

# ANALYTICA CHIMICA ACTA

International journal devoted to all branches of analytical chemistry

## EDITORS

**A. M. G. MACDONALD** (Birmingham, Great Britain)

**D. M. W. ANDERSON** (Edinburgh, Great Britain)

## Editorial Advisers

- |                                  |                                      |
|----------------------------------|--------------------------------------|
| F. C. Adams, Antwerp             | E. Pungor, Budapest                  |
| R. P. Buck, Chapel Hill, N.C.    | J. P. Riley, Liverpool               |
| E. A. M. F. Dahmen, Enschede     | J. W. Robinson, Baton Rouge, La.     |
| G. den Boef, Amsterdam           | J. Růžička, Copenhagen               |
| G. Duyckaerts, Liège             | D. E. Ryan, Halifax, N.S.            |
| D. Dyrssen, Göteborg             | W. Simon, Zürich                     |
| W. Haerdi, Geneva                | R. K. Skogerboe, Fort Collins, Colo. |
| G. M. Hieftje, Bloomington, Ind. | W. I. Stephen, Birmingham            |
| J. Hoste, Ghent                  | G. Tölg, Schwäbisch Gmünd, B.R.D.    |
| A. Hulanicki, Warsaw             | A. Townshend, Birmingham             |
| E. Jackwerth, Bochum             | B. Trémillon, Paris                  |
| G. Johansson, Lund               | A. Walsh, Melbourne                  |
| D. C. Johnson, Ames, Iowa        | H. Weisz, Freiburg i Br.             |
| J. H. Knox, Edinburgh            | P. W. West, Baton Rouge, La.         |
| P. D. LaFleur, Washington, D.C.  | T. S. West, Aberdeen                 |
| D. E. Leyden, Denver, Colo.      | J. B. Willis, Melbourne              |
| H. Malissa, Vienna               | Yu. A. Zolotov, Moscow               |
| A. Mizuike, Nagoya               | P. Zuman, Potsdam, N.Y.              |
| G. H. Morrison, Ithaca, N.Y.     |                                      |

# ANALYTICA CHIMICA ACTA

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

**PUBLICATION SCHEDULE FOR 1979** (incorporating the section on Computer Techniques and Optimization).

	J	F	M	A	M	J	J	A	S	O	N	D
Analytica Chimica Acta	104/1	104/2	105	106/1	106/2	107	108	109/1	109/2	110/1	110/2	111
Section on Computer Techniques and Optimization			112/1			112/2			112/3			112/4

**Scope.** *Analytica Chimica Acta* publishes original papers, short communications, and reviews dealing with every aspect of modern chemical analysis, both fundamental and applied. The section on *Computer Techniques and Optimization* is devoted to new developments in chemical analysis by the application of computer techniques and by interdisciplinary approaches, including statistics, systems theory and operation research. The section deals with the following topics: Computerized acquisition, processing and evaluation of data. Computerized methods for the interpretation of analytical data including chemometrics, cluster analysis, and pattern recognition. Storage and retrieval systems. Optimization procedures and their application. Automated analysis for industrial processes and quality control. Organizational problems.

**Submission of Papers.** Manuscripts (three copies) should be submitted to:

for *Analytica Chimica Acta*: Dr. A. M. G. Macdonald, Department of Chemistry, The University, P.O. Box 363, Birmingham B15 2TT, England;

for the section on *Computer Techniques and Optimization*: Dr. J. T. Clerc, Universität Bern, Pharmazeutisches Institut, Sahlstrasse 10, CH-3012 Bern, Switzerland.

American authors are recommended to send manuscripts and proofs by **INTERNATIONAL AIRMAIL**.

**Information for Authors.** Papers in English, French and German are published. There are no page charges. Manuscripts should conform in layout and style to the papers published in this Volume. Authors should consult Vol. 102, p. 253 for detailed information. Reprints of this information are available from the Editors or from: Elsevier Editorial Services Ltd., Mayfield House, 256 Banbury Road, Oxford OX2 7DE (Great Britain).

**Reprints.** Fifty reprints will be supplied free of charge. Additional reprints (minimum 100) can be ordered. An order form containing price quotations will be sent to the authors together with the proofs of their article.

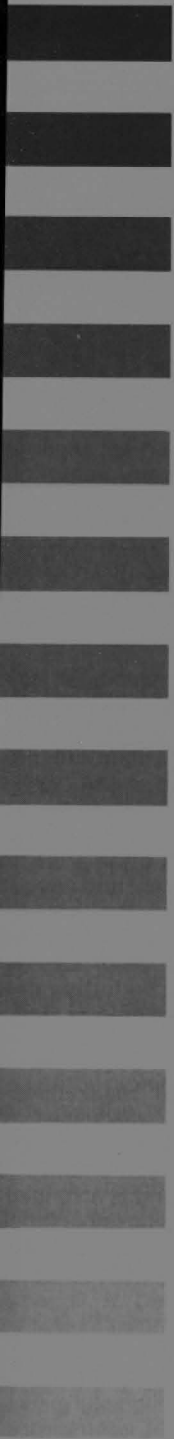
**Advertisements.** Advertisement rates are available from the publisher.

**Subscriptions.** Subscriptions should be sent to: Elsevier Scientific Publishing Company, P.O. Box 211, 1000 AE Amsterdam, The Netherlands. The section on *Computer Techniques and Optimization* can be subscribed to separately.

**Publication.** *Analytica Chimica Acta* (including the section on *Computer Techniques and Optimization*) appears in 9 volumes in 1979. The subscription for 1979 (Vols. 104–112) is Dfl. 1179.00 plus Dfl. 135.00 (postage) (total approx. U.S. \$641.00). The subscription for the *Computer Techniques and Optimization* section only (Vol. 112) is Dfl. 131.00 plus Dfl. 15.00 (postage) (total approx. U.S. \$71.00). Journals are sent automatically by air mail to the U.S.A. and Canada at no extra cost and to Japan, Australia and New Zealand for a small additional postal charge. All earlier volumes (Vols. 1–103) except Vols. 23 and 28 are available at Dfl. 150.00 (U.S. \$73.00), plus Dfl. 10.00 (U.S. \$5.00) postage and handling, per volume.

Claims for issues not received should be made within three months of publication of the issue, otherwise they cannot be honoured free of charge.

Customers in the U.S.A. and Canada who wish to obtain additional bibliographic information on this and other Elsevier journals should contact Elsevier/North Holland Inc., Journal Information Center, 52 Vanderbilt Avenue, New York, NY 10017. Tel: (212) 867-9040.



*Full information  
on the latest volumes in the*

# **JOURNAL OF CHROMATOGRAPHY LIBRARY**

*A Series of Books Devoted to  
Chromatographic Techniques and  
Their Applications*

Although complementary to the Journal of Chromatography, each volume in the library series is an important and independent contribution to the field of chromatography. It should be stressed that the library contains no material reprinted from the journal itself.

**ELSEVIER SCIENTIFIC PUBLISHING COMPANY**  
Amsterdam and New York

**Volume 18  
ELECTROPHORESIS  
A Survey of Techniques and  
Applications. Part A: Techniques**

*edited by Z. Deyl*  
*co-editors: F. M. Everaerts, Z. Prusik and P. J. Svendsen*

**1979 xvi + 392 pages**  
**Price: US \$83.00 / Dfl. 170.00**  
**ISBN 0-444-41721-4**

This first volume in a two-part set, deals with the principles, theory and instrumentation of modern electromigration techniques. The second part will be concerned with the detailed applications of electromigration methods to all diverse categories of compounds, although to a limited extent some applications are discussed in Part A.

Electromigration methods have been so extensively used in the past for both analytical and preparative separations that several of these methods have become standard procedures. These are discussed in the book together with newer developments in the field. Hints are included to help the reader to overcome the difficulties which often arise from the lack of available equipment and adequate theoretical background of the individual techniques is also given. A theoretical approach to the deteriorative processes is presented in order to facilitate further development of a particular technique and its application to a special problem.

In each chapter practical realizations of different techniques are discussed and examples are presented to demonstrate the limits of each method. The mathematical and physicochemical background is arranged so as to make it as coherent as possible for both non-professionals, such as post-graduate students, and experts using electromigration techniques.

**CONTENTS:** Preface. Foreword. Introduction  
Chapters: 1. Theory of electromigration processes (*J. Vacík*). 2. Classification of electromigrator methods (*J. Vacík*). 3. Evaluation of the results of electrophoretic separations (*J. Vacík*). 4. Molecular size and shape in electrophoresis (*Z. Deyl*). 5. Zone electrophoresis (except gel-type technique) and immunoelectrophoresis (*W. Ostrowski*). 6. Gel-type techniques (*Z. Hrkal*). 7. Quantitative immunoelectrophoresis (*P. J. Svendsen*). 8. Moving boundary electrophoresis in narrow-bore tubes (*F. M. Everaerts and J. L. Beckers*). 9. Isoelectric focusing (*N. Catsimpoolas*). 10. Analytical

ctachophoresis (J. Vacík and F. M. Everaerts) 11. Continuous flow-through electrophoresis (Z. Husík). 12. Continuous flow deviation electrophoresis (A. Kolin). 13. Preparative electrophoresis in media (Z. Hrkal). 14. Preparative electrophoresis in columns (P. J. Svendsen). 15. Preparative electric focusing (P. Blanický). 16. Preparative ctachophoresis (P. J. Svendsen). 17. Preparative ctachophoresis on the micro scale (L. Arlinger). st of frequently occurring symbols. Subject dex.

## Volume 17 5 YEARS OF CHROMATO- GRAPHY – A HISTORICAL DIALOGUE

Edited by L. S. Ettre and A. Zlatkiss

1979 xiv + 502 pages  
Price: US \$54.75 / Dfl. 112.00  
ISBN 0-444-41754-0

On the occasion of the 75th anniversary of the invention of chromatography, this book compiles the personal stories of 59 pioneers of the various chromatographic techniques including five Nobel Prize laureates).

In their contributions to this volume, these pioneers review the events which influenced them to enter the field; explain the background of their inventions; summarize their activities and results during their professional lives; and discuss their interactions with other scientists and other disciplines. The book is completed by a chapter devoted to those who are no longer with us".

This book is more than a nostalgic recollection of the past for those who have been in chromatography for some time. It also provides, for the younger generation of chromatographers, a unique record of how recent-day knowledge was accumulated as well as an insight into the background of the methods and techniques which they use in their daily work.

**CONTRIBUTORS:** E. R. Adlard, H. Boer, E. Bremer, D. H. Desty, G. Dijkstra, L. S. Ettre, P. Godin, C. W. Gehrke, J. C. Giddings, E. Glueckauf, J. J. E. Golay, D. W. Grant, E. Heftmann, G. Hesse, H. Higgins, E. C. Horning, M. G. Horning, Cs. Orváth, J. F. K. Huber, A. T. James, J. Janák, R. E. Kaiser, A. Karmen, J. G. Kirchner, J. J. Kirkland, A. Kiselev, E. sz. Kováts, E. Lederer, M. Lederer, A. Bertini, S. R. Lipsky, J. E. Lovelock, A. J. P. Martin, Moore, H. W. Patton, C. S. G. Phillips, J. Porath, Pretorius, G. R. Primavesi, N. H. Ray, L. Rohrhneider, K. I. Sakodynskii, G. Schomburg, G.-M. Schwab, R. D. Schwartz, C. D. Scott, R. P. W. Scott, T. Seaborg, M. S. Shraiber, L. R. Snyder, E. Stahl, W. H. Stein, H. H. Strain, F. H. Stross, R. L. M. Yngve, R. Teranishi, J. J. van Deemter, A. A. hukhovitskii, A. Zlatkiss.

## Volume 16 POROUS SILICA

### Its Properties and Use as Support in Column Liquid Chromatography

by K. K. Unger

1979 xii + 336 pages  
Price: US \$58.50 / Dfl. 120.00  
ISBN 0-444-41683-8

Although an enormous amount of literature exists about basic surface chemistry of silica on the one hand, and about its use as packing in high-performance liquid chromatography on the other, no comprehensive and systematic survey has previously been published to cover both subjects.

This book covers both treatments and provides the chromatographer with full information on the properties of silica and its chemically bonded derivatives in context with its chromatographic behaviour. The text is divided into two parts: the first deals with the physical and chemical properties of silica including pore structure, surface chemistry, particle preparation and characterization, while the second surveys the wide-spread application of untreated and chemically modified silica as adsorbent, support and ion exchanger in the four modes of HPLC, i.e. adsorption, partition, ion exchange and size exclusion chromatography. A separate chapter is devoted to packing procedures and performance of silica columns.

**CONTENTS:** 1. General Chemistry of Silica. 2. Pore Structure of Silica. 3. Surface Chemistry of Porous Silica. 4. Particle Characteristics. 5. Silica Columns – Packing Procedures and Performance Characteristics. 6. Silica and Its Chemically Bonded Derivatives as Adsorbents in Liquid-Solid Chromatography. 7. Silica as a Support in Liquid-Liquid Chromatography. 8. Chemically Modified Silica as Packing in Ion-Exchange Chromatography. 9. Silica as Packing in Size-Exclusion Chromatography. Appendix: Commercially Available Silica Packings. List of Symbols and Abbreviations. Subject Index.

## Volume 15 ANTIBIOTICS

### Isolation, Separation and Purification

edited by M. J. Weinstein and G. H. Wagman

1978 x + 772 pages  
Price: US \$95.00 / Dfl. 195.00  
ISBN 0-444-41727-3

This book has been written in response to the great interest currently being shown in modification of some of the older, and many newer

antibiotics to improve upon existing, naturally produced compounds.

Twenty-four eminent scientists in the field of antibiotic isolation have contributed chapters on key chemical families of antibiotics, with emphasis placed on isolation, separation and purification of these substances, many of which can be used as starting materials for further modification. In addition the authors have provided brief summaries of the chemical, physical and biological properties, usage and structural formulae of many of the compounds. Isolation methods include solvent and resin extractions, counter-current distribution, gas-liquid and high-pressure chromatography and electrophoresis. Many of the recently discovered naturally produced antibiotics are also discussed.

**CONTENTS:** Actinomycins (*A. Mauger and E. Katz*). Ansamycins (*A. Ganguly*). Cephalosporin Antibiotics (*R. L. Hamill and L. W. Crandall*). Coumarin-Glycoside Antibiotics (*J. Berger and A. D. Batcho*). 2-Deoxystreptamine-Containing Antibiotics (*J. A. Marquez and A. Kershner*). Griseofulvins (*G. H. Wagman and M. J. Weinstein*). Lincomycin Related Antibiotics (*T. E. Eble*). Macrolide Antibiotics (*J. P. Majer*). Marine-Derived Antibiotics (*L. S. Shield and K. L. Rinehart, Jr.*). Penicillins and Related Antibiotics (*B. B. Mukherjee and B. K. Lee*). Peptide Antibiotics (*E. Gross*). Plant-Derived Antibiotics (*L. A. Mitscher*). Polyether Antibiotics (*R. L. Hamill and L. W. Crandall*). Siderochromes (*H. Maehr*). Streptomycin-Containing Antibiotics (*D. Perlman and Y. Ogawa*). Streptothricins and Related Antibiotics (*A. S. Khokhlov*). Tetracyclines (*S. Neidleman*). Subject Index.

## Volume 14 RADIOCHROMATOGRAPHY The Chromatography and Electrophoresis of Radiolabelled Compounds

by *T. R. Roberts*

1978 x + 174 pages  
Price: US \$44.00 / Dfl. 90.00  
ISBN 0-444-41656-0

The aim of this book is to describe and discuss all of the various radiochromatography and radioelectrophoresis methods in a single volume. For each technique, the historical development is outlined and the relative merits of the radiochemical detection methods currently available are assessed. This is followed by a discussion of the method of choice for any particular application. Each chapter also describes in detail the practical aspects of the various techniques and provides examples of applications taken from the recent literature.

**CONTENTS:** Introduction. Radioactivity detectors used in chromatography. Radio-paper chromatography. Radio-thin-layer chromatography. Radio-electrophoresis. Radio-column chromatography. Radio-gas-liquid chromatography. Miscellaneous applications related to radiochromatography. Appendix. Subject Index.

## Volume 13 INSTRUMENTATION FOR HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

edited by *J. F. K. Huber*

1978 xii + 204 pages  
Price: US \$39.00 / Dfl. 80.00  
ISBN 0-444-41648-X

A practical guide for all those involved in the application of column liquid chromatography, this book provides a valuable, up-to-date review of the large selection of instrumentation currently available, describing the general design features and the specific technical solutions in the instrumentation for high-performance liquid chromatography. For the purposes of this survey, the chromatographic system has been divided into a number of interacting sub-systems and these are described in detail by experts in the field. Special emphasis is given to discussion of the general principles of design which will remain relevant even if new technical solutions are found in the future.

**CONTENTS:** The chromatographic apparatus from the viewpoint of system theory (*J. F. K. Huber*). Pump systems (*M. Martin and G. Guiochon*). Solvent gradient systems (*M. Martin and G. Guiochon*). Sample introduction systems (*J. C. Kraak*). Column design selection (*J. C. Kraak*). Components and accessories for preparative high-performance liquid chromatography (*A. Wehrli*). Detectors based on the measurement of optical and electrical properties of the mobile phase (*H. Poppe*). Electrochemical detectors (*H. Poppe*). Radiometric detectors (*P. Markl*). Combination of liquid chromatography and mass spectrometry (*E. Kenndler and E. R. Schmid*). Specifications of commercial liquid chromatographs (*R. R. Becker*). Subject index. Manufacturer index.

## Volume 12 AFFINITY CHROMATOGRAPHY

by *J. Turková*

1978 x + 406 pages  
Price: US \$81.50 / Dfl. 167.00  
ISBN 0-444-41605-6

This book reviews the application of affinity chromatography for the isolation of various

biologically active substances. The reviewing volume comprises almost 1,400 references and is completed by data on use of solid supports and spacers. Great attention is given to the review of the most commonly used solid supports and to the method of attachment, together with the methods of characterization of both the carriers and the immobilized affinity ligands.

