I

TITRATION OF VANADIUM(IV) TO DIFFERENT INDICATORS

| *V(IV) taken, (mmoles)* | *V(IV) found, mmoles* | | | | | |
|---|---|---|---|---|---|---|
| | *Ferroin*[a] | *Erio-glaucine A*[b] | *Erio-green B*[b] | *Xylene-cyanol FF*[c] | *Seto-glaucine O*[d] | *Setocyanine Supra*[d] |
| *Titration with permanganate* | | | | | | |
| 0.05300 | 0.05306 | 0.05302 | 0.05302 | 0.05302 | 0.05304 | 0.05304 |
| 0.1260 | 0.1264 | 0.1264 | 0.1262 | 0.1260 | 0.1254 | 0.1262 |
| 0.4684 | 0.4688 | 0.4684 | 0.4688 | 0.4690 | 0.4680 | 0.4682 |
| 0.6486 | 0.6492 | 0.6488 | 0.6490 | 0.6492 | 0.6482 | 0.6480 |
| 0.8004 | 0.8014 | 0.8008 | 0.8002 | 0.8006 | 0.8002 | 0.8012 |
| 1.040 | 1.042 | 1.041 | 1.041 | 1.040 | 1.039 | 1.041 |
| *Titration with cerium(IV)* | | | | | | |
| 0.06150 | 0.06160 | 0.06156 | 0.06156 | 0.06152 | 0.06156 | 0.06154 |
| 0.1040 | 0.1046 | 0.1044 | 0.1042 | 0.1044 | 0.1046 | 0.1044 |
| 0.3466 | 0.3470 | 0.3462 | 0.3464 | 0.3468 | 0.3466 | 0.3470 |
| 0.5280 | 0.5290 | 0.5288 | 0.5286 | 0.5284 | 0.5284 | 0.5288 |
| 0.7462 | 0.7474 | 0.7466 | 0.7460 | 0.7466 | 0.7462 | 0.7470 |
| 0.9284 | 0.9294 | 0.9288 | 0.9280 | 0.9284 | 0.9286 | 0.9290 |

[a] Colour change, orange to yellow,
[b] Colour change, yellow-green to orange,
[c] Colour change, blue-green to orange,
[d] Colour change, green to orange.

*Indicator corrections.* In titrations with 0.05 *N* solutions, no indicator correction is necessary, but in titrations with 0.01 *N* solutions, indicator corrections are needed as follows:

ferroin: 0.08 ml for each 0.1 ml of 0.01 $M$ solution;
triphenylmethane dyes: 0.06 ml for each 0.5 ml of 0.1% solution.
Some typical results obtained by the proposed method are given in Table I.

*Interferences.* 50 mg Each of iron(III) and chromium(III) did not interfere.

*Reverse titrations.* Reverse titrations, *i.e.*, titration of cerium(IV) or permanganate with vanadium(IV) sulphate, can also be carried out as described above, provided that ferroin is used as indicator. The triphenylmethane dyes are unsuitable because they are destroyed by the excess of oxidant.

*Titrations in hydrochloric acid medium.* Vanadium(IV) can be titrated with cerium(IV) (but not with permanganate) in 0.1–0.3 $N$ hydrochloric acid medium in the presence of hexacyanoferrate(III).

*Differential titration of iron(II) and vanadium(IV).* The method can also be applied for the differential titration of iron(II) and vanadium(IV). Titration of one aliquot with cerium(IV) or permanganate in 10–11 $N$ sulphuric acid medium, in presence of the above indicators, gives only the iron(II) content, whereas the titration of a second aliquot by the above procedure gives the total of iron(II) and vanadium(IV). In titrating the second aliquot, it is essential to add the hexacyanoferrate(III) after the iron(II) has been completely titrated in order to avoid the formation of iron(II) hexacyanoferrate(III).