This extensive and up-to-date review is included mainly for biochemists and biologists. It will be particularly useful to technicians engaged in human or veterinary medicine, as well as to those dealing with chromatography and industrial chemistry.

**CONTENTS:** Introduction. The principle, history and use of affinity chromatography. Theory of affinity chromatography. Application of affinity chromatography to the quantitative evaluation of specific complexes. General considerations on ion-exchange sorbent bonding. Choice of affinity supports for attachment. Hydrophobic chromatography, covalent affinity chromatography, affinity ion and related methods. Solid matrix supports and the most used methods of binding. Characterization of supports and immobilized affinity ligands. General considerations on adsorption, elution and non-specific binding. Examples of the use of affinity chromatography. Immobilized enzymes. Subject Index. List of compounds chromatographed.

## Volume 11 LIQUID CHROMATOGRAPHY DETECTORS

*R. P. W. Scott*

1977 **x + 248 pages**  
**Price: US \$41.00 / Dfl. 84.00**  
**ISBN 0-444-41580-7**

The rapid development of liquid chromatography over the past decade has been due to the introduction of highly sensitive linear liquid chromatography detectors. This book provides a comprehensive treatment of the action and optimal working conditions of liquid chromatography detectors. It is divided into four parts.

Part 1 includes a detailed discussion of properties of the detecting system that can impair column performance and how these defects can be minimized. In Parts 2 and 3, the various types of detectors that have been developed are described and a detailed treatment given of commercially available detectors. Part 4 discusses the practical operation of liquid chromatography, including methods for quantitative analysis as well as practical hints on detector operation and special detector techniques. The final

chapter deals with spectroscopic detectors and provides a detailed description of LC/UV and LC/MS systems.

This work is particularly useful because of the presentation of the necessary detector specifications which enables readers to make a rational comparison of the performance of one detector with that of another.

**CONTENTS:** Introduction. General characteristics of liquid chromatography detectors. Bulk property detectors. Solute property detectors. The use of detectors in liquid chromatography. Subject Index.

## Volume 10 GAS CHROMATOGRAPHY OF POLYMERS

*by V. G. Berezkin, V. R. Alishoyev and I. B. Nemirovskaya*

1977 **xiv + 226 pages**  
**Price: US \$50.25 / Dfl. 103.00**  
**ISBN 0-444-41514-9**

This book is devoted to the strategy of application of gas chromatography in polymer chemistry and discusses, in detail, the use of gas chromatography in research work and the polymeric compounds industry. It is the second, revised and enlarged edition of the original version published in the USSR in 1972.

## Volume 9 HPTLC - HIGH PERFORMANCE THIN-LAYER CHROMATOGRAPHY

*edited by A. Zlatkis and R. E. Kaiser*

1977 **240 pages**  
**Price: US \$53.75 / Dfl. 110.00**  
**ISBN 0-444-41525-4**

HPTLC is the advanced technology of thin-layer chromatography and is defined as the combined action of several variables which include: an optimized coating material with a separation power superior to the best high performance liquid chromatographic separation material; a new method of feeding the mobile phase; a novel procedure for layer conditioning; a considerably improved dosage method and a competent data acquisition and processing system. Thus a complete system and procedure is discussed here. This should be understood as a step-wise improvement of an analytical method,

which has been a powerful tool since the pioneering work of E. Stahl.

**CONTENTS:** Simplified theory of TLC (*R. E. Kaiser*). The separation number in linear and circular TLC (*J. Blome*). Advantages, limits and disadvantages of the ring developing technique (*J. Blome*). The U-chamber (*R. E. Kaiser*). Dosage techniques in HPTLC (*R. E. Kaiser*). High performance thin-layer chromatography: development, data and results (*H. Halpaap and J. Rippahn*). Consideration on the reproducibility of TLC separations (*D. Jaenchen*). Potential and experience in quantitative HPTLC (*U. B. Hezel*). Application of a new high-performance layer in quantitative TLC (*J. Rippahn and H. Halpaap*). Appendix. Index.

## Volume 8 CHROMATOGRAPHY OF STEROIDS

by *E. Heftmann*

1976 xiv + 204 pages  
Price: US \$44.00 / Dfl. 90.00  
ISBN 0-444-41441-X

Although some theory is included, this is mainly a laboratory handbook, arranged according to the steroids analyzed as well as according to the methods used. Currently used techniques are described in detail.

**CONTENTS:** Introduction. Liquid column chromatography. Paper and thin-layer chromatography. Gas chromatography. Relations between structure and chromatographic mobility. Sterols. Bile acids and alcohols. Estrogens. Androstane derivatives. Pregnane derivatives. Corticosteroids. Miscellaneous steroid hormones. Vitamins D. Molting hormones. Steroid sapogenins and alkaloids. Cardenolides and bufadienolides. List of Abbreviations. References. Subject Index.

## Volume 7 CHEMICAL DERIVATIZATION IN LIQUID CHROMATOGRAPHY

by *J. F. Lawrence and R. W. Frei*

1976 viii + 214 pages  
Price: US \$44.00 / Dfl. 90.00  
ISBN 0-444-41429-0

This book is intended for all investigators concerned with the use of physical separation techniques for solving complex analytical problems. It provides a comprehensive account of modern derivatization in liquid chromatography with special emphasis on the practical aspects.

## Volume 6 ISOTACHOPHORESIS Theory, Instrumentation and Applications

by *F. M. Everaerts, J. L. Beckers and  
Th. P. E. M. Verheggen*

1976 xiv + 418 pages  
Price: US \$78.00 / Dfl. 160.00  
ISBN 0-444-41430-4

This book is the only text currently available providing full information on the new separation technique known as Isotachopheresis. The various chapters can be referred to more or less independently by scientists interested in fundamental aspects, by research group intending to construct an instrument and by workers concerned mainly with the analytical aspects.

## Volume 5 INSTRUMENTAL LIQUID CHROMATOGRAPHY A Practical Manual on High-Performance Liquid Chromatographic Methods

by *N. A. Parris*

1976 second impression 1979  
x + 330 pages  
Price: US \$48.75 / Dfl. 100.00  
ISBN 0-444-41427-4

Available texts on liquid chromatography have tended to emphasize the development in the theoretical understanding of the technique and methodology or to list numerous applications, complete with experimental details.

This work intends to bridge the gap between these two treatments by providing, with the minimum of theory, a practical guide to the use of the technique for the development of separations. The material is based largely on practical experience and highlights detail which may have important operational value for laboratory workers.

**CONTENTS:** Introduction and historical background. Basic principles and terminology. Chromatographic support and column. Liquid chromatographic instrumentation. Liquid chromatographic detection systems. Nature of the mobile phase. Liquid-solid (adsorption) chromatography. Liquid-liquid (partition) chromatography.



hy. Ion-exchange chromatography. Steric exclusion chromatography. Qualitative analysis. Titrimetric analysis. Practical aspects of trace analysis. Practical aspects of preparative liquid chromatography. Published LC applications information. The latest trends and a glimpse into the future. Subject Index.

## Volume 4 FACTORS IN GAS CHROMATOGRAPHY

Edited by Ševčík

5 192 pages  
Price: US \$34.25 / Dfl. 70.00  
ISBN 0-444-99857-8

The first systematic treatment of gas chromatographic techniques, this publication draws special attention to so-called specific factors and working conditions which strongly influence results (e.g. gas flow, effect of additives in gases, working temperature, detector form and dimensions).

## Volume 3 LIQUID COLUMN CHROMATOGRAPHY

Survey of Modern Techniques and Applications

Edited by Z. Deyl, K. Macek and J. Janák

5 xxiii + 1176 pages  
Price: US \$141.50 / Dfl. 290.00  
ISBN 0-444-41156-9

A wide selection of applications in various fields of chemistry and biochemistry, written by specialists in the area, makes this volume an essential reference work for those interested in chromatographic investigations.

## Volume 2 GRAVITY CHROMATOGRAPHY

Edited by T. Braun and G. Ghersini

5 xviii + 566 pages  
Price: US \$68.25 / Dfl. 140.00  
ISBN 0-444-99878-0

This volume is the result of the collective work of many specialists, each responsible

for a chapter in which a definite aspect of column extraction chromatography is thoroughly presented and discussed.

## Volume 1 CHROMATOGRAPHY OF ANTIBIOTICS

by G. H. Wagman and M. J. Weinstein

1973 x + 238 pages  
Price: US \$46.25 / Dfl. 95.00  
ISBN 0-444-41106-2

This book has been written to aid the identification of very similar compounds by use of specific chromatographic techniques. It contains detailed data on paper and thin-layer chromatography, electrophoresis, counter-current distribution and gas chromatographic systems for over 1,200 antibiotics and their derivatives, and provides information on chromatographic media, solvents, detection methodology and mobility of the antibiotics.

Announcing a New Elsevier Series:

## CHROMATOGRAPHY SYMPOSIA SERIES

Volume 1

### RECENT DEVELOPMENTS IN CHROMATOGRAPHY AND ELECTROPHORESIS

Proceedings of the 9th International Symposium on Chromatography and Electrophoresis, Riva del Garda, 15-17 May, 1978

edited by A. Frigerio and L. Renoz

1979 x + 358 pages  
Price: US \$58.50 / Dfl. 120.00  
ISBN 0-444-41785-0

# ORDER FORM

Send to your bookseller or

For the U.S.A. and Canada:

ELSEVIER NORTH-HOLLAND INC.,  
52 Vanderbilt Avenue, New York, N.Y. 10017

For Australia and New Zealand:

D.A. BOOK DEPOT PTY. LTD.,  
11-13 Station Street, Mitcham, Vic. 3132

For India:

ALLIED PUBLISHERS PRIVATE LTD.,  
Bombay, New Delhi, Calcutta, Madras, Bangalore

For all other countries:

ELSEVIER SCIENTIFIC PUBLISHING CO.,  
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

Please send me the following books \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

Please enter my continuation order for the

JOURNAL OF CHROMATOGRAPHY LIBRARY beginning with volume \_\_\_\_\_

CHROMATOGRAPHY SYMPOSIA SERIES

Customers in North America wishing information on library series direct order plans are requested to contact Elsevier North-Holland Inc  
52 Vanderbilt Avenue, New York, N.Y. 10017.

Orders from individuals must be accompanied by a remittance, following which books will be sent postfree.

I enclose

my personal cheque

bank draft

UNESCO coupons

Name \_\_\_\_\_

Address \_\_\_\_\_  
\_\_\_\_\_

Postal Code \_\_\_\_\_

Signature \_\_\_\_\_

Date \_\_\_\_\_

## INTERFACIAL PROPERTIES OF PRECIPITATE-BASED ION-SELECTIVE ELECTRODES

### Rotating Disk Impedance Measurements of the $\text{Ag}_2\text{S}/\text{Ag}^+$ (aqueous) Interface

RATHBUN K. RHODES and RICHARD P. BUCK\*

*William Rand Kenan, Jr. Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514 (U.S.A.)*

(Received 1st May 1979)

#### SUMMARY

Three-electrode rotating disk impedance measurements were made from 31.6 kHz to 0.0178 Hz on  $\text{Ag}_2\text{S}/\text{Ag}^+$  (aqueous) and  $\text{Ag}_2\text{S}/\text{Ag}$  systems. Membranes were prepared from materials precipitated in excess of silver or sulfide ions, and stoichiometric mixtures. Impedances were analyzed, as a function of rotation rate and bathing activities, to isolate bulk conductivities, internal diffusion, surface kinetic and dissolution/crystallization impedances. High-frequency bulk resistivities,  $R_\infty$ , varied by four with precipitation and pressing conditions. Resistivities were the same for solution and ohmic configurations for each preparation. For ohmic contacts,  $R_\infty$  and  $R(\text{DC})$  were identical. Solution contact cells in  $10^{-1}$  M and  $10^{-2}$  M bathing silver ion solution gave identical frequency-dependent impedances which were independent of rotation rate. Thus, solution diffusional impedances and solution dependent surface kinetics were eliminated, and a finite Warburg, interior- $\text{Ag}^+$ -defect, diffusion impedance was indicated. Summation of bulk membrane and contact resistances, and this Warburg impedance served as a 'background' correction in analyzing dilute bathing solution interfacial impedances for surface effects. Corrected impedances in  $10^{-3}$ – $10^{-5}$  M  $\text{AgNO}_3$  showed solution diffusional behaviour combined with surface kinetic and dissolution impedances. An iterative linear least-squares method resolved these quantities. The surface resistance suggests a potential-dependent rate constant; dissolution time constants were solution-independent and smaller than those for solution diffusion. Thus, dissolution can be a rate-limiting step in establishment of steady-state potentials.

Since the introduction of precipitate-based ion-selective electrodes, there have been many theoretical and experimental studies of their response mechanisms. Buck [1] applied the theory of reversible ion exchange at the membrane surface as the potential-determining mechanism for silver halide, silver sulfide and mixed sulfide electrodes. Brand and Rechnitz [2] made dual-probe impedance measurements, at high electroactive ion concentrations, on the first commercially available silver sulfide-based electrodes. They concluded that these electrodes behaved like blocking capacitors in series with the solution and membrane resistances. However, later exchange-current measurements by Cammann and Rechnitz [3] and conductivity studies by Koebel et al. [4] demonstrated that this result, inconsistent with interfacial reversibility, could be attributed to background reference elec-

trode impedance. Both of these studies demonstrated extremely fast ion exchange with no measurably slow surface kinetics at silver ion concentrations of  $10^{-3}$  M or higher. At lower concentrations, solution diffusional polarization makes it impossible to resolve surface and bulk diffusion effects by these methods.

However, since slower time responses occur at very low concentrations of responsive salts [5, 6], especially near the limits of detection, it is obvious that some surface kinetic limiting process may be occurring and may be coupled with slow mass transport. Buffle and Parthasarathy [7, 8] monitored the change of solution conductivity in dilute  $\text{Ag}^+$  and  $\text{Cl}^-$  solutions for mixed silver sulfide—silver chloride electrodes, and showed a correlation of membrane dissolution with the time required to reach a steady potential. Shatkay [9] reported concentration step experiments to develop and test empirical equations for electrode time responses. Our experimental preference for studying these phenomena is the three-electrode rotating disk impedance method. Three-electrode potentiostating removes the large reference electrode impedance observed in two-probe measurements at low concentrations and the rotating disk configuration reduces solution diffusional impedances in an exact form. Both effects combine to improve greatly resolution of any ongoing surface processes. In addition, the impedance method allows separation of processes in the frequency domain [10], although the ease of separation will depend on the respective time constants and magnitudes of the apparent impedances. In the best cases, inspection of resolved impedance plots is all that is required to determine response parameters, while some form of least-squares fitting must be applied to more strongly melded cases [11, 12].

## EXPERIMENTAL

### *Preparation of electrodes*

The silver sulfide used to make the electrodes was prepared at room temperature by mixing of 1.0 M  $\text{AgNO}_3$  and 0.4 M  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  solutions. One reagent was added slowly to a stirred solution containing excess of the other reagent. The precipitates were prepared with (1) 100% excess  $\text{Ag}^+$ , (2) 100% excess  $\text{S}^{2-}$ , and (3) stoichiometric quantities of reagents. These were heated and digested at  $75^\circ\text{C}$  with constant stirring for 45 min. The supernatant solutions were decanted and the precipitates washed 4 times with 200-ml portions of distilled water at  $75^\circ\text{C}$ , twice with 0.1 M nitric acid at room temperature and twice more with distilled water at room temperature. Lastly, the precipitates were washed with 100 ml of reagent-grade acetone and suction-filtered for 15 min. The resultant fine powder was dried overnight at  $90^\circ\text{C}$ .

Preparation of low-resistance ohmic contacts to silver sulfide membranes at room temperature has been discussed in depth by Koebel et al. [4]. Instead of pressing silver metal directly to the silver sulfide, which results in a changing contact resistance, they recommended an intermediate layer

of silver powder mixed with silver sulfide between layers of silver powder and silver sulfide. This procedure provides a greater effective contact area to minimize contact resistance. Accordingly, the present electrodes were prepared by this three-layer sandwich technique; the layers consisted of 0.5 g of silver powder, 0.6 g of equal portions of silver powder and  $\text{Ag}_2\text{S}$ , and 0.8 g of  $\text{Ag}_2\text{S}$ , to give membranes for the solution contact configuration with the format

$\text{Ag}|\text{Ag}, \text{Ag}_2\text{S}|\text{Ag}_2\text{S}|\text{Ag}^+$  (aqueous)

A membrane of each preparation was also pressed in the symmetric ohmic contact configuration

$\text{Ag}|\text{Ag}, \text{Ag}_2\text{S}|\text{Ag}_2\text{S}|\text{Ag}, \text{Ag}_2\text{S}|\text{Ag}$

to allow comparison of bulk conductivity measurements with electronically unblocked, as well as blocked contacts. These layers were packed in a 13-mm KBr die and two pellets of each preparation pressed, one at room temperature and the other at 300°C. A final pressure of 75,000 psi was applied for 20 min during room-temperature pressing and for 3 h during the hot pressing. The alternative modes of pellet preparation allowed comparison of impedance characteristics as a function of material preparation and pressing conditions.

After pressing, the solution contact membranes were epoxy-sealed, silver side inward, into precut Teflon bodies (0.570-in. o.d., 0.510-in. i.d., 0.075-in. lip). Polishing with 180-grain sandpaper down to 1- $\mu\text{m}$  Metadi diamond compound gave a smooth continuous surface across the face of the membrane and the electrode body. The electrode was threaded from the top to allow ohmic contact of the silver to the shaft of a Beckman rotating electrode. Electrical continuity from the rotating shaft of the electrode to the impedance instrumentation was provided by a carbon wiper on copper contact.

### *Measurement procedures*

From the rotating disk configuration the potentiometric response of the  $\text{Ag}_2\text{S}$  electrodes versus an Orion double-junction reference electrode was verified in serial diluted solutions of  $\text{pAg}$  1–5. In all solutions sufficient potassium nitrate was added to increase the ionic strength to 0.1 M. Slopes of the responses were 57–59 mV/(log  $a_{\text{Ag}^+}$ ). Reproducibility of points was better than 0.5 mV over three calibrations, and standard potentials were within 2 mV of the theoretical value [13].

When equilibrium behaviour of the electrodes had been established, impedance measurements were made. The bridge operated on the same principles described previously [14] with the addition of a three-electrode potentiostat and a more versatile integrator. For the symmetric ohmic configuration, measurements were made in the two-probe mode at the equilibrium potential. For the solution contact configuration, measurements

were made in the three-electrode mode at the equilibrium potential with controlled rotation of the working electrode. In both cases the a.c. excitation was less than 25 mV peak-to-peak. In solution contact experiments, the auxiliary electrode was a 4-cm<sup>2</sup> silver flag surface anodized to Ag<sub>2</sub>S and positioned 3 cm below the working electrode. The reference electrode was a silver wire (0.1-cm diameter) partially anodized to Ag<sub>2</sub>S and positioned 0.2 cm from the working electrode. Solution volumes were ca. 100 ml and temperature was maintained to within 0.1°C by a Beckman thermocirculator. Measurements were made at 20.0 ± 0.1°C unless otherwise specified. Nitrogen degassing of dilute solutions was found not to affect the impedance characteristics of these electrodes and was discontinued for the remainder of the runs.

Bulk membrane conductivities were measured for all preparations at the lowest frequency that provided a zero quadrature impedance component. Values for membranes in the solution contact configuration were also measured as a function of temperature (20–35°C) to give activation energies of transport. Variation of electrode impedance as a function of solution pAg was measured for all preparations at a working electrode rotation speed of 36 rps and for selected preparations at 0 rps. This experiment allowed comparison of finite and infinite solution diffusion conditions of the electroactive species. This effect was further investigated at several rotation rates in 10<sup>-5</sup> M AgNO<sub>3</sub> for one of the electrodes.

For all runs, applied frequency was systematically varied from 31.6 kHz to 0.0178 Hz in quarter-decade intervals on a log frequency scale. The resulting admittance data were converted through the usual transforms to impedances. All impedance plotting, data regression and parametric data fitting were done with the aid of an IBM 360.

### *Reagents*

The silver used to make ohmic contact to the silver sulfide membranes was 100-mesh powder of 99.99% purity (Alpha Research Chemicals). The Na<sub>2</sub>S·9H<sub>2</sub>O, AgNO<sub>3</sub> and KNO<sub>3</sub> used for preparing standard solutions and synthesizing the membrane materials were Fisher Scientific A.C.S. grade. Distilled water used showed resistivity greater than 6MΩ-cm and the nitrogen used was electrochemical grade.

## RESULTS

### *Determination of bulk membrane and other "background" impedances*

Silver sulfide is a mixed electronic-ionic conductor. Thus, its conductivity will vary as preparation conditions vary the concentrations of electrons, holes, and silver ion interstitials. At high temperatures, extrinsic electronic donor/acceptor doping and ionic doping dominate conductivity in a reproducible way. However, at room temperature, equilibration is slow and even trace impurities and grain boundaries influence conductivity and render

measurements dependent on many uncontrollable factors in the preparation. As shown in Table 1, the high-frequency bulk conductivity values for the solution contact configuration varied as a function of precipitation and pressing conditions from  $1.94 \times 10^{-3} \text{ S cm}^{-1}$  to  $4.32 \times 10^{-4} \text{ S cm}^{-1}$ . The value of  $1.75 \times 10^{-3} \text{ S cm}^{-1}$  for all pressing conditions of the stoichiometric composition is comparable with  $1.5 \times 10^{-3} \text{ S cm}^{-1}$  reported by Koebel et al. [4], and is higher than the  $7 \times 10^{-4} \text{ S cm}^{-1}$  reported by Cammann and Rechnitz [3]. The present values decreased by as much as 50% during a period of a month. This effect indicates that the silver/silver sulfide interface was not at equilibrium and that the contact resistance increased. In addition, values for transport activation energies, calculated from the temperature-dependence of the bulk conductivity by the equation  $\sigma = \sigma_0 \exp(-E_a/kT)$ , were much higher (0.30–0.45 eV) than the high-temperature intrinsic value 0.16 eV [15]. It is probable that the resistivity observed at room temperature is a series combination of bulk membrane and contact resistances.

When the symmetric ohmic contact configuration was used, the bulk conductivity measurements were frequency-independent as expected, since no mobile charge carriers were blocked at the Ag/Ag<sub>2</sub>S interface and the extremely fast diffusion coefficient of electrons (ca.  $10^{-1} \text{ cm}^2 \text{ s}^{-1}$ ) [16] precludes internal diffusion polarization. However, in the solution contact configuration, the conductivity decreased and capacitance increased with decreasing frequency. To verify that this was not merely a solution diffusion or surface kinetic effect, rotating disk measurements were made at 0 and 36 rps in  $10^{-1} \text{ M}$  and  $10^{-2} \text{ M}$  AgNO<sub>3</sub> at constant ionic strength. The resulting impedance plane plots from these four measurements for each electrode were identical within experimental error and are shown for the hot-pressed pellets in Fig. 1. Since electron transport is blocked at the solution interface while silver ions are transported, conditions exist which allow prediction of a finite Warburg impedance caused by the internal diffusion of silver ion interstitials within the pellet thickness. As expected for finite Warburg behaviour, the quadrature component decreases at the lowest frequency (0.01 Hz) while the usual 45° slope is seen at the highest frequencies.

TABLE 1

High-frequency bulk membrane conductivities (17 kHz)

Type <sup>a</sup>	$R_\infty (\Omega)$	$\sigma (\text{S cm}^{-1})$	$E_a (\text{eV})$
CP1	159	$4.3 \times 10^{-4}$	0.32
CP2	46.6	$1.9 \times 10^{-3}$	0.30
CP3	43.9	$1.8 \times 10^{-3}$	0.35
HP1	53.7	$1.2 \times 10^{-3}$	—
HP2	139	$4.5 \times 10^{-4}$	0.45
HP3	39.9	$1.7 \times 10^{-3}$	—

<sup>a</sup>CP = cold-pressed, HP = hot-pressed, 1 = excess Ag<sup>+</sup>, 2 = excess S<sup>2-</sup>, 3 = stoichiometric.

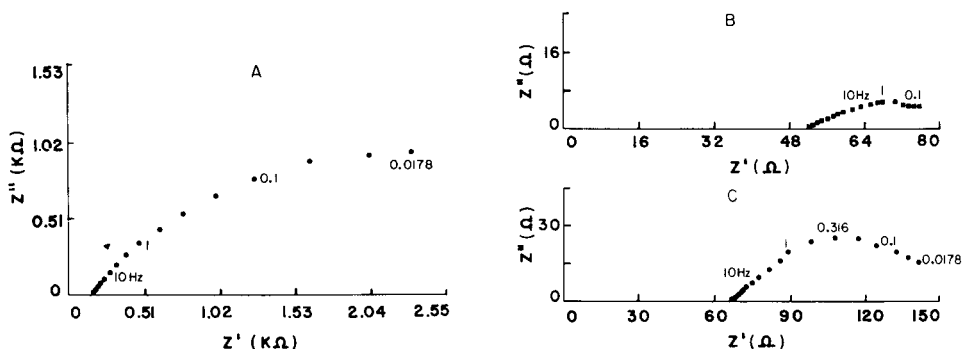


Fig. 1. Impedance plane plot of hot-pressed  $\text{Ag}_2\text{S}$  membranes in stirred and unstirred solutions of  $10^{-4}$  M and  $10^{-2}$  M  $\text{AgNO}_3$ . (A) Excess  $\text{S}^{2-}$ ; (B) stoichiometric; (C) excess  $\text{Ag}^+$ .

The magnitude of the diffusional Warburg impedance varied with membrane preparation. Both hot- and cold-pressed pellets from stoichiometric and excessive silver ion mixtures show Warburg impedances of from 25 to 100 ohms, while pellets prepared with excess of sulfide show Warburg impedances of about 100 ohms for cold-pressed pellets and 2500 ohms for the hot-pressed pellets. The large increase with hot pressing is probably connected with high-temperature oxidation of excess of sulfide to elemental sulfur with resultant depression in electron and interstitial ion concentrations. Since summation of solution, bulk membrane and contact resistances is seldom more than 200 ohms, this internal Warburg effect makes up a large part of the background impedance.

#### Determination and analysis of surface impedances

The measured background impedance was subtracted as each frequency point from the impedance components of the more dilute solution contact measurements to give the impedance of the membrane/solution interface. Results for background-corrected solution contact in  $10^{-4}$  M and  $10^{-5}$  M  $\text{AgNO}_3$  at a rotation rate of 36 rps are shown in Fig. 2. Trends are similar for all electrodes. The striking feature of these plots is the appearance of a finite solution Warburg impedance. (That this is, in fact, a solution-dependent diffusion effect is shown in Fig. 3 by the corresponding infinite Warburg plot in unstirred solution.) Theory [17] and literature values for kinematic viscosity and the silver ion diffusion coefficient [18] predict a concentration-independent maximum quadrature impedance at 3.16 Hz for the diffusion process at this rotation rate. However, with decreasing silver ion concentration the frequency of maximum quadrature impedance also decreases. This result means that a resolvable surface process is occurring and is melded (probably in series) with solution diffusion to cause this maximum quadrature frequency dependence.

To resolve this surface process, assumptions were made on the form



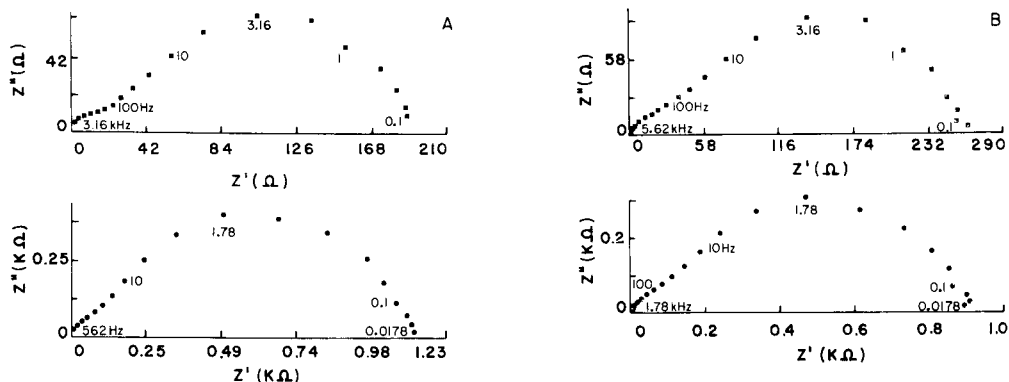


Fig. 2. Impedance plane plots at a rotation rate of 36 rps in (■)  $10^{-4}$  M  $\text{AgNO}_3$  (●)  $10^{-5}$  M  $\text{AgNO}_3$  for (A) cold-pressed  $\text{Ag}_2\text{S}$  membrane (excess  $\text{S}^{2-}$ ) and (B) hot-pressed  $\text{Ag}_2\text{S}$  membrane (stoichiometric).

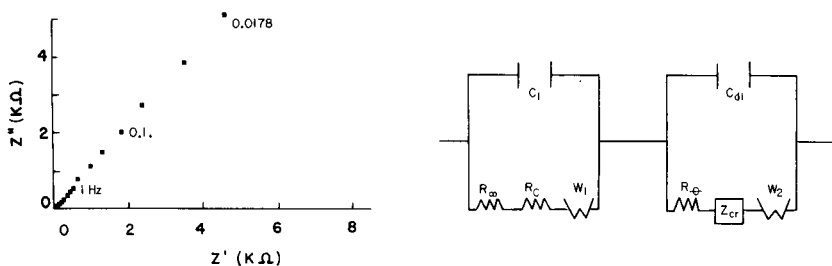


Fig. 3. Impedance plane plot of cold-pressed  $\text{Ag}_2\text{S}$  membrane (excess  $\text{S}^{2-}$ ) in an unstirred solution of  $10^{-5}$  M  $\text{AgNO}_3$ .

Fig. 4. Equivalent circuit representation for the  $\text{Ag}_2\text{S}$  electrode.

of the analogous equivalent circuit (Fig. 4). The bulk membrane resistance ( $R_\infty$ ), contact resistance ( $R_c$ ), internal Warburg impedance ( $W_1$ ) and associated capacitances ( $C_1$ ) are lumped together into one series "element" which serves as the background impedance. The second series element is a parallel kinetic  $RC$  termed  $R_\theta$  and  $C_{d1}$ . The physical significance may be due to a leached layer similar to the glass electrode [19] or an ion-transfer resistance. In series with  $R_\theta$  is a nonequilibrium dissolution/crystallization impedance ( $Z_{cr}$ ) as postulated by Buffle and Parthasarathy [7, 8] and the form of which has been quantitatively described by Vetter [20] and Canagaratna and Karunathilaka [21]. Also included is the finite solution Warburg impedance ( $W_2$ ).

To separate these processes and quantities, the iterative method described by Canagaratna and Karunathilaka [11, 21] was used. First, the impedance of each component is defined

$$Z(R_\theta) = \theta, Z(C_{d1}) = 1/j\omega C_{d1} \quad (1)$$

$$Z(\text{cr}) = \gamma(1 - j(\omega/K))/(1 + (\omega/K)^2) \quad (2)$$

$$Z(W_2) = (\bar{\sigma}/\omega^{1/2})(1 - j)\tanh(\delta_N(j\omega/D_0)^{1/2}) \quad (3)$$

where  $\theta$  is the "surface" resistance,  $j = (-1)^{1/2}$ ,  $\omega$  the angular frequency,  $C_{\text{dl}}$  the relaxed double-layer capacitance,  $\gamma$  the crystallization resistance,  $K$  the crystallization rate constant,  $\bar{\sigma}$  the Warburg coefficient,  $D_0$  the silver ion diffusion coefficient, and  $\delta_N$  the thickness of the Nernst solution diffusion layer. The diffusion thickness is further defined by  $\delta_N = 1.61 D_0^{1/3} \nu^{1/6} \bar{\Omega}^{-1/2}$ , where  $\nu$  is the kinematic viscosity and  $\bar{\Omega}$  the electrode rotation rate. The frequency character of the circuit is then described and analyzed to give expressions for the series resistance and capacitance

$$R_s = [\theta b^2 + ab\bar{\sigma}\omega^{-1/2} + b^2\gamma/(1 + \omega^2K^{-2})]/D \quad (4)$$

$$(1/C_s) = (1/C_{\text{dl}}) [1 - b^2/D - b^2c\omega^{1/2}\bar{\sigma}C_{\text{dl}}/D - b^2\gamma\omega^2K^{-1}C_{\text{dl}}/(1 + \omega^2K^{-2})D] \quad (5)$$

$$D = [b + c\omega^{1/2}\bar{\sigma}C_{\text{dl}} + b\gamma\omega^2K^{-1}C_{\text{dl}}/(1 + \omega^2K^{-2})]^2 + (\omega^2C_{\text{dl}}^2)[b\gamma/(1 + \omega^2K^{-2}) + \theta b + a\bar{\sigma}\omega^{-1/2}]^2 \quad (6)$$

where  $a$ ,  $b$ ,  $c$ , and  $x$  are constants derived from the tanh function of the finite Warburg expression:  $a = \sinh(x) + \sin(x)$ ,  $b = \cosh(x) + \cos(x)$ ,  $c = \sinh(x) - \sin(x)$ , and  $x = (\delta_N^2 2\omega/D_0)^{1/2}$ .

The expressions for  $R_s$  and  $C_s$  are combined into a single expression to give

$$(R_s C_s) [b(b + c\omega^{1/2}\bar{\sigma}C_{\text{dl}})(1 + \omega^2K^{-2}) + (b^2\gamma C_{\text{dl}})(\omega^2K^{-1})] \quad (7)$$

$$= (C_s - C_{\text{dl}}) [(\theta b^2 + ab\bar{\sigma}\omega^{-1/2})(1 + \omega^2K^{-2}) + b^2\gamma]$$

Equation (7) can be expanded at each frequency point about initial guesses for  $\theta$ ,  $C_{\text{dl}}$ ,  $\bar{\sigma}$ ,  $\gamma$  and  $K$  and linearized. Through least-squares normalization the matrix equation  $\hat{A} \cdot \hat{X} = \hat{B}$  results where  $\hat{X} = (\Delta\theta, \Delta C_{\text{dl}}, \Delta\bar{\sigma}, \Delta\gamma, \Delta K)$  and  $\hat{A}$  is a symmetric matrix.  $\hat{X}$  is used to define new guesses for the variables and the process repeated until the  $\Delta$  are sufficiently small. After the final iteration the covariance matrix can be calculated through  $\hat{A}^{-1}$  to give parameter standard deviations.

The estimation of the initial guess for  $\bar{\sigma}$ , the Warburg coefficient, can be made from theory:  $\bar{\sigma} = [RT]/[AF^2N^2C_0(2D_0)^{1/2}]$ , where  $R$  is the gas constant ( $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $A$  the electrode area,  $N$  the ionic charge,  $F$  the Faraday and  $C_0$  the concentration in  $\text{mol cm}^{-3}$ . Values for  $\theta$  and  $C_{\text{dl}}$  were taken from experimental intercept data for  $10^{-3} \text{ M}$  and  $10^{-4} \text{ M}$   $\text{AgNO}_3$  solutions. These quantities were also still visually resolvable from the solution Warburg plot. The same  $C_{\text{dl}}$  value was used as an estimate for the  $10^{-5} \text{ M}$  runs and estimated  $\theta$  value was increased by a factor of 3 over previous runs.  $\gamma$  was estimated from the difference between the total d.c. resistance and the sum of the d.c. resistances caused by  $\bar{\sigma}$  and  $\theta$ .  $K$  was estimated by the shift in the quadrature impedance maximum from that for a pure Warburg impedance. For  $10^{-4} \text{ M}$  and  $10^{-5} \text{ M}$  solutions, con-

vergence for all parameters occurred in 8–10 iterations. Stability conditions were met as long as initial estimates were within a factor of three of the final values. For  $10^{-3}$  M solutions, convergence could not be obtained for  $\bar{\sigma}$ ,  $\gamma$  and  $K$  because of the similar sizes of background and signal, and uncertainty in the background low-frequency data. However, good values for  $\theta$  and  $C_{dl}$  could be obtained and were used to estimate less concentrated solution parameters.