### *Results and discussion*

The reactions involved in the titration of vanadium(IV) with permanganate are as follows:

(1) V(IV) + Mn(VII) → V(V) + Mn(II) Slow
(2a) Mn(VII) + ferroin → Mn(II) + ferriin Fast
(2b) Mn(VII) + triphenylmethane dyes → Mn(II) + oxidised triphenylmethane dyes Fast
(3a) V(IV) + ferriin → ferroin + V(V) Slow
(3b) V(IV) + oxidised triphenylmethane dyes → V(V) + triphenylmethane dyes Slow

Reaction (1), is slow at room temperature, but fast at elevated temperatures[1,2]; reactions (1) and (3a) are fast at room temperature in presence of orthophosphoric acid.[3] Hexacyanoferrate(III) exerts a marked catalytic effect on reactions (3a) and (3b), but not on reaction (1), at room temperature. The practicability of the titration of vanadium(IV) with permanganate at room temperature, can be explained as follows: permanganate first oxidises the indicators to their oxidised forms and the latter oxidise the vanadium(IV) to vanadium(V) rapidly in presence of hexacyanoferrate(III) as catalyst. When all the vanadium(IV) has been oxidised to vanadium(V), the colour of the oxidised form of the indicators persists and indicates the end-point of the titration.

In the titration of vanadium(IV) with cerium(IV), the scheme is entirely analogous, except that the reaction: V(IV) + Ce(IV) → V(V) + Ce(III) is fast.

The time taken for the complete reduction of the oxidised indicator by vanadium(IV) (as evidenced by the appearance of the colour of original intensity) in the presence of hexacyanoferrate(III), for ferroin and the five triphenylmethane dyes is about 3–5 sec, whereas it is more than 5 min in absence of hexacyanoferrate(III). The transition potentials of the triphenylmethane dyes are all in the range 1000–1020 mV under these conditions.

Thanks are due to the Council of Scientific & Industrial Research, India, for the award of a Junior Research Fellowship for one of us (V.V.S.E.D.).

*Chemistry Department,*
*Andhra University,*
*Waltair (India)*

N. VENKATESWARA RAO
V. V. S. ESWARA DUTT

1 E. MÜLLER AND H. JUST, *Z. anorg. u. allgem. Chem.*, 125 (1922) 155.
2 H. H. WILLARD AND P. YOUNG, *Ind. Eng. Chem., Anal. Ed.*, 6 (1934) 48.
3 L. S. A. DIKSHITULU AND G. GOPALA RAO, *Z. Anal. Chem.*, 189 (1962) 421.
4 N. H. FURMAN, *J. Am. Chem. Soc.*, 50 (1928) 1675.
5 H. H. WILLARD AND P. YOUNG, *Ind. Eng. Chem.*, 20 (1928) 972.
6 G. A. RECHNITZ AND G. N. RAO, *Anal. Chem.*, 39 (1967) 1192.
7 K. SRIRAMAM AND G. GOPALA RAO, *Talanta*, 13 (1966) 1469.
8 N. VENKATESWARA RAO AND V. V. S. ESWARA DUTT, *Z. Anal. Chem.*. (in press).
9 G. GOPALA RAO AND L. S. A. DIKSHITULU, *Talanta*, 9 (1962) 289.

Received April 6th, 1970

# ANNOUNCEMENTS

---

## 3RD ROMANIAN NATIONAL CONFERENCE ON ANALYTICAL CHEMISTRY

*September 22–26, 1971*

The Chemistry Division of the Romanian National Council of Engineers and Technicians will sponsor the 3rd National Conference on Analytical Chemistry between 22nd and 26th of September 1971 in Brașov, Romania.

Sessions on electrometric methods, optical methods, and separation methods are planned.

Further information on this meeting is available from the Secretary: Dr. CONSTANTIN LUCA, Consiliul Național al Inginerilor și Technicienilor, Conferința de Chimie Analitică, Calea Victoriei 118, București, Romania.

# FOURTEENTH CONFERENCE ON ANALYTICAL CHEMISTRY IN NUCLEAR TECHNOLOGY

*Mountain View Hotel and Motor Lodge, Gatlinburg, Tenn.*

*October 13–15, 1970*

The Fourteenth Conference on Analytical Chemistry in Nuclear Technology will be held in Gatlinburg, Tenn., October 13–15, 1970, under the sponsorship of the Analytical Chemistry Division, Oak Ridge National Laboratory. The Laboratory is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

All sessions of the conference will be held in the Mountain View Hotel. Registration will begin on October 12 at 4 p.m. in the hotel lobby and continue each day for the duration of the conference. Sessions will begin at 9 a.m. each day.