### Experimental impedance parameters

Impedance parameter values and their standard deviations are given in Table 2. Values of  $\theta$ ,  $\bar{\sigma}$  and  $\gamma$  increased as the silver ion concentration decreased for all electrodes.  $\theta$  increased by a factor of 2–4 with a tenfold change in concentration. This effect is similar to that documented for leached surface layers in glass [22] and lanthanum fluoride [23] electrodes. This result agrees with a model for membrane surface resistance developed by Buck [24]. The apparent rate depends on the square root of the product of external (bathing)  $\text{Ag}^+$  and internal (mobile)  $\text{Ag}^+$  species concentrations as

$$k_0 = (RT)/(AN^2F^2)(\bar{a}_{\text{Ag}}a_{\text{Ag}^+})^{1/2}\theta \quad (8)$$

to give a solution-independent value of  $2.1 \times 10^{-4}$  cm s $^{-1}$  in  $10^{-4}$  M and  $10^{-5}$  M silver nitrate solutions. The experimental result is consistent with a potential-dependent rate constant as potential varies through the surface space charge region (ca.  $10^{-4}$  cm) where silver ions adjust from bulk membrane concentration levels (ca.  $10^{-2}$  mol cm $^{-3}$ ) to bulk solution concentrations ( $10^{-8}$  mol cm $^{-3}$ ).

TABLE 2

Impedance parameters from least-squares regression

Type <sup>a</sup>	AgNO <sub>3</sub> (M)	$\bar{\Omega}$ (rps)	$\theta$ ( $\Omega$ )	$C_{dl}$ ( $\mu\text{F}$ )	$\bar{\sigma}$ ( $\Omega$ s $^{-1/2}$ )	$\gamma$ ( $\Omega$ )	$K$ (s $^{-1}$ )
HP2	$10^{-4}$	36	$93 \pm 3$	$6.0 \pm 0.2$	$406 \pm 15$	$15 \pm 10$	$24.1 \pm 1.0$
HP3	$10^{-4}$	36	$44 \pm 3$	$9.3 \pm 1.1$	$502 \pm 8$	$63 \pm 2$	$5.1 \pm 0.1$
CP2	$10^{-4}$	36	$24 \pm 23$	$12.3 \pm 19.1$	$426 \pm 49$	$34 \pm 5$	$2.1 \pm 0.2$
CP3	$10^{-4}$	36	$25 \pm 7$	$8.9 \pm 6.5$	$406 \pm 16$	$36 \pm 3$	$3.3 \pm 0.3$
HP2	$10^{-5}$	36	$150 \pm 12$	$4.0 \pm 4.7$	$1242 \pm 66$	$662 \pm 21$	$5.8 \pm 0.3$
HP3	$10^{-5}$	36	$126 \pm 39$	$5.4 \pm 2.3$	$1185 \pm 147$	$484 \pm 45$	$5.2 \pm 0.4$
HP1	$10^{-5}$	36	$30 \pm 11$	$7.2 \pm 1.4$	$1268 \pm 50$	$379 \pm 19$	$7.0 \pm 0.4$
CP3	$10^{-5}$	36	$85 \pm 38$	$6.3 \pm 2.4$	$1515 \pm 91$	$458 \pm 22$	$2.9 \pm 0.1$
CP2	$10^{-5}$	20	$149 \pm 14$	$8.2 \pm 0.7$	$1174 \pm 61$	$967 \pm 27$	$3.5 \pm 0.1$
CP2	$10^{-5}$	36	$125 \pm 16$	$6.7 \pm 0.8$	$1283 \pm 68$	$687 \pm 22$	$5.1 \pm 0.2$
CP2	$10^{-5}$	49	$108 \pm 16$	$6.3 \pm 0.9$	$1377 \pm 66$	$571 \pm 18$	$6.1 \pm 0.2$

<sup>a</sup>See footnote to Table 1.

The dependence of the "surface" resistance  $\theta$  (at constant solution  $\text{Ag}^+$  concentration) on electrode type and preparation appears to be random. At constant concentration the Warburg coefficient is electrode-independent, as expected, since this quantity is a measure only of solution diffusion to the electrode surface.  $K$  values are essentially concentration-independent for any one electrode, although they varied by as much as a factor of three among electrodes studied here. Since electrodes can never receive exactly the same surface treatment, a factor of 2–3 for  $\gamma$  and  $K$  within a group of electrodes is quite reasonable. An earlier similar study of the  $\text{Ag}/\text{Ag}^+$  system [21] showed variations by an order of magnitude for the same parameters after repeated polishing of the same electrode. The large uncertainty in  $C_{dl}$  makes its dependence on concentration and electrode preparation impossible to determine, although most of the electrodes were grouped between 4 and 10  $\mu\text{F}$ . Regenerated data from the fitting parameters are compared with real data in Fig. 5.

As seen in Fig. 6, impedance parameters varied as a function of electrode rotation rate in the  $10^{-5}$  M  $\text{AgNO}_3$  solution tested. Analysis of the

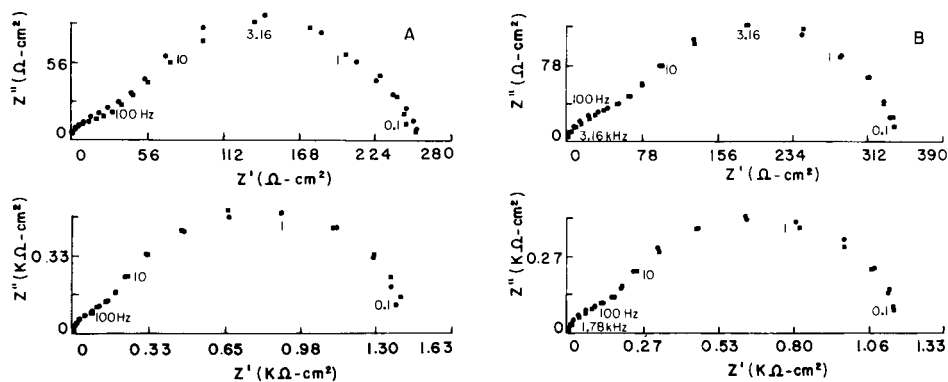


Fig. 5. Comparison of regenerated data (●) versus real data (■) for (A) cold-pressed  $\text{Ag}_2\text{S}$  membrane (excess  $\text{S}^{2-}$ ) and (B) hot-pressed  $\text{Ag}_2\text{S}$  membrane (stoichiometric), in (top)  $10^{-4}$  M  $\text{AgNO}_3$ , (bottom)  $10^{-5}$  M  $\text{AgNO}_3$ .

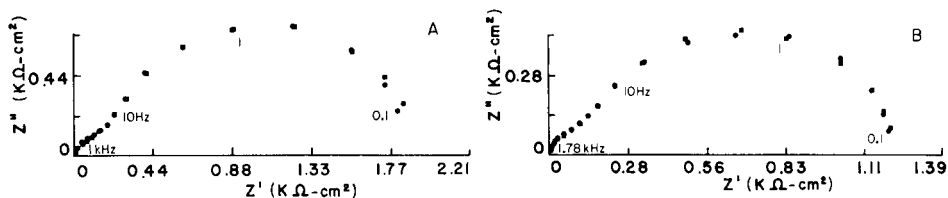


Fig. 6. Comparison of regenerated data (●) versus real data (■) for cold-pressed  $\text{Ag}_2\text{S}$  membrane (excess  $\text{S}^{2-}$ ) in  $10^{-5}$  M  $\text{AgNO}_3$  at (A) 20 rps and (B) 49 rps.

data showed that increasing the rotation rate from 20 to 49 rps increased the dissolution rate constant and decreased the dissolution resistance by approximately 2. The surface resistance and capacitance also decreased by 25–30% and the Warburg coefficient remained nearly constant. That the dissolution kinetics increased with rotation rate indicates that this is a steady-state rather than equilibrium process, because the solutions are not equilibrated with powdered  $\text{Ag}_2\text{S}$ . This increased dissolution rate is consistent with a thinner Nernst diffusion layer, higher surface concentration and consequent decreased values for the "surface" resistance.

## CONCLUSIONS

For silver sulfide, bulk conductivity at room temperature varies only by a factor of 4 depending on the type of material preparation and type of contact. After careful extensive washing of precipitates, gross effects of preparation conditions, such as precipitation from excess of silver ion or excess of sulfide ion or from stoichiometric mixtures, are apparently not important. Evidently only residual coprecipitated matter remains. With symmetric ohmic contacts, conductivity is frequency-independent as both electrons and silver ion interstitials are totally unblocked. However, when a solution contact is used, electrons are blocked at the interface and an internal diffusional Warburg impedance of silver defect species becomes easily observable. The impedance is very small for all cold-pressed membranes and for hot-pressed membranes prepared from stoichiometric mixtures or with an excess of silver ions. However, with hot-pressed membranes prepared from excess of sulfide ions, the Warburg impedance is very large (2500 ohms). This observation indicates a depression of the charge carrier (probably interstitial silver ion) concentration. In all cases, combination of the bulk membrane and internal Warburg impedances was measured and subtracted as background correction from less concentrated solution impedances to separate and determine interfacial properties of these electrodes.

These background-corrected measurements in  $10^{-3}$ – $10^{-5}$  M  $\text{AgNO}_3$  demonstrated the presence of a surface ion-transfer resistance which appears to depend on the potential profile, as deduced from the dependence on bathing silver ion concentrations. The measurements also showed measurable total salt crystallization/dissolution impedances with a time constant slower than that for solution diffusion. This latter result indicates that the salt dissolution process can be a limiting process in the establishment of the steady-state potential.

The authors thank Drs J. R. Macdonald and S. G. Canagaratna for their helpful discussions of least squares fitting of impedance data. This work was supported by NSF Grant MPS 75-00970.

## REFERENCES

- 1 R. P. Buck, *Anal. Chem.*, 40 (1968) 1432.
- 2 M. J. D. Brand and G. A. Rechnitz, *Anal. Chem.*, 42 (1970) 478.
- 3 K. Cammann and G. A. Rechnitz, *Anal. Chem.*, 48 (1976) 856.
- 4 M. Koebel, N. Ibl and A. M. Frei, *Electrochim. Acta.*, 19 (1974) 287.
- 5 D. J. Crombie, G. J. Moody and J. D. R. Thomas, *Anal. Chim. Acta.*, 80 (1975) 1.
- 6 J. Gulens and B. Ikeda, *Anal. Chem.*, 50 (1978) 782.
- 7 J. Buffle and N. Parthasarathy, *Anal. Chim. Acta.*, 93 (1977) 111.
- 8 J. Buffle and N. Parthasarathy, *Anal. Chim. Acta.*, 93 (1977) 121.
- 9 A. Shatkey, *Anal. Chem.*, 48 (1976) 1039.
- 10 J. R. Macdonald, *J. Chem. Phys.*, 10 (1974) 3977.
- 11 S. G. Canagaratna and S. A. G. R. Karunathilaka, *J. Electroanal. Chem.*, 48 (1973) 183.
- 12 J. R. Macdonald and J. A. Garber, *J. Electrochem. Soc.*, 124 (1977) 1022.
- 13 R. P. Buck and V. R. Sheppard, Jr., *Anal. Chem.*, 46 (1974) 2097.
- 14 D. E. Mathis and R. P. Buck, *Anal. Chem.*, 48 (1976) 2033.
- 15 H. Okazaki, *J. Phys. Soc. Jpn.*, 23 (1967) 355.
- 16 H. P. Gesserich and W. Suppanz, *Phys. Status Solidi*, 35 (1969) 381.
- 17 R. D. Armstrong, T. Dickinson and M. Reid, *Electrochim. Acta*, 21 (1976) 935.
- 18 R. N. Adams, *Electrochemistry at Solid Electrodes*, M. Dekker, N.Y., 1969, p. 269.
- 19 J. R. Sandifer and R. P. Buck, *J. Electroanal. Chem.*, 56 (1974) 385.
- 20 K. J. Vetter, *Electrochemical Kinetics*, Academic Press, N.Y., 1967, p. 333.
- 21 S. G. Canagaratna and S. A. G. R. Karunathilaka, *J. Electroanal. Chem.*, 60 (1975) 65.
- 22 A. Wikby, *J. Electroanal. Chem.*, 33 (1971) 145.
- 23 P. Van den Winkel, J. Mertens, T. Boel and J. Vereecken, *J. Electrochem. Soc.*, 124 (1977) 1338.
- 24 R. P. Buck, *Electroanalytical Chemistry of Membranes*, CRC Review, CRC Press, 1976.

## THE MECHANISM OF THE POTENTIAL RESPONSE OF BROMIDE-SELECTIVE ELECTRODES BASED ON MERCURY SALTS

ADAM HULANICKI,\* RYSZARD LEWANDOWSKI and ANDRZEJ LEWENSTAM

*Institute of Fundamental Problems in Chemistry, University of Warsaw, Warszawa (Poland)*

(Received 23rd April 1979)

### SUMMARY

Bromide-selective electrodes based on  $\text{Hg}_2\text{Br}_2\text{-HgS-Ag}_2\text{S}$  membranes are discussed. X-ray diffraction studies indicate the formation of  $\text{HgBr}_2$  and mercury under certain conditions. Improved preparations are reported. Electrode response can be interpreted on the basis of the theory for second-kind electrodes. In very dilute nitric acid solutions ( $3 \times 10^{-4} \text{ mol dm}^{-3}$ ), the linear range extends almost to pBr 6 and the electrodes are useful at pBr > 7.

Solid-state bromide-selective electrodes based on silver salts were among the first successfully applied ion-selective electrodes [1, 2], and their preparation, theory and application have been described by numerous authors [3, 4]. Their linear response range extends to about pBr 5, while their analytical utility reaches to about pBr 6.

In 1976, Sekerka and Lechner [5], and somewhat later Tseng and Gutknecht [6], indicated the possibility of preparing bromide-selective electrodes from insoluble mercury salts ( $\text{HgS}$  and  $\text{Hg}_2\text{Br}_2$ ). It was mentioned that such electrodes are characterized by a broader working range (to pBr  $\approx$  7), a better linear range (to pBr  $\approx$  6) and a shorter response time. The remaining parameters of these electrodes were said to be similar to those of silver-based electrodes. In some respects, the mercury-based electrodes were more troublesome, especially with regard to preparation of membranes, internal liquid mercury contact and long conditioning before measurements, which can require up to two days.

Improvement of the electrode action is difficult, however, because of lack of knowledge about the mechanism of the electrode function, especially in connection with standard potential, charge-transfer mechanism and electrode behaviour at low activities of bromide ions. In the work described here, attempts were made to elucidate these phenomena connected with electrode mechanism in order to improve the practical construction and utilization of this type of electrode.

## EXPERIMENTAL

*Apparatus and reagents*

For potential measurements, a Radiometer PHM 64 pH-meter and a Servograph REC 61 recorder were used. All solutions were thermostated at 20°C and stirred at constant speed. A double-junction saturated calomel electrode was used as reference electrode. Calibration curves were prepared by the spiking technique with a Radiometer ABU 13 autoburette, or by series dilution. X-ray diffractograms were obtained with an x-ray powder diffractometer (DRON-1.5, USSR).

All reagents were of analytical grade, and solutions were prepared with twice-distilled water.

*Electrodes*

Mercury(I) bromide and mercury(II) sulphide were precipitated as described by Tseng and Gutknecht [6] by slow precipitation from mercury(I) nitrate and mercury(II) nitrate solutions, respectively, acidified initially with nitric acid to about pH 1. In the case of  $\text{Hg}_2\text{Br}_2$  a small excess of mercury(I) ions was left in the solution; for  $\text{HgS}$ , a small excess of sulphide ions was added. The filtered and washed precipitates were dried and powdered to a particle size of less than 0.1-mm diameter.

Silver sulphide was obtained from the powdered elements by heating in a hydrogen sulphide atmosphere; the powdered product was washed with carbon disulphide and acetone, and dried at 110°C. The purity of the electroactive materials was tested by x-ray diffraction. The entire preparation of electroactive substances was done under red light.

The membranes were prepared by pressing at room temperature to give disks of 8-mm diameter and 3-mm thickness. The molar compositions of the membranes prepared were  $\text{Hg}_2\text{Br}_2:\text{HgS}$  ratios of 1:1 and  $\text{Hg}_2\text{Br}_2:\text{HgS}:\text{Ag}_2\text{S}$  ratios of 2:1:1. For the  $\text{Hg}_2\text{Br}_2\text{—HgS}$  membranes, the optimal pressure was 200 MPa; at lower pressures, the membranes were not sufficiently compact whereas higher pressures led to disintegration of the disks during the further procedure. To improve the plastic properties of the membranes, silver sulphide was added; for these  $\text{Hg}_2\text{Br}_2\text{—HgS—Ag}_2\text{S}$  membranes, pressures up to 500 MPa gave disks with good mechanical properties. These membranes were used in all later tests, unless otherwise specified.

The membranes were heated at 200°C in an argon atmosphere for 3 h, and a 0.5-mm layer of metallic silver was pressed onto one side as the internal contact. After this treatment, the membranes were sealed in epoxy resin bodies and the outer surface was polished with abrasive paper and felt cloth.

Some tests were also done with electrodes prepared from membranes which had not been thermally treated, and with liquid mercury internal contacts.



## RESULTS AND DISCUSSION

In the course of membrane preparation, it was noted that thermal treatment of membrane disks was accompanied by sublimation of a crystalline substance which deposited on the internal walls of the heating chamber; this was identified as mercury(II) bromide. In addition, when a freshly prepared membrane disk was pressed under the slight pressure necessary to affix the silver contact, small droplets of mercury appeared on the wall of the die. When the electroactive substances were analysed by x-ray diffraction before and after pressing and thermal treatment, the formation of  $\text{HgBr}_2$  was confirmed, with loss of  $\text{Hg}_2\text{Br}_2$ ; the continuous background found at small angles was attributed to the presence of elemental mercury.

These results indicate that the dismutation reaction  $\text{Hg}_2\text{Br}_2 \rightarrow \text{Hg} + \text{HgBr}_2$  occurs during the membrane preparation. Such behaviour may explain several problems connected with the action of these mercury salt-based electrodes.

### Potential response

The previous reports on the behaviour of mercury salt-based electrodes [5, 6] indicated that several days of electrode conditioning could be necessary for proper electrode response, but no explanation of this fact was given. The electrodes prepared here were tested immediately after preparation or after two or five days of conditioning in water or in very dilute nitric acid (Fig. 1). On the basis of the above-mentioned dismutation reaction,

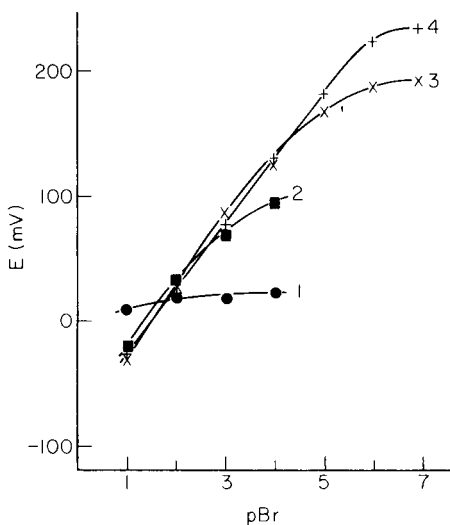


Fig. 1. The influence of conditioning on the potential response of bromide-selective electrodes. (1) Freshly prepared, unconditioned; (2) conditioned for 2 days in water; (3) conditioned for 5 days in water; (4) conditioned for 5 days in  $3 \times 10^{-4}$  mol  $\text{dm}^{-3}$  nitric acid.

it seems probable that conditioning consists of leaching out soluble mercury(II) bromide, at least from the surface layer, and it may be supposed that membranes which do not contain this salt do not need to be conditioned before use.

Calibration curves obtained in solutions of soluble mercury(I) and mercury(II) salts were compared for a mercury metal electrode and the mercury(I) bromide ion-selective electrode. (Fig. 2). Their responses are very similar in shape as well as in potential values; this is in agreement with the theoretical explanations provided by Kolthoff and Miller [7].

When the electrodes were tested in bromide solutions of different concentration, the potential response for  $pBr < 5$  was linear with a slope equal to 57.7 mV/pBr (Fig. 3). The electrode potential for more dilute bromide solutions depended strongly on the electrode preparation and on the pre-treatment of the electrode. When the electrode before measurements was washed with very dilute (ca.  $3 \times 10^{-4}$  mol dm $^{-3}$ ) nitric acid, and the analyte solutions were similarly acidic, the linear range was the longest obtained, extending nearly to pBr 6. However, the potential response was not very stable in this low concentration range and the potentials drifted slowly in the negative direction. It may be suspected that the electrode behaviour is affected in a complex manner which is similar in character to that observed for iodide-selective electrodes based on silver salts [8], though less pronounced. The positive deviations would be caused by the appearance of Hg $^{2+}$  ions at the membrane surface; these originate from leaching of residual mercury(II) ions, or by oxidation of membrane components. The negative deviations are connected with reduction processes, adsorption of bromide ions at the electrode surface or dissolution of Hg $_2$ Br $_2$ , as well as from hydroxide interferences.

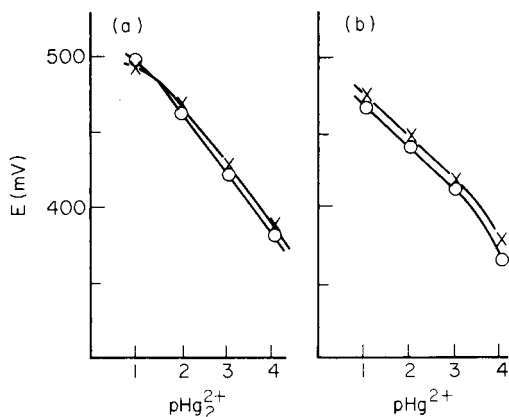


Fig. 2. Potential response of electrodes in (a) mercury(I) nitrate and (b) mercury(II) nitrate solutions containing 1 mol dm $^{-3}$  nitric acid: (x) mercury electrode; (o) Hg $_2$ Br $_2$  ion-selective electrode.

The advantageous influence of nitric acid is connected not only with elimination of interference from hydroxide, but also with the overall redox potential in solution (Fig. 4) which compensates better for negative deviations.

#### *The mechanism of the electrode action and its consequences*

The results obtained in this study strongly support the idea that the bromide-selective electrodes based on mercury salts are in fact second-order electrodes with the  $\text{Hg}/\text{Hg}_2\text{Br}_2$  couple dispersed in the electron-conducting matrix containing  $\text{HgS}$  and/or  $\text{Ag}_2\text{S}$  [5]. The half-cell can therefore be described by  $\text{Hg}(\text{m}), \text{Hg}_2\text{Br}_2(\text{s})/\text{Br}^-(\text{soln.})$ , which does not exclude the electrodes from being considered as typical membrane ion-selective electrodes with the mercury metal activity equal to unity. It cannot, however, be decided on the basis of the present tests whether or not the mercury has an activity less than one. According to Koebel [9] and Buck and Shepard [10], this is one of the characteristics that differentiate the silver-based membrane electrodes from the corresponding second-order electrodes.

The electrode potential of these bromide-selective electrodes can be described by

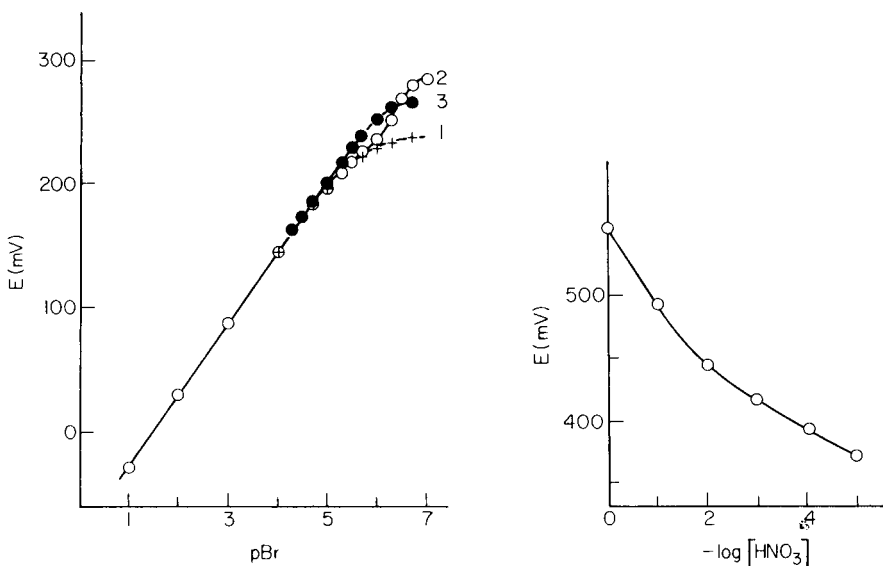


Fig. 3. Calibration curves for bromide-selective electrodes: (1) after conditioning for 6 h in  $10^{-4}$  mol  $\text{dm}^{-3}$  KBr; (2) after conditioning for 10 min in 1 mol  $\text{dm}^{-3}$   $\text{Hg}(\text{NO}_3)_2$ ; (3) after washing with  $3 \times 10^{-4}$  mol  $\text{dm}^{-3}$   $\text{HNO}_3$ . The measurements for curve 1 and 2 were done at pH 7, and those for curve 3 at pH 3.5. Potential readings after 3 min.

Fig. 4. Redox potential (Pt—SCE couple) as a function of nitric acid concentration.

$$E = E_{\text{Hg}_2^{2+}, \text{Hg}}^0 + \frac{RT}{2F} \ln K_{\text{so}} - \frac{RT}{2F} \ln [\text{Br}^-]^2$$

(where  $K_{\text{so}}$  refers to  $\text{Hg}_2\text{Br}_2$ ) when the surface concentration of bromide ions is visualised as the contributions from several sources, as was shown in the case of iodide-selective electrodes [8]. The basic feature of the equation is then its interpretation of electrode behaviour for  $\text{pBr} > 5$ .

Extrapolation of the calibration curves shown in Fig. 3 to  $\text{pBr} 0$  gives the standard potential of the system as  $-86$  mV vs. SCE. If the value of the standard potential  $E_{(\text{Hg}_2^{2+}/\text{Hg})}^0$  is assumed to be  $546$  mV vs. SCE, which corresponds well to the extrapolated value from the electrode calibration in  $\text{Hg}_2^{2+}$  solution ( $530$  mV vs. SCE, Fig. 2), the solubility product of mercury(I) bromide may be calculated as  $\text{p}K_{\text{so}} = 21.8$ , which is in good agreement with literature data [11].

From the calculated value of the solubility product, the molar solubility in the absence of hydroxide interference ( $\text{pH} < 4$ ) is  $10^{-7.46}$ . This suggests that membrane surface processes rather than the solubility itself influence the limit of detection and electrode response at  $\text{pBr} > 5$ .

In conclusion it may be stated that a simpler procedure for membrane construction is possible. The thermal treatment can be omitted when the membrane is composed of  $\text{Hg}_2\text{Br}_2$ ,  $\text{HgS}$  and  $\text{Ag}_2\text{S}$  in a 2:1:1 ratio and a small amount of mercury metal, the excess of which is removed during pressing. A series of membranes was prepared by mixing and pressing these substances at a pressure of  $500$  MPa. The properties of these electrodes were similar to those described in Fig. 3, without lengthy preconditioning.

The authors are indebted to Dr. T. M. Krygowski and Mr. T. Więckowski for the x-ray diffractograms and their interpretation. This study was supported financially by the Polish Academy of Sciences (project 03.10.6.05.09).

## REFERENCES

- 1 I. M. Kolthoff and H. L. Sanders, *J. Am. Chem. Soc.*, **59** (1937) 416.
- 2 E. Pungor, *Anal. Chem.*, **39** (1967) 28A.
- 3 See, e.g., J. Koryta, *Anal. Chim. Acta*, **91** (1977) 1.
- 4 See, e.g., R. P. Buck, *Anal. Chem.*, **50** (1978) 17R.
- 5 I. Sekerka and J. F. Lechner, *Anal. Chim. Acta*, **69** (1976) 339.
- 6 P. K. C. Tseng and W. F. Gutknecht, *Anal. Lett.*, **9** (1976) 795.
- 7 I. M. Kolthoff and C. S. Miller, *J. Am. Chem. Soc.*, **63** (1941) 2732.
- 8 A. Hulanicki, A. Lewenstam and M. Maj-Żurawska, *Anal. Chim. Acta*, **107** (1979) 121.
- 9 M. Koebel, *Anal. Chem.*, **46** (1974) 1559.
- 10 R. P. Buck and V. R. Shepard, Jr., *Anal. Chem.*, **46** (1974) 2097.
- 11 A. Ringbom, *Complexation in Analytical Chemistry*, J. Wiley, New York, 1963.

## ELECTROCHEMICAL ENZYMATIC DETERMINATIONS OF ETHANOL AND L-LACTIC ACID WITH A CARBON PASTE ELECTRODE MODIFIED CHEMICALLY WITH NICOTINAMIDE ADENINE DINUCLEOTIDE

TOSHIO YAO\* and SOICHIRO MUSHA

*Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Mozu-umemachi, Sakai 591 (Japan)*

(Received 28th February 1979)

### SUMMARY

The oxidized form of nicotinamide adenine dinucleotide ( $\text{NAD}^+$ ) is chemically immobilized at the surface of a carbon paste electrode containing *n*-octaldehyde. The  $\text{NAD}^+$  is converted to NADH by oxidation of ethanol and L-lactic acid catalyzed by their respective dehydrogenases, and the NADH formed is oxidized electrochemically to the original  $\text{NAD}^+$ , thus giving a well defined linear-sweep voltammetric peak. The peak area is linearly related to the amount of ethanol or L-lactic acid in the range  $0.05\text{--}2 \times 10^{-9}$  mol.

In recent years there has been considerable interest in applying immobilized enzymes to specific assays. Among these applications, the so-called enzyme electrode is unique because it combines enzyme specificity with the sensitivity and convenience of electroanalytical techniques in a compact form to facilitate analysis. The enzyme electrode is usually prepared by attaching an immobilized enzyme layer to an electrochemical sensor so that changes occurring as a result of the enzyme reaction can be monitored either potentiometrically or amperometrically [1, 2].

As with immobilized enzymes, studies and applications [3] of immobilized coenzymes have recently been growing noticeably. In this paper, a method for bonding the oxidized form of nicotinamide adenine dinucleotide ( $\text{NAD}^+$ ) to the electrode surface is described.  $\text{NAD}^+$  is an important coenzyme physiologically because it furnishes the redox driving force for many enzyme-catalyzed reactions. The determination of many clinically important substrates involves the use of enzymes requiring  $\text{NAD}^+$  as a cofactor, and virtually all of these methods are based on the spectrophotometric measurements of NADH (reduced NAD) at 340 nm.

The electrochemical reduction of  $\text{NAD}^+$  has been thoroughly investigated [4, 5]; a biologically inactive dimer is the main product. However, the electrochemical oxidation of NADH is less well understood. Although there have been some reports on the electrochemical oxidation of NADH analogues [6–8], the current–potential curves of these compounds were poorly defined. Recently, conditions under which reproducible current–potential

curves may be obtained for the electrochemical oxidation of NADH have been described [9, 10], making possible the amperometric determination of  $\mu\text{M}$  levels of NADH. A few studies [11, 12] have also demonstrated that the electrochemical oxidation product of NADH is  $\text{NAD}^+$ .

In this paper, an investigation of the voltammetric oxidation of NADH is described; linear-sweep voltammetry is used with carbon paste and glassy carbon electrodes. An immobilized coenzyme electrode fabricated by modifying chemically the surface of the carbon paste electrode is applied to the determination of traces of ethanol by using alcohol dehydrogenase (ADH) as catalyst, and to traces of L-lactate, by using lactate dehydrogenase (LDH). For example, the lactate is enzymatically oxidized to pyruvate, while  $\text{NAD}^+$  (bonded to the electrode surface) is converted to NADH, which gives an oxidation peak by linear-sweep voltammetry. The peak area can be related to the amount of L-lactate in the solution. Such methods offer high analytical selectivity as well as sensitivity.

## EXPERIMENTAL

### *Reagents and equipment*

$\text{NAD}^+$ , NADH, ADH ( $305 \text{ IU mg}^{-1}$ ), LDH ( $10 \text{ mg protein ml}^{-1}$ ,  $550 \text{ IU mg}^{-1}$  protein), L-lactic acid, and D-lactic acid (all from Sigma Chemical Company) were stored in a refrigerator. All supporting electrolyte solutions were prepared from analytical-grade chemicals without further purification. All other chemicals were reagent grade.

Voltammograms were recorded with a Yanagimoto P-8 polarograph. Cyclic voltammograms were obtained by using a solid-state instrument constructed in this laboratory. A three-electrode voltammetric cell was used for all the experiments. A saturated calomel electrode (SCE) served as the reference electrode and a platinum wire as the counter electrode.

*Glassy carbon electrode (GCE)*. This was constructed as described previously [13]. It was polished for ca. 30 s with 1500-grade emery paper and then with a paste of cerium dioxide on asphalt pitch until the surface of the electrode was brought to a mirror finish.

*Carbon paste electrode (CPE)*. The paste was prepared by mixing with a spatula 5 g of carbon (Shimadzu spectroscopically pure graphite powder TSP-1, 280 mesh) and 3 ml of liquid paraffin (Kishida Chemical Co.) until the entire mixture appeared uniformly wetted. The paste was packed firmly into one end of a glass tube (5 mm diam.) equipped with a piston rod. The surface of the CPE was smoothed off by rubbing the electrode across a piece of wax-paper. The electrode surface was renewed before recording each voltammogram.

*Platinum disc electrode (PDE)*. This was constructed by Adams' method [14]; the area of the electrode was  $3.1 \text{ mm}^2$ . The PDE was polished with 800-grade and then with 1500-grade emery paper.

*$\text{NAD}^+$ -modified carbon paste electrode*. The carbon paste was prepared as

above from 5 g of graphite powder and 3 ml of liquid paraffin, except that 0.5 ml of n-octaldehyde was also added. The thoroughly mixed carbon paste was packed firmly into one end of a glass tube (5 mm diam.) equipped with a piston rod. The surface of the electrode was smoothed off by rubbing the electrode across a piece of wax-paper, and was dipped into 2 ml of  $\text{NAD}^+$  solution ( $50 \text{ mg ml}^{-1}$ ) stirred with a 3-mm magnetic stirring bar. The reaction was allowed to proceed for 6 min. The electrode was then washed several times with a cold phosphate buffer to remove physically entrapped or weakly bonded coenzyme. The electrode was immersed in a phosphate buffer and stored at  $5^\circ\text{C}$  overnight before use.