## *Technical program*

Papers up to 25 minutes in length, that describe original, unpublished work related to the following topics are solicited by the Program Committee.

1. Applications of Digital Computers in Analytical Chemistry.
2. New Sensors and Detectors for use in Studies Related to Environmental Pollution.
3. Problems Associated with the Purity of Reagents for use in Chemical Analysis.
4. Sample Preparation and Dissolution—Vital Steps in Chemical Analysis.
5. Papers on Topics of General Interest Related to Analytical Chemistry in Nuclear Technology.

## *Exhibition of modern analytical instruments and laboratory equipment*

Facilities will be available to manufacturers and dealers in laboratory supplies for the installation of 14 exhibits on modern developments in analytical instrumentation, equipment, and supplies. Information concerning the availability of and rental charge for exhibit space may be secured by writing to H. R. BEATTY, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tenn. 37830.

## *General information*

*Abstracts.* Those who wish to make contributions should submit an abstract of 200–500 words not later than June 20, 1970. The title, name of the author, an estimate of the time that will be required for the presentation, and in case of multiple authorship, an indication of the name of the speaker should accompany the abstract.

Abstracts of papers and inquiries concerning the conference, including request for programs, should be directed to the Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tenn. 37830, Attention: L. J. BRADY, Chairman.

*Registration fee.* The registration fee, except for full-time students, is $10.00 per person. A registration fee of $5.00 will be required for attendance of one day or any part thereof.

*Reservations.* Reservation for lodging should be made by direct communication with: The Mountain View Hotel and Motor Lodge, Gatlinburg, Tenn. 37738.

# BOOK REVIEWS

---

A. SANFELD, *Introduction to the Thermodynamics of Charged and Polarized Layers*, John Wiley and Sons Ltd., London–New York–Sydney–Toronto, 1968, xxiv + 258 pp., price £ 4.5.

The study of polarized interfaces has great relevance to many problems in electrochemistry (*e.g.* adsorption phenomena) and colloid chemistry (colloid stability, electrophoresis).

In the classical thermodynamic method of analysis, no reference is made to the manner in which the discontinuities at an interface appear; for instance, in GUGGENHEIM's approach, the interfacial region is treated as a separate phase. The purpose of this book is to generalize a local thermodynamic formulation and apply it to the case of a polarized system. In contrast with global thermodynamics, a local formulation attempts to give a connection between the thermodynamic functions and the values of the local variables (*i.e.* temperature, concentration, electric field).

The conservation laws in the presence of an electromagnetic field and the local definition of the thermodynamic functions are primarily presented. The thermodynamic relations are then extended to systems where the polarization is not a linear function of the electric field (dielectric saturation). Following this, a generalized distribution function for ions and dipoles is derived. This distribution function takes into account the specific volume of the components, differences in electrostatic pressure within the interface, dielectric saturation phenomena, and variation of dielectric properties with changes in concentration of the components, as well as the classical electrostatic energy. The individual activity coefficient of the constituents appears also as a separate variable, although in the present work, its calculation has not been attempted. The generalized distribution function is applied to the case of a diffuse double layer, and both the potential at the outer Helmholtz plane and the differential capacitance are calculated for several ions.

There is a basic difficulty in general in comparing experimental diffuse double layer results with calculated values using various distribution functions. With the exception of the most dilute solutions and at potentials very close to the point of zero charge, most of the potential drop occurs in the inner region of the double layer (where, in the absence of specific adsorption, no electrolyte is present) and hence the diffuse layer makes a small contribution to the overall measured capacitance. Furthermore, to estimate "experimental" values of the diffuse layer contribution, some assumption has to be made with regard to the constancy of the inner layer capacitance with changes of concentration. These points make it difficult to assess the relative merits of distribution functions of a more complex nature than the simple Boltzmann distribution law. Therefore, for dilute solutions, results with a higher degree of accuracy than those presently available seem to be necessary.