#### *Determination of ethanol—calibration*

The  $\text{NAD}^+$ -modified CPE was dipped into 2 ml of 0.2 M phosphate buffer solution (pH 8.0) which was 0.02 M in semicarbazide hydrochloride and contained 0.2 mg of ADH. Then known amounts of ethanol ( $1 \text{ mg l}^{-1}$  solution) in the range  $0.05\text{--}1.5 \times 10^{-9}$  mol were added. After stirring for 10 min with a 3-mm magnetic stirring bar, the electrode was washed with the cold phosphate buffer. The electrode was transferred to a voltammetric cell containing 0.1 M phosphate buffer at pH 7.5. The voltammograms for the oxidation of immobilized NADH converted by the enzymatic reaction were recorded at  $10 \text{ mV s}^{-1}$ . The quantity of electricity (Q) consumed during the oxidation of the immobilized NADH was calculated from the area of each peak.

#### *Determination of L-lactic acid—calibration*

The  $\text{NAD}^+$ -modified electrode was dipped into 2 ml of 0.1 M pyrophosphate buffer solution (pH 9.0) which was 0.25 M in hydrazine and contained  $10 \mu\text{g}$  of LDH. Known amounts of L-lactic acid in the range  $0.05\text{--}2.0 \times 10^{-9}$  mol were added. The reaction was allowed to proceed for ca. 10 min, with magnetic stirring. The voltammograms for the oxidation of immobilized NADH were recorded in 0.1 M phosphate buffer at pH 7.5 as described for ethanol.

## RESULTS AND DISCUSSION

#### *Voltammetric waves of $\text{NAD}^+$ at the solid electrodes*

$\text{NAD}^+$  is unstable in alkaline solutions, while NADH is unstable in acidic solutions. Consequently, the electrochemical behavior of  $\text{NAD}^+$  and NADH was investigated at pH 6.5–8.2. At the PDE, the residual current was very large and the voltammetric wave was poorly defined, in agreement with a previous report [11]. At the CPE, the residual current was much smaller and a well-defined wave was obtained for the oxidation of NADH with a half-peak potential ( $E_{p/2}$ ) of 0.38 V vs. SCE. At the GCE, a well-defined oxidation wave was also obtained, at almost the same potential as that at the CPE. In this case, however, an additional oxidation wave appeared at 1.28 V vs.

SCE, which corresponded to the oxidation of the adenosine in the NADH molecule [13].

NAD<sup>+</sup> gave both a reduction wave ( $E_{p/2} = -1.08$  V vs. SCE) and an oxidation wave corresponding to the oxidation of adenosine at the GCE. The half-peak potentials of the oxidation wave (0.38 V) of NADH and the reduction wave (-1.08 V) of NAD<sup>+</sup> stayed almost constant in spite of pH variations between 6.5 and 8.2. In addition, no significant change in their peak currents was observed within that pH range. A linear dependence of the peak current on concentration was observed for the oxidation and reduction waves over the range 0.1–3 mM. Also, the peak current was directly proportional to the square root of the scan rate. These results imply that the electrode process is diffusion-controlled.

A cyclic voltammogram of NADH is shown in Fig. 1. The point of interest is that a new cathodic peak was observed on the return sweep toward negative potentials. This peak was independent of the pH of the electrolyte solution and its potential was the same as that of the cathodic reduction peak of NAD<sup>+</sup>. Also, the coulometric  $n$ -value for NADH was about two and most of the oxidation product was NAD<sup>+</sup>.

#### *NAD<sup>+</sup>-modified carbon paste electrode*

In order to retain the coenzyme at the CPE surface, the presence of a small amount of aldehyde in the carbon paste is essential. In this work, *n*-octaldehyde, a hydrophobic aldehyde, was used rather than glutaraldehyde, which diffused back into the solution. Carbon pastes containing different amounts of *n*-octaldehyde were prepared, and their background currents were measured in the phosphate buffer solutions. If the aldehyde concentration was increased to five times the recommended amount, the residual current rapidly grew larger.

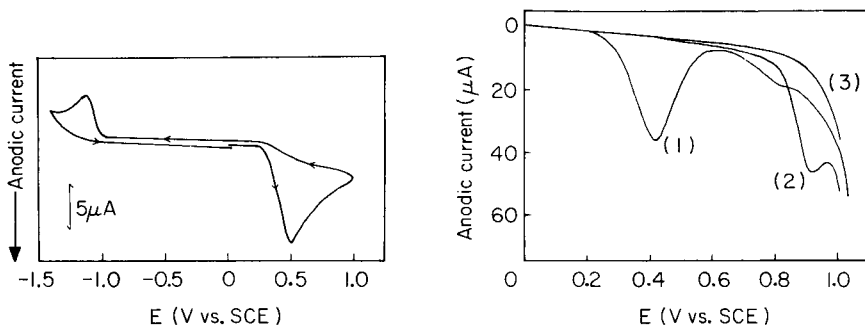
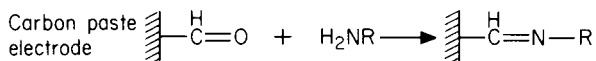


Fig. 1. Cyclic voltammogram of 1.0 mM NADH at the GCE in 0.2 M phosphate buffer at pH 8.1. GCE area 7.1 mm<sup>2</sup>; scan rate 0.25 V s<sup>-1</sup>.

Fig. 2. Anodic voltammograms obtained after reaction of the carbon paste electrode containing *n*-octaldehyde with (1) NADH, (2) adenine, and (3) reduced nicotinamide adenine mononucleotide.



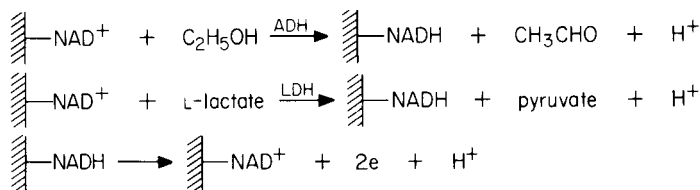
After the CPE containing n-octaldehyde had reacted with a NADH solution, a voltammogram for NADH immobilized at the CPE surface was recorded in the phosphate buffer at pH 7.5. A well-defined peak corresponding to the oxidation of the immobilized NADH was obtained (Fig. 2). Adenine also gave a voltammetric peak by reacting with the CPE containing n-octaldehyde, while nicotinamide adenine mononucleotide (reduced form) was not immobilized at the surface of the electrode (Fig. 2). Consequently, the reaction responsible for immobilization of the coenzyme probably involves the formation of a Schiff's base with the primary amino group of the adenosine in the NAD molecule:



The relationship between the quantity of electricity ( $Q$ ) involved (the area of the voltammetric peak) and the reaction time was investigated. The results are shown in Fig. 3 for two CPE differing only in n-octaldehyde content. The rate of the reaction was sufficiently rapid at room temperature, and the reaction went nearly to completion in ca. 6 min. From the charge required to oxidize the NADH immobilized at the electrode (Fig. 3, curve 2), corrected for background, the surface coverage of NADH was calculated to be  $1.2 \times 10^{-7}$  mol  $\text{cm}^{-2}$  (geometric area) assuming a two-electron process. The coenzyme immobilized by this procedure was quite stable in buffer solutions, ranging from pH 5.5 to 9.5 kept at 5°C.

#### *Analytical applications of the NAD<sup>+</sup>-modified electrode*

NAD<sup>+</sup> immobilized at the electrode surface can be converted to NADH by enzymatic reactions such as the oxidation of ethanol or L-lactate catalyzed by ADH and LDH, respectively. The NADH produced (immobilized at the electrode surface) was oxidized to NAD<sup>+</sup> electrochemically and showed a well-defined peak by linear-sweep voltammetry. The overall reactions are as follows:



#### *Determination of traces of ethanol*

Trace amounts of ethanol were determined as described in the experimental section. The results are shown in Fig. 4. The number of moles of NADH calculated from the  $Q$  values ( $0.41 \times 10^{-4}$  C,  $0.80 \times 10^{-4}$  C and  $1.54 \times 10^{-4}$  C for curves 1–3, respectively) varies linearly with the amount of ethanol added. Accordingly, the enzymatic reaction seems to proceed to completion at the surface of the modified electrode.

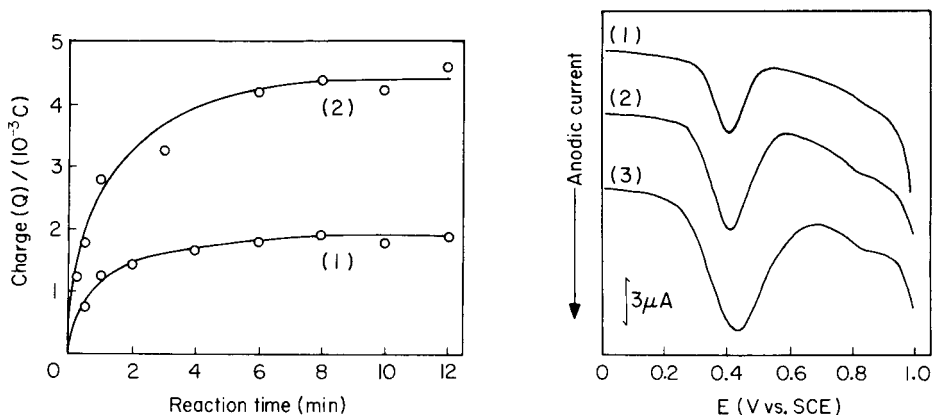


Fig. 3. Relationships between reaction time and the charge (area under the peak) for NADH immobilized at the electrode. Composition of carbon paste used: 5 g of graphite powder and 3 ml of liquid paraffin with (1) 0.2 ml of *n*-octaldehyde, (2) 0.5 ml of *n*-octaldehyde. Reaction solution: 2 ml of a 50 mg ml<sup>-1</sup> NADH solution.

Fig. 4. Current—voltage curves for immobilized NADH produced by enzymatic oxidation of ethanol at a NAD<sup>+</sup>-modified carbon paste electrode by the recommended procedure. Added ethanol: (1) 13 ng (2.2 × 10<sup>-10</sup> mol); (2) 25 ng (4.3 × 10<sup>-10</sup> mol); (3) 50 ng (8.6 × 10<sup>-10</sup> mol).

There is a linear relationship between the amount of added ethanol and the charge passed to oxidize NADH converted from NAD<sup>+</sup> at the electrode surface by the enzymatic oxidation of ethanol over the range 0.05–1.5 × 10<sup>-9</sup> mol of ethanol. For larger amounts, the quantity of electricity was less than expected. Therefore, the method appears to be suitable for the determination of trace amounts of ethanol.

#### Determination of traces of *L*-lactic acid

The method of measurement used was similar to that described for ethanol. The relationship between the amount of added *L*-lactic acid and the *Q* values determined from peak voltammograms was linear over the range 0.05–2.0 × 10<sup>-9</sup> mol of lactic acid. LDH catalyzes the oxidation of *L*-lactic acid, but not that of the *D*-isomer. This specificity was applied to the determination of the *L*-isomer in commercial *D*-lactic acid. The results are shown in Table 1; the trace amounts of the *L*-isomer found in the commercial sample (average of 0.017 wt. %) closely agreed with the analytical data (ca. 0.02%) indicated on the label.

#### Stability and reproducibility of the NAD<sup>+</sup>-modified electrode

After the electrode had been used five times, the response of the NAD<sup>+</sup>-modified CPE decreased by about 6–10% compared to that of the fresh electrode. Such lack of stability suggests loss or deactivation of the im-

TABLE 1

Determination of L-lactic acid in a commercial D-lactic acid sample (Sigma Chemical Co., No. L-1000)

D-Lactic acid taken ( $10^{-6}$ mol)	Q ( $10^{-4}$ C)	L-Lactic acid found ( $10^{-9}$ mol)	L-Lactic acid (% by weight)
1.67	0.56	0.29	0.017
3.33	1.11	0.63	0.019
4.44	1.29	0.67	0.015
6.67	2.15	1.12	0.017

mobilized  $\text{NAD}^+$ . Electrochemical studies at the GCE and CPE have indicated that NADH is quite stable in phosphate buffer solutions, losing only about 1–2% of its electrochemical activity during several hours. Thus the loss of response of the modified electrode is probably due to the instability of the bond between NADH and the electrode surface. It is thought that some bond breakage is caused by the electrochemical oxidation of the immobilized NADH, so that some of the  $\text{NAD}^+$  produced is free to be leached from the electrode. Therefore, the  $\text{NAD}^+$ -modified electrode had to be freshly prepared after every 2–3 analyses, but the time taken to prepare the electrode was short (ca. 7 min).

The reproducibility of the response of the freshly prepared  $\text{NAD}^+$ -modified electrode was measured for various amounts of ethanol. The coefficient of variation of the charge for seven voltammetric peak measurements was 6–7% at the  $10^{-10}$ -mol level and 2–3% at the  $10^{-9}$ -mol level.

#### REFERENCES

- 1 G. G. Guilbault and J. G. Montalvo, *J. Am. Chem. Soc.*, 91 (1969) 2164.
- 2 G. G. Guilbault and G. J. Lubrano, *Anal. Chim. Acta*, 64 (1973) 439.
- 3 D. C. Tse and T. Kuwana, *Anal. Chem.*, 50 (1978) 1315.
- 4 D. Thevenot and R. Buvet, *J. Electroanal. Chem.*, 39 (1972) 429.
- 5 D. Thevenot and R. Buvet, *J. Electroanal. Chem.*, 40 (1972) 197.
- 6 P. Leduc and D. Thevenot, *J. Electroanal. Chem.*, 47 (1973) 543.
- 7 W. J. Blaedel and R. G. Haas, *Anal. Chem.*, 42 (1970) 918.
- 8 C. O. Schmamel, K. S. V. Santhanam and P. J. Elving, *J. Electrochem. Soc.*, 121 (1974) 1033.
- 9 W. J. Blaedel and R. A. Jenkins, *Anal. Chem.*, 47 (1975) 1337.
- 10 L. C. Thomas and G. D. Christian, *Anal. Chim. Acta*, 78 (1975) 271.
- 11 J. N. Burnett and A. L. Underwood, *Biochemistry*, 4 (1965) 2060.
- 12 M. Aizawa, R. W. Coughlin and M. Charles, *Biochim. Biophys. Acta*, 385 (1975) 362.
- 13 T. Yao, T. Wasa and S. Musha, *Bull. Chem. Soc. Jpn.*, 50 (1977) 2917.
- 14 R. N. Adams, *Electrochemistry at Solid Electrode*, M. Dekker, New York, 1969, p. 273.

## DETERMINATION DES CONSTANTES DE DISSOCIATION IONIQUE DU CHLORURE DE NITROSYLE ET DE N<sub>2</sub>O<sub>4</sub> DANS LE SULFOLANE

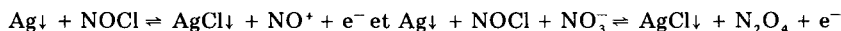
MICHEL WARTEL\*, ABDELHATEF BOUGHRIET et JEAN-CLAUDE FISCHER

Université des Sciences et Techniques de Lille, Laboratoire de chimie minérale I, Bât. C8, B.P. 36, 59 650 Villeneuve d'Ascq (France)

(Reçu le 10 avril 1979)

### RESUME

L'utilisation d'une électrode d'argent recouverte de AgCl a permis l'étude dans le sulfolane des systèmes électrochimiques suivants:

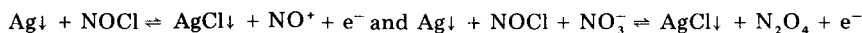


et la détermination des constantes de dissociation des donneurs de NO<sup>+</sup>:  $K_{(\text{NOCl})} = 10^{-11,8} \text{ mol l}^{-1}$  et  $K_{(\text{N}_2\text{O}_4)} = 10^{-7,2} \text{ mol l}^{-1}$ . Nous en avons déduit un dosage des solutions de N<sub>2</sub>O<sub>4</sub> seul ou en présence d'acide nitrique. Ce dosage est possible pour des mélanges contenant en poids au maximum 90% d'acide nitrique.

### SUMMARY

*Determination of the ionic dissociation constants of nitrosyl chloride and dinitrogen tetroxide in sulpholane.*

A silver chloride—silver electrode is used to study electrochemical systems involving nitrosyl chloride and dinitrogen tetroxide in sulpholane:



The dissociation constants of these two NO<sup>+</sup> donors determined in this way are:  $K_{(\text{NOCl})} = 10^{-11,8} \text{ mol l}^{-1}$  and  $K_{(\text{N}_2\text{O}_4)} = 10^{-7,2} \text{ mol l}^{-1}$ . A titration of N<sub>2</sub>O<sub>4</sub> solutions alone or in the presence of nitric acid is described. This titration is possible in mixtures which contain up to 90% (w/w) nitric acid.

Ce mémoire s'insère dans une étude générale du comportement électrochimique des dérivés oxygénés et chlorooxygénés de l'azote dans le but d'obtenir une meilleure connaissance des réactions de nitration. Nous nous sommes intéressés en premier lieu à l'équilibre de dissociation ionique de N<sub>2</sub>O<sub>4</sub> selon



Cette dissociation hétérolytique, très faible dans N<sub>2</sub>O<sub>4</sub> liquide [1], peut être exaltée par l'utilisation d'un solvant dissociant. Nous avons choisi d'effectuer ce travail dans le sulfolane en raison, d'une part, de son utilisation dans l'étude du mécanisme des réactions de nitration [2, 3] et, d'autre part, en

raison de son pouvoir donneur, selon Gutmann [4], assez élevé. Cette dernière propriété aura pour conséquence de rétrograder l'équilibre de dissociation homolytique  $N_2O_4 \rightleftharpoons 2NO_2$ , par stabilisation de l'acide de Lewis  $N_2O_4$  plus fort que  $NO_2$  [5].

Afin d'accéder à la valeur de la constante de l'équilibre (1) qui met en jeu des concentrations très faibles des produits de dissociation, nous avons cherché à intégrer cet équilibre dans un couple électrochimique. L'électrode de platine n'est pas bien adaptée à l'étude du comportement électrochimique des dérivés oxygénés de l'azote en milieu non aqueux, les systèmes étudiés se révélant en général peu rapides [6, 7]. Nous avons été amenés à utiliser un complexe intermédiaire de  $NO^+$  moins dissocié:  $NOCl$ , et un autre type d'électrode indicatrice: l'électrode d'argent. En effet, cette électrode étant indicatrice de la concentration du chlorure dans le sulfolane, nous avons pu dans une première étape déterminer la constante de dissociation de  $NOCl$  selon l'équilibre



Le chlorure de nitrosyle étant moins dissocié que  $N_2O_4$ , il est possible d'accéder à la valeur de la constante de l'équilibre (1) en suivant la neutralisation d'une solution de  $N_2O_4$  par une solution de chlorure, à l'électrode d'argent. Nous avons pu en déduire une méthode de dosage de solutions de  $N_2O_4$ .

## PARTIE EXPERIMENTALE

Le sulfolane (Merck) est purifié selon la méthode déjà décrite [8].  $N_2O_4$  est préparé par oxydation de  $NO$  par l'oxygène. L'oxyde azotique est préparé par addition d'une solution aqueuse saturée de nitrite de sodium à une solution sulfurique de sulfate ferrique. Le produit obtenu est redistillé sous courant d'oxygène. L'oxygène dissous est ensuite éliminé sous pression réduite à la température de l'azote liquide. Le chlorure et le nitrate de tétraéthylammonium (Eastman-Kodak) sont séchés sous vide dynamique pendant 8 jours à  $30^\circ C$ . Les perchlorates d'argent (Fluka) et de tétraéthylammonium (Carlo Erba) sont séchés à  $60^\circ C$  sous pression réduite. Le perchlorate de nitrosyle est préparé selon Goddard et al. [9].

L'électrode d'argent est recouverte d'un dépôt de  $AgCl$ , avant chaque manipulation, par oxydation de l'électrode d'argent dans une solution de chlorosulfate de tétraéthylammonium dans le sulfolane. Nous avons utilisé ce complexe du chlorure pour éviter la formation d'ion  $AgCl_2^-$ . La préparation de  $(C_2H_5)_4NSO_3Cl$  a été décrite [8]. L'électrode est ensuite rincée soigneusement par du sulfolane pur.

Les courbes  $i = f(E)$  ont été tracées à l'aide d'un ensemble voltampérométrique Tacussel. Nous avons utilisé un millivoltmètre Isis 20 000 Tacussel pour la potentiométrie. La stabilité des mesures est contrôlée sur un enregistreur Tacussel EPL 2, relié au millivoltmètre. Toutes les préparations de

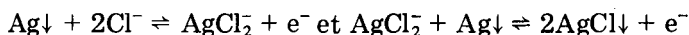
solutions sont effectuées en boîte sèche. Les manipulations ont été réalisées à  $30 \pm 0,10^\circ\text{C}$ . L'électrode de référence est constituée par un fil d'argent plongeant dans une solution de  $\text{AgClO}_4$  0,1 M reliée à la cellule de mesure par un pont rempli d'une solution de  $(\text{C}_2\text{H}_5)_4\text{NClO}_4$  0,1 M.

Le potentiel de demi-vague du système ferrocène—ferricinium ( $\text{Fc}/\text{Fc}^+$ ) est pris comme origine de l'échelle des potentiels.

## RESULTATS ET DISCUSSION

### *Etude des solutions de NOCl dans le sulfolane*

La Fig. 1 représente la courbe intensité—potentiel obtenue pour une solution de NOCl en milieu perchlorate de tétraéthylammonium 0,1 M. L'électrode indicatrice est une microélectrode d'argent de 1 mm de diamètre. Cette courbe a été tracée dans le sens des potentiels croissants. Les deux vagues observées peuvent être considérées comme étant la résultante de la réduction de NOCl, suivant:  $2\text{NOCl} + 2\text{e}^- \rightleftharpoons 2\text{NO} + 2\text{Cl}^-$ , et de l'oxydation simultanée de l'argent en présence de chlorure selon



La vague anodique correspond à l'oxydation de l'argent en présence de NOCl selon:



Le courant limite de diffusion relatif à cette oxydation est égal en valeur absolue à la somme des courants limites de diffusion des deux vagues cathodiques, ce qui est en accord avec les mécanismes proposés. Le potentiel de demi-vague correspondant à l'équilibre (3) ne varie pas en fonction de la concentration tant que l'on n'observe pas de "passivation". L'étude mathématique de cette vague anodique montre alors que le système électrochimique (3) est rapide. L'électrode d'argent recouverte de AgCl est donc bien adaptée à l'étude de ce système.

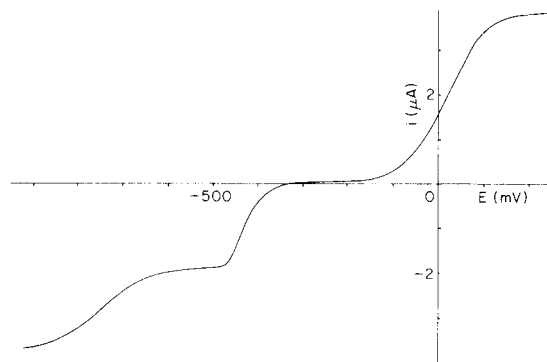
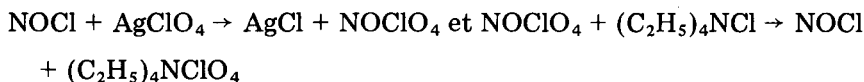


Fig. 1. Courbe  $i = f(E)$  d'une solution de NOCl ( $5 \times 10^{-3} \text{ mol l}^{-1}$ ) dans le sulfolane (électrode indicatrice d'argent).

Ayant vérifié, par conductimétrie, que le chlorure de tétraéthylammonium et les perchlorates d'argent et de nitrosyle sont des électrolytes forts dans le sulfolane, nous avons entrepris l'étude des réactions suivantes:



Les courbes potentiométriques obtenues sont représentées sur la Fig. 2.

La transformée logarithmique de ces courbes confirme la réversibilité du système électrochimique mis en jeu (le coefficient moyen de la loi de Nernst est trouvé égal à  $60 \pm 2$  mV par unité de logarithme). Le potentiel normal du système (3) est  $E^0 = -22 \pm 3$  mV (par rapport au potentiel de demi-vague du système Fc/Fc<sup>+</sup>). Le faible écart observé entre cette valeur et celle du potentiel de demi-vague, tirée des courbes  $i = f(E)$ , peut être dû aux valeurs différentes des constantes de diffusion des espèces NOCl et NO<sup>+</sup>. En tenant compte du potentiel normal du système Ag/Ag<sup>+</sup> [8],  $E^0 = 373$  mV, et du produit de solubilité de AgCl ( $K_{so} = 3,7 \times 10^{-19} \text{ mol}^2 \text{ l}^{-2}$ ), la constante de dissociation de NOCl suivant l'équilibre (2) est, ramenée à force ionique nulle:

$$K_{(\text{NOCl})} = [\text{NO}^+][\text{Cl}^-]/[\text{NOCl}] = 10^{-11,8 \pm 0,2} \text{ mol l}^{-1}$$

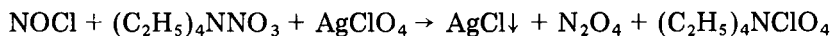
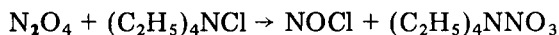
Le chlorure de nitrosyle, peu dissocié dans le sulfolane, doit donc permettre l'étude de complexes donneurs de NO<sup>+</sup> plus dissociés.

#### *Etude des solutions de N<sub>2</sub>O<sub>4</sub> dans le sulfolane*

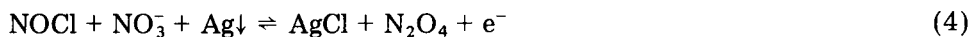
Dans cette étude, nous ne tiendrons pas compte de la dissociation de N<sub>2</sub>O<sub>4</sub> selon  $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2^+ + \text{NO}_2^-$ . En effet, une telle dissociation, si elle existe, ne peut être que très faible en raison du fort pouvoir oxydant de NO<sub>2</sub><sup>+</sup> et du caractère réducteur marqué du nitrite dans ce solvant. Une étude en cours montre que les potentiels de demi-vague des systèmes électrochimiques faisant intervenir ces deux entités chimiques sont séparés par plus de 1 V dans le sulfolane. On peut donc admettre que la seule dissociation ionique de N<sub>2</sub>O<sub>4</sub> dans le sulfolane est  $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}^+ + \text{NO}_3^-$ .

Notons que N<sub>2</sub>O<sub>4</sub> peut également donner lieu à la dissociation homolytique  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ . La constante de cet équilibre a été mesurée dans différents solvants. Ainsi, à 25°C, elle est égale à  $1,78 \times 10^{-4} \text{ mol l}^{-1}$  dans CCl<sub>4</sub>[5]. Cette constante diminue en utilisant un solvant de nombre donneur (DN) de Gutmann [4] plus élevé. Ainsi, dans l'acétonitrile (DN = 14,1), cette constante est égale à  $3 \times 10^{-5} \text{ mol l}^{-1}$  à 25°C et  $5 \times 10^{-5}$  à 30°C, valeur calculée à partir des valeurs de  $\Delta H$  et  $\Delta S$  données par Redmond et Wayland [5]. Ces derniers, remarquant que la dissociation en NO<sub>2</sub> augmente si la basicité du solvant diminue, concluent que N<sub>2</sub>O<sub>4</sub> est un acide de Lewis plus fort que NO<sub>2</sub>. On peut donc admettre que, dans le sulfolane (DN = 14,8), cette constante sera de même ordre de grandeur que dans l'acétonitrile. Cette hypothèse est en accord avec la légère coloration jaune pâle des solutions de N<sub>2</sub>O<sub>4</sub> dans le sulfolane à 30°C.

Nous avons montré précédemment que l'électrode d'argent recouverte de AgCl est indicatrice du rapport  $(\text{NO}^+)/(\text{NOCl})$ . Il est donc possible de suivre avec une telle électrode le dosage, par une solution de chlorure, de complexes de  $\text{NO}^+$  plus dissociés que  $\text{NOCl}$ . Les courbes potentiométriques (courbes 3 et 4) représentées sur la Fig. 2 ont été obtenues lors des réactions:



Cette dernière réaction est effectuée en présence d'un excès de nitrate. Il est nécessaire que le dépôt de chlorure d'argent recouvre entièrement l'électrode pour éviter son attaque par  $\text{N}_2\text{O}_4$ . L'étude mathématique de ces courbes montre que l'influence de la dissociation homolytique de  $\text{N}_2\text{O}_4$  est quasi-négligeable, (si l'on prend pour constante de dissociation celle calculée dans l'acétonitrile à 30°C) et que le système



est rapide à cette électrode, le coefficient de la loi de Nernst étant égal à  $62 \pm 3$  mV par unité de logarithme (l'écart-type sur les droites de régression est dans tous les essais inférieur à 1 mV).

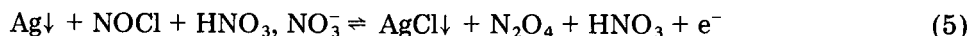
Le potentiel normal du système (4) est  $E^0 = -456 \pm 2$  mV. Nous pouvons en déduire la constante de dissociation de  $\text{N}_2\text{O}_4$  selon équilibre (1) soit, ramenée à force ionique nulle:

$$K_{(\text{N}_2\text{O}_4)} = [\text{NO}^+][\text{NO}_3^-]/[\text{N}_2\text{O}_4] = 10^{-7.2 \pm 0.3} \text{ mol l}^{-1}$$

Cette valeur est en accord avec les résultats conductimétriques qui montrent que  $\text{N}_2\text{O}_4$  est un électrolyte très faible dans le sulfolane. Remarquons cependant que, l'acide nitrique étant un acide très faible dans ce solvant ( $\text{p}K_{\text{HNO}_3} > \text{p}K_{\text{HCl}} = 14,5$  [10]),  $\text{N}_2\text{O}_4$  sera ionisé par de nombreux acides.

#### *Titration de $\text{N}_2\text{O}_4$ dans les mélanges $\text{N}_2\text{O}_4$ - $\text{HNO}_3$*

La Fig. 2 montre donc qu'il est possible de titrer des solutions de  $\text{N}_2\text{O}_4$  par une solution de chlorure. Nous avons voulu étendre ce dosage au cas des mélanges  $\text{HNO}_3$ - $\text{N}_2\text{O}_4$ . Il existe en effet peu de méthodes permettant la détermination de faibles quantités de  $\text{N}_2\text{O}_4$  dans l'acide nitrique. La Fig. 3 (courbe 2) représente le dosage de  $\text{N}_2\text{O}_4$  en présence de  $\text{HNO}_3$ . On peut remarquer que les potentiels sont plus élevés que lors du dosage de  $\text{N}_2\text{O}_4$  seul, en raison du faible pouvoir solvatant du sulfolane envers les anions. Il faut donc tenir compte de l'équilibre d'homoconjugaison entre  $\text{NO}_3^-$  et  $\text{HNO}_3$ . Le système électrochimique mis en jeu avant l'équivalence est donc:



L'étude mathématique de la courbe montre que le système (5) est rapide, et que la constante d'homoconjugaison relative à l'équilibre  $\text{NO}_3^- + \text{HNO}_3 \rightleftharpoons \text{HNO}_3, \text{NO}_3^-$  a pour valeur  $K = [\text{NO}_3^-][\text{HNO}_3]/[\text{HNO}_3, \text{NO}_3^-] = 10^{-3.1 \pm 0.3} \text{ mol l}^{-1}$ .



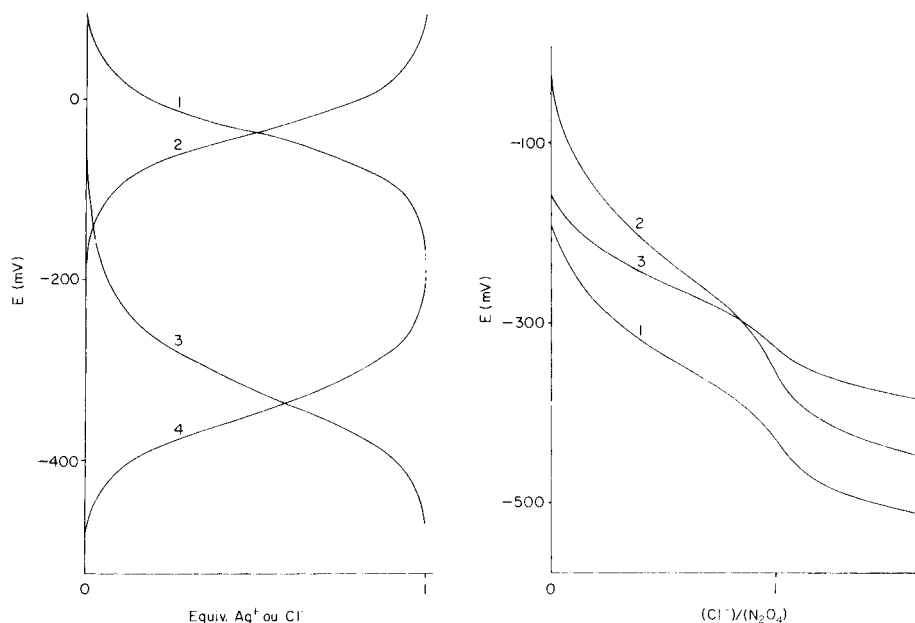
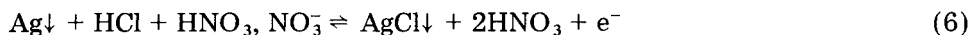


Fig. 2. Courbes potentiométriques (électrodes Ag/AgCl) obtenues dans le sulfolane lors des réactions: (1)  $\text{NOClO}_4$  ( $4 \times 10^{-2} \text{ mol l}^{-1}$ ) +  $(\text{C}_2\text{H}_5)_4\text{NCl}$ ; (2)  $\text{NOCl}$  ( $3,5 \times 10^{-2} \text{ mol l}^{-1}$ ) +  $\text{AgClO}_4$ ; (3)  $\text{N}_2\text{O}_4$  ( $2,2 \times 10^{-2} \text{ mol l}^{-1}$ ) +  $(\text{C}_2\text{H}_5)_4\text{NCl}$ ; (4)  $\text{NOCl}$  ( $2,3 \times 10^{-2} \text{ mol l}^{-1}$ ) +  $(\text{C}_2\text{H}_5)_4\text{NNO}_3$  ( $4,1 \times 10^{-2} \text{ mol l}^{-1}$ ) +  $\text{AgClO}_4$ .

Fig. 3. Courbes potentiométriques (électrode Ag/AgCl) de dosage d'une solution de  $\text{N}_2\text{O}_4$  ( $0,04 \text{ mol l}^{-1}$ ) par une solution de  $(\text{C}_2\text{H}_5)_4\text{NCl}$ , en présence de (1)  $[\text{HNO}_3] = 0$ ; (2)  $[\text{HNO}_3] = 0,1 \text{ mol l}^{-1}$ ; (3)  $[\text{HNO}_3] = 0,5 \text{ mol l}^{-1}$ , électrolyte  $((\text{C}_2\text{H}_5)_4\text{NNO}_3) = 0,1 \text{ mol l}^{-1}$ .

La valeur élevée de cette constante montre bien qu'il est nécessaire de tenir compte de cet équilibre. Si l'on augmente la concentration d'acide nitrique, l'amplitude du saut de potentiel diminue. Après l'équivalence, le système électrochimique intervenant est



La présence de l'acide chlorhydrique, acide plus fort que l'acide nitrique, est due au gros excès de  $\text{HNO}_3$  par rapport au chlorure introduit après l'équivalence.