The electrical potential, field and charge density distribution functions are derived for the diffuse double layer. Also, ionic association in the presence of an electric field and interaction of two diffuse double layers are presented.

The book is very well presented and abundant references are given. The inclusion of well explained numerical examples to show the relative order of magnitude of variables is highly commendable. This monograph does manage to present a unified picture of a thermodynamic formulation of charged and polarized matter as the author intended and should prove a useful basic reference book for research workers in this field.

D. J. SCHIFFRIN (Southampton)

*Anal. Chim. Acta*, 51 (1970) 558–559

---

*Analytical Chemistry in Space*, Edited by R. E. WAINERDI (International Series of Monographs in Analytical Chemistry, Vol. 35), Pergamon Press, Oxford, 1970, vii + 275 pp., price £7.00.

With all the current excitement about the analysis of lunar samples, this is a timely book. Although it was written well before the first lunar samples arrived on Earth, it serves a useful purpose in indicating the problems involved not only in extraterrestrial analysis but in analysis of returned extraterrestrial materials. The book has been capably edited by R. E. WAINERDI and contains seven chapters on various relevant aspects by different authors.

L. F. HERZOG summarizes the pre-Apollo state of knowledge and hypotheses on the composition of the solar system, and F. S. JOHNSON discusses what is known about solar system atmospheres; both these chapters contain data which should perhaps have been treated with a greater degree of scepticism. Chapters on the applications and possibilities of several techniques for space analysis *in situ* follow: HERZOG discusses mass spectrometry, J. A. WAGGONER describes neutron scattering, and J. S. HISLOP and R. E. WAINERDI review 14-MeV neutron activation. E. C. MACKANNAN provides an interesting chapter on space engineering in which the mechanics and electronics of space-worthy analytical instruments are discussed; anyone with ideas for analytical space projects should find this chapter rewarding. Finally, D. E. MAPPER and A. A. SMALES discuss the analysis of recovered extraterrestrial materials, which chapter deals with meteorites, but the type of analysis has immediate relevance to lunar samples.

This book was, of course, outdated in some respects by the recent reports on the analysis of lunar samples. Nevertheless, it is full of interest and anyone who has perused it will be the better qualified to assimilate the achievements that will follow from the continuation of manned space flights.

A. M. G. MACDONALD (Birmingham)

*Anal. Chim. Acta*, 51 (1970) 559

M. TSUTSUI (Editor), *Characterisation of Organometallic Compounds. Part 1. Chemical Analysis*, Vol. 26, Edited by P. J. ELVING AND I. M. KOLTHOFF, Interscience Publishers–J. Wiley and Sons, Inc., New York, 1969, vii + 371 pp., price £7.00.

As stressed by the Editor in his Preface, organometallic chemistry has undergone an extremely rapid expansion in recent years and in many instances preparative techniques have outstripped the ability of the chemist to characterise and analyse his products.

This very timely volume attempts to remedy this deficiency by gathering under one cover details of various physical techniques which have attained widespread use but have heretofore been available largely in specific research papers.

Following a general introduction to the subject, designed mainly for the student but nevertheless providing a useful summary of the types of systems needing characterisation, chapters are contributed by distinguished authors on chemical characterisation, infrared spectroscopy, mass spectroscopy, X-ray diffraction, microwave and Mössbauer spectroscopy. While the last two topics are of a more specialised nature all will be of considerable use to workers in the field. Articles are accompanied by extensive lists of references and there are full author and subject indexes. Subsequent parts of this series will without doubt be awaited with considerable anticipation.

P. C. UDEN (Birmingham)

---

*Computer Programs for Chemistry*, Vol. II, Edited by DELOS. F. DETAR, W. A. Benjamin, Inc., New York, 1969, xix+260 pp., price $14.75.

The programmes given in this second volume will be of considerable interest to both physical chemists and biochemists since they are concerned with simulating kinetic situations. Extensive use of numerical integration of sequential rate equations makes it possible to simulate very complex reactions. This situation is possibly more important in biochemistry than chemistry and since the programmes allow the user to formulate his reactions in any sequence or combination he wishes, they should have extensive use in the future. The programmers are to be congratulated on the care they have taken to ensure that false input-data is not accepted by the programme.

S. P. SPRAGG (Birmingham)

G. CHARLOT AND B. TRÉMILLON, *Chemical Reactions of Solvents and Melts*, Translated from the French by P. J. J. HARVEY, Pergamon Press, Oxford, 1969, viii+528 pp., price £10 ($27.00).

The use of non-aqueous solvents in chemical analysis is constantly increasing, and the analytical chemistry of melts has grown in importance with studies of fuel cells. It is therefore surprising that very few large groups work on fundamental chemical problems in these media and that the use of solvents or melts is so often empirical; the school of Professor CHARLOT is a notable exception.

This book summarizes accumulated experience in two parts. The first is devoted to general properties (acid–base reactions, complex formation, oxidation–reduction phenomena and solubility) and the second is descriptive, discussing the information available according to the chemical nature of the investigated solvent (hydrocarbons, halo-derivatives, acids, bases, alcohols, amides, nitro compounds, nitriles, ketones, anhydrides, ethers and esters, halides and ionized melts). Particularly useful are the numerous tables and graphs that illustrate relative acid–base and oxidation–reduction properties. The only pity is that the book, which is a translation of a 1963 French edition, has not been augmented with later information.

The volume is, nevertheless, of great practical importance for all analytical chemists interested in non-aqueous solvents and melts.

P. ZUMAN (Potsdam, N.Y.)

---

L. S. BIRKS, *X-Ray Spectrochemical Analysis*, 2nd Edn., Interscience Publishers–J. Wiley & Sons, New York, 1969, xv + 143 pp., price £ 4.75.

X-Ray fluorescence spectrometry is now universally recognised as a highly versatile and rapid means of analysis, and whilst several good text books covering the basic fundamentals of the subject are currently available, this revised edition will be of special interest to owners of the first edition of the book which is now ten years old.

The book deals with the principles and practices involved in the generation, dispersion, and detection of X-ray wavelengths, and highlights the ways in which they are used to distinguish one element from another, and how line intensities are used in quantitative analysis.

Two features of this latest edition are a new chapter on energy dispersion and a considerably revised and reorganised applications chapter.

W. T. ELWELL (Birmingham)

CODATA (Committee on Data for Science and Technology), *International Compendium of Numerical Data Projects*, Springer-Verlag, Berlin, 1969, xxiii +295 pp., price DM 48.—.

This is an unusual but useful book, which has been produced by CODATA —the Committee on Data for Science and Technology of ICSU—as a preliminary step in their efforts to rationalize the compilation of numerical data. In Chapter 1, the National Data Programmes for the U.S., U.S.S.R. and U.K. and the various national committees are listed. Chapter 2 summarizes the credentials of well-known data compilations such as Landolt-Börnstein and those of the American Petroleum Institute. In subsequent chapters, the data compilations available are listed by subject: nuclear properties, atomic and molecular properties, solid-state properties, thermodynamic and transport properties, chemical kinetics, crystallographic data, etc. All of these collections are continuing projects and new and other specialized projects are listed separately. The many Handbooks available are also listed, and the sources for basic physical constants, nomenclature, etc. are given.

Altogether about 150 data compilation projects are mentioned. In each case, the organization responsible for the data collection is described and the coverage is described in one or two paragraphs; an analysis of the contents is then given, with a brief assessment of the reliability of the data and method of compilation.

This is, of course, a listing of lists, but given so many lists, it should prove useful in indicating where a particular type of data should be sought. The great variety of data already compiled and published by different organizations seems to show a good deal of overlap and CODATA's aims of coordinating existing programmes as well as initiating new projects appear to be well justified.

A. M. G. MACDONALD (Birmingham)

*Anal. Chim. Acta*, 51 (1970) 562

---

J. H. VAN DER MAAS, *Basic Infrared Spectroscopy*, Heyden and Sons, Ltd., London, iii+108 pp. Price 30s, \$3.50, DM13.50.

This book is intended "as a guide to those starting infrared spectroscopy and as a convenient source of fundamental data for graduate workers". It consists of 5 short chapters and 4 appendices. Chapter 1 gives a concise introduction to the basic principles involved. Chapter 2 attempts to cover the basic theory of the absorption of infrared radiation by molecules, and is the weakest section of the book. There are at least two bad errors, (particularly a completely erroneous definition of the Born-Oppenheimer approximation), and a number of misprints—such as confusion between $\nu$ and $v$ for frequency, $f$ and $k$ for force constant, degeneration and degeneracy. It also seems unnecessary for the author to introduce centrifugal distortion into a topic in which the emphasis is on simplicity. Chapters 3 and 4 deal adequately with the basic components of a spectrometer and their functions, and with sampling techniques. However, Chapter 5, on interpretation of spectra consists of 3 pages only, and gives but the briefest synopsis of the basic rules; for advice here, one must look elsewhere. The appendices give a list of sources of reference spectra, a few "typical band contours" (some without adequate wave number scales), and the inevitable correlation charts, and lists of absorption frequencies of functional groups.

The book is priced at 30/-, which for a paperback, containing a mere 108 pages, seems rather high.

J. LINDSAY DUNCAN, Aberdeen

*Anal. Chim. Acta*, 51 (1970) 562–563

---

N. H. HARTSHORNE AND A. STUART, *Practical Optical Crystallography*, 2nd Edn., Edward Arnold (Publishers) Ltd., London, 1969, ix + 326 pp., price £3.75.

This new edition of *Practical Optical Crystallography* has followed the 1964 edition rapidly, which indicates the considerable interest which this book has aroused, particularly for students of geology and crystallography. The present book can be considered as a somewhat simpler and condensed version of the authors' well-known *Crystals and the Polarising Microscope*, the third edition of which appeared in 1960.

Most chemists at some time have occasion to examine crystalline material under the microscope and the present book provides a valuable source of the simpler practical techniques which, for the non-specialist, are more than sufficient for characterization of crystal properties. The eight chapters deal in turn with the general morphology of crystals, their optical properties, the polarising microscope, the microscopic examination of crystals by parallel and by converged light, stereographic projection, preparation, mounting and manipulation of material, and finally some practical examples on the determination of optical crystallographic properties.

This new edition has been purged of the minor errors in the first edition and has been brought thoroughly up-to-date. Dr. HARTSHORNE and Professor STUART have a reputation second to none in this field and this revised edition can be warmly recommended wherever a polarising microscope is used.

W. I. STEPHEN (Birmingham)

*Anal. Chim. Acta*, 51 (1970) 563

# PUBLICATIONS RECEIVED

C. Duval, *L'Iode* (Que sais-je? No. 1370), Presses Universitaires de France, Paris, 1969, 126 pp.

G. Nedey, *Peintures et Vernis* (Que sais-je? No. 1348), Presses Universitaires de France, Paris, 1969, 124 pp.

*British Ceramic Abstracts No. 1, 1969*, The British Ceramic Research Association, Penkhull, Stoke-on-Trent, England, subscription price, £10 per annum. This is the first of a new series of abstracts on ceramics science.

H. Bennett and W. G. Hawley, *The Accuracy of Industrial Ceramic Analysis*, The British Ceramic Research Association, Spec. Publ. No. 53, 1969, 60 pp., price £1.50.

H. Guerin, *Chimie Industrielle. Tome II. Du Sel au Teflon*, Presses Universitaires de France, Paris, 1969, 577 pp.

# ANALYTICA CHIMICA ACTA, VOL. 51 (1970)
# AUTHOR INDEX

# ANALYTICA CHIMICA ACTA, VOL. 51 (1970)

# AUTHOR INDEX

VOL. 51 NO. 3 ANALYTICA CHIMICA ACTA SEPTEMBER 1970

# CONTENTS

*(continued on page 4 of cover)*

*(contents, continued from page 3 of cover)*

PRINTED IN THE NETHERLANDS