L'application de la loi de Nernst aux systèmes (5) et (6) confirme la diminution du saut de potentiel si la concentration en acide nitrique croît. Le dosage de  $\text{N}_2\text{O}_4$  en présence d'acide nitrique est possible tant que le rapport de concentration  $(\text{HNO}_3)/(\text{N}_2\text{O}_4)$  est inférieur à 10. La valeur de ce rapport peut être augmentée en utilisant le nitrate de tétraéthylammonium comme électrolyte "indifférent" (courbe 3, Fig. 3). En effet, ce dernier diminue par complexation, l'influence de l'acide nitrique. Le dosage est ainsi possible pour des concentrations en  $\text{HNO}_3$  allant jusqu'à 90% en poids.

## CONCLUSION

Ainsi, nous avons pu, en utilisant l'électrode d'argent recouverte de AgCl, déterminer les constantes de dissociation des complexes de  $\text{NO}^+$ :  $\text{NOCl}$  et  $\text{N}_2\text{O}_4$ , en solution dans le sulfolane, solvant moyennement dissociant. Le chlorure de nitrosyle est moins dissocié que  $\text{N}_2\text{O}_4$ , ce qui devrait permettre de généraliser cette étude à d'autres donneurs de  $\text{NO}^+$  et à l'influence de l'addition de bases ou d'acides de Lewis (catalyseurs de nitration) sur la dissociation ionique de  $\text{N}_2\text{O}_4$ .

Le dosage de  $\text{N}_2\text{O}_4$  seul ou en présence d'acide nitrique est possible par une solution de chlorure. Une étude de l'hydrolyse de  $\text{N}_2\text{O}_4$ , en cours, devrait permettre de généraliser ce dosage au cas des mélanges  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_4$ ,  $\text{H}_2\text{O}$ , dosage qui est d'un grand intérêt dans la synthèse industrielle de l'acide nitrique.

Nous remercions Monsieur le Professeur Trémillon pour ses discussions fructueuses et ses encouragements, et la Délégation Générale à la Recherche Scientifique pour l'aide financière apportée à ces travaux. Contrat D.G.R.S.T. C.N. 77.7.0777.

## BIBLIOGRAPHIE

- 1 C. C. Addison, Chemistry in Non-aqueous Ionizing Solvents, Part I, Vol. 3, Pergamon, Oxford, 1967.
- 2 S. J. Kuhn et G. A. Olah, J. Am. Chem. Soc., 83 (1961) 4564.
- 3 G. A. Olah et S. J. Kuhn, Friedel and Related Reactions. Acylation and Related Reactions, Vol. 3, Part II, Interscience, New York, 1964, p. 1393.
- 4 V. Gutmann, Chem. Tech., (1977) 255.
- 5 T. F. Redmond et B. B. Wayland, J. Phys. Chem., 72 (1968) 1626.
- 6 D. Serve, Thèse, Grenoble (1972), n° AO 7174.
- 7 G. Bontempelli, G. A. Mazzochin et F. Magno, J. Electroanal. Chem., 55 (1974) 91.
- 8 P. Pierens, Y. Auger, J. C. Fischer et M. Wartel, Can. J. Chem., 53 (1975) 2989.
- 9 D. R. Goddard, E. D. Hughes et C. K. Ingold, J. Chem. Soc., (195) 2559.
- 10 J. F. Coetzee et R. J. Bertozzi, Anal. Chem., 45 (1973) 1064.

## DOSAGE ELECTROCHIMIQUE DU COBALT

### I. Etude des Courbes Intensité—Potentiel du Système cobalt(III)/cobalt(II) en Milieu Picolique

G. CLEMENT

*Ecole Nationale Supérieure des Arts et Métiers, 71250 Cluny (France)*

M. R. PÂRIS\*

*Laboratoire de Chimie de Coordination, Université de Dijon, B.P. 138, 21004 Dijon Cédex (France)*

(Reçu le 1 mai 1979)

#### RESUME

En vue de mettre au point un dosage électrochimique du cobalt dans les aciers, les auteurs décrivent les courbes intensité—potentiel, tracées sur platine et relatives aux couples Co(III)/Co(II) et Fe(III)/Fe(II) en milieu complexant d'acide picolique. Ils montrent que le fer(III) oxyde le cobalt(II) dans ce milieu et que l'on peut doser le fer(II) formé par un oxydant tel que le cérium(IV).

#### SUMMARY

*Electrochemical determination of cobalt. Part I. Studies of current—voltage curves of the cobalt(III)/cobalt(II) system in picolinic acid media*

As a preliminary to the development of electrochemical determinations of cobalt in steels, current—voltage curves at a platinum electrode were studied for the systems cobalt(III)/cobalt(II) and iron(III)/iron(II) in media containing picolinic acid as complexing agent. Iron(III) oxidizes cobalt(II) in this complexing medium, and the iron(II) formed can be determined by an oxidant such as cerium(IV).

Si l'une des tendances actuelles des analystes est de s'orienter vers des analyses de traces par des méthodes de plus en plus sophistiquées, il subsiste, dans le domaine des éléments qualifiés "d'abondants", des méthodes de dosage laissant souvent à désirer, parce que reposant encore sur des techniques archaïques comme la gravimétrie (citons à ce sujet la dispersion des résultats observés [1] sur le dosage de l'aluminium dans les bauxites) ou bien faisant appel à la technique spectrophotométrique tributaire de nombreuses interférences malgré le recours "aux blancs" pour réaliser des étalonnages d'une fiabilité douteuse. En dépit de leur développement continu depuis de nombreuses années, les techniques électrochimiques semblent encore boudées dans la panoplie des méthodes de référence: il suffit pour s'en convaincre d'examiner les recueils de normes d'analyses (AFNOR) par exemple

[2] qui donnent une seule méthode de dosage potentiométrique: celle du manganèse connue depuis 1941; deux autres titrages électrochimiques doivent être proposées pour le vanadium et le chrome.

Nous envisageons dans le présent travail de développer une méthode électrochimique, de dosage du cobalt adaptée aux aciers, notamment ceux destinés à la fabrication d'aimants ou d'outils de coupe rapide; cette méthode sera étendue au cas plus délicat des aciers destinés à la technologie nucléaire, dont la teneur en cobalt ne doit pas dépasser 0,02%. On trouvera une bibliographie exhaustive de ce problème dans les ouvrages spécialisés de chimie analytique [3—5]. Du point de vue électrochimique, en dehors de la réduction cathodique du cobalt [6] qui donne des résultats peu fiables, il est intéressant de mettre à profit les possibilités d'oxydo-réduction du couple Co(III)/Co(II), à condition de se trouver en milieu complexant puisque l'ion  $\text{Co}^{3+}$  simplement hydraté oxyde l'eau. Cette possibilité a été proposée depuis longtemps [7] avec la 1,10-phénanthroline, mais ce réactif est coûteux. Ceci nous conduit à utiliser un composé plus commode d'emploi: l'acide picolique ou carboxy-2-pyridine que nous symboliserons par HL.

#### *Les complexes du cobalt avec l'acide picolique*

Cet acide a fait l'objet de plusieurs études sur ses possibilités de coordination [8—10]. En ce qui concerne le cobalt(II), on observe la formation de trois complexes successifs  $\text{CoL}^+$ ,  $\text{CoL}_2$  et  $\text{CoL}_3^-$  dont les constantes de stabilité sont respectivement:  $\log \beta_1 = 5,32$ ;  $\log \beta_2 = 10,06$  et  $\log \beta_3 = 13,78$  à 25°C et en milieu 0,5 M en  $\text{NaClO}_4$  [11]. Ces constantes permettent de conclure, par l'examen des courbes de distribution (Fig. 1) tracées dans les conditions du dosage, que la totalité de l'ion Co(II) est complexé à pH2 (sous forme de  $\text{CoL}_2$  essentiellement). En ce qui concerne le cobalt(III), il se forme un seul complexe  $\text{CoL}_3$  rouge violacé peu soluble [8] dont la constante de stabilité est très élevée ( $\log K = 34,17$  [12]); nous avons observé que le spectre d'absorption du complexe  $\text{CoL}_3$  demeurerait inchangé dans le tout le domaine de pH habituel (de 2 à 10).

#### EXAMEN DES COURBES INTENSITE—POTENTIEL DES DIVERS SYSTEMES OXYDO-REDUCTEURS

Pour doser le cobalt en milieu picolique, il suffit de trouver un titrant oxydant et de suivre le potentiel d'une électrode indicatrice en fonction du volume de titrant versé. De nombreux oxydants permettent d'oxyder les complexes cobalt(II) en complexes cobalt(III) (peroxodisulfate d'ammonium, eau oxygénée, brome, fer(III) et cérium(IV), permanganate, etc.). Nous avons fixé notre choix sur le cérium(IV) du fait de la stabilité de ces solutions. Il est néanmoins nécessaire de travailler en milieu suffisamment acide pour éviter l'hydrolyse des ions cérium et du fer qui est présent comme oxydant intermédiaire (cf. ci-dessous); inversement, il est indispensable de ne pas opérer en milieu trop acide afin de ne pas inhiber la complexation du

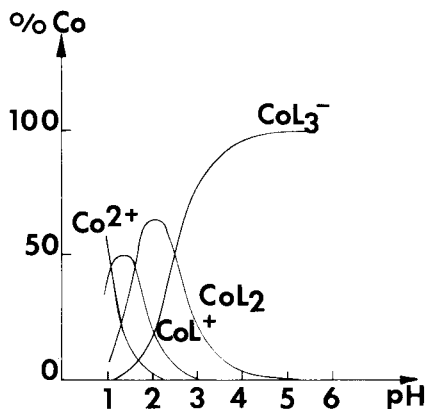


Fig. 1. Courbes de distribution des complexes du Co(II) en milieu picolique (HL); HL: Co = 50.

cobalt(II) (cf. Fig. 1). Le meilleur compromis se situe à  $\text{pH } 2 \pm 0,1$  sur des quantités de l'ordre de  $10^{-4}$  mol de cobalt. En outre des essais de dosages potentiométriques effectués parallèlement au tracé des courbes intensité—potentiel, montrent que les conditions optimales de concentration en acide picolique sont de  $1,5 \text{ g}/100 \text{ cm}^3$  soit  $0,12 \text{ M}$ . Enfin nous avons utilisé une électrode de platine poli pour effectuer ces courbes intensité—potentiel.

#### *Couple Co(III)/Co(II) en milieu picolique 0,12 M*

Comme le montre la Fig. 2, le système Co(III)/Co(II) en milieu picolique est un système lent sur platine poli. La vague d'oxydation se situe vers  $0,6 \text{ V}$  vs. ECS (courbe 1) et la vague de réduction vers  $0,0 \text{ V}$  vs. ECS (courbe 2). Lorsque l'on ajoute graduellement une solution de cérium(IV) à une solution de Co(II) complexé par l'acide picolique, on constate qu'au point d'équivalence (correspondant à la courbe 2) le courant de diffusion est nul entre  $0,3$  et  $1 \text{ V}$ . Au-delà il apparaît le courant de diffusion traduisant la réduction de Ce(IV) en excès (courbe 3). Il est donc possible de suivre l'oxydation du cobalt par le cérium par potentiométrie à intensité nulle; toutefois les expériences montrent que les potentiels sont instables avant le point d'équivalence du fait de la lenteur du système Co(III)/Co(II). Il convient de signaler que nous avons montré par ailleurs [12] la rapidité du couple Co(III)/Co(II) sur électrode d'or; on obtient alors une valeur de  $0,17 \text{ V}$  pour le potentiel de ce couple oxydo-réducteur.

#### *Couple Fe(III)/Fe(II) en milieu picolique 0,12 M*

La présence du fer dans les aciers au cobalt, nous a bien entendu amenés à considérer les caractéristiques d'oxydoréduction du système Fe(II)/Fe(III) en milieu picolique  $0,12 \text{ M}$  et  $\text{pH}2$ . La Fig. 3 reproduit quelques courbes

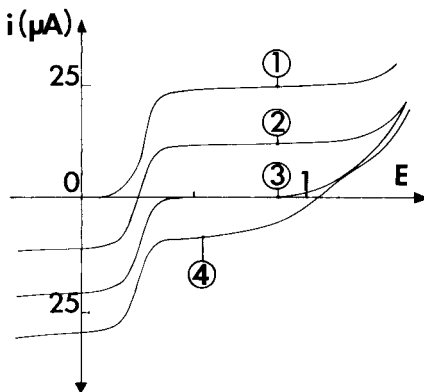
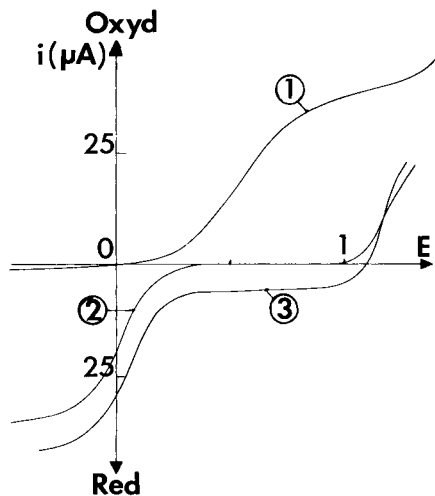


Fig. 2. Courbes intensité—potential du couple  $\text{Co(III)/Co(II)}$  en milieu picolique: (1)  $\text{Co(II)}$ ; (2)  $\text{Co(III)}$ ; (3)  $\text{Co(III) + Ce(IV)}$ .

Fig. 3. Courbes intensité—potential du couple  $\text{Fe(III)/Fe(II)}$  en milieu picolique: (1)  $\text{Fe(II)}$  seul; (2) addition d'une quantité de  $\text{Ce(IV)}$ ; (3) addition de  $\text{Ce(IV)}$  en quantité égale; (4) addition d'un excès de  $\text{Ce(IV)}$ .

intensité—potential qui montrent que le système considéré est rapide; ces courbes ont été obtenues en ajoutant du sulfate de cérium(IV) à une solution de picolate de fer(II), la quantité stoechiométrique correspondant à la courbe 3. Le potentiel du couple  $\text{Fe(III)/Fe(II)}$  dans les conditions expérimentales choisies est de + 0,25 V sur électrode de platine poli.

#### *Oxydation du cobalt(II) par le fer(III) en milieu picolique 0,12 M*

La faible différence des potentiels des couples  $\text{Fe(III)/Fe(II)}$  (0,25 V) et  $\text{Co(III)/Co(II)}$  (0,17 V) autorise à penser qu'en milieu picolique, le picolate de fer(III) doit oxyder le picolate de cobalt(II). C'est effectivement ce que l'on observe sur la Fig. 4 où l'on a rassemblé les courbes intensité—potential tracées sur platine poli à partir de solutions de picolate cobalteux additionnées graduellement de sel ferrique. La courbe 1 est relative à l'électrolyte support et la courbe 2 à la solution de picolate de cobalt(II) pour laquelle on observe la vague d'oxydation irréversible à 0,6 V environ. Au cours de l'oxydation progressive par le picolate de fer(III) (courbes 2—8) on observe l'apparition de la vague du complexe de fer(II) à 0,25 V, la diminution progressive de celle du complexe de cobalt(II) à 0,6 V et enfin l'augmentation de celle du complexe de cobalt(III) vers 0,0 V.

La courbe 8 qui correspond à un léger excès de fer(III) par rapport à la quantité de cobalt présente, traduit bien la vague réversible du couple  $\text{Fe(III)/Fe(II)}$  en milieu picolique; toutefois on constate qu'il subsiste encore

un peu de Co(II) non oxydé (inflexion sur la courbe 8 vers 0,6 V) cet épaulement disparaît par contre en présence d'un plus grand excès de fer (pour une quantité de fer 5 fois égale à la quantité de cobalt). Ces observations permettent de conclure que l'oxydation du cobalt(II) par le fer(III) en milieu picolique, du fait du faible écart entre les deux potentiels, n'est totale que si le milieu renferme un excès de fer(III): ceci est précisément le cas rencontré lors du dosage d'un acier où le fer est le constituant prédominant.

Alors qu'habituellement, il faut l'éliminer par des extractions fastidieuses, nous nous proposons ici de l'utiliser comme oxydant insitu du cobalt(II): le dosage se ramène donc à celui du fer(II) formé. Il suffit alors d'effectuer un dosage potentiométrique par le Ce(IV) ce qui permettra d'obtenir un saut de potentiel important au point d'équivalence: on passe en effet du potentiel du couple réversible Fe(III)/Fe(II) en milieu picolique (0,25 V) à celui du couple Ce(IV)/Ce(III) situé à plus de 1,0V.

## RESULTATS ET INTERFERENCES

Afin de connaître les possibilités d'application de la méthode proposée, nous avons étudié la dispersion des résultats sur 12 essais identiques sur une solution synthétique de cobalt obtenue par dissolution du cobalt de pureté spectroscopique (Johnson-Matthey). Pour une valeur moyenne  $x_m = 9,149 \times 10^{-5}$  mol, l'écart absolu était égal à  $2,3 \times 10^{-7}$  mol, soit un écart relatif moyen de 0,09%.

Du point de vue des interférences induites par la présence d'autres cations métalliques, on peut penser que les ions à valences multiples auront une action perturbatrice. Le Tableau 1 résume les résultats obtenus.

On constate que les ions colorés (Cu, Ni par exemple) modifient simplement la couleur jaune des complexes de cobalt(II) et fer(III). Pour ce qui concerne le manganèse nous avons pu montrer [14] que l'ion  $Mn^{2+}$  n'étant pas complexé dans les conditions du dosage (pH 2) ne subit aucune oxydation en  $Mn^{3+}$ ; cette dernière ne devient appréciable qu'à partir de pH 3-3,5. Le titane(IV) provoque une précipitation due à l'hydrolyse dès que la teneur dépasse  $5 \times 10^{-3}$  mol  $l^{-1}$ ; mais les dosages effectués dans ces conditions montrent que les résultats demeurent corrects. Seul le vanadium présente une interférence notable car le complexe de cobalt(II) réduit le vanadium(V) résultant de l'attaque nitro-chlorhydrique de l'échantillon; le complexe picolique du vanadyle obtenu est oxydé lentement par le cérium(IV).

Le rôle d'oxydant intermédiaire du vanadium(V) est donc nuisible à la rapidité du dosage. Toutefois les essais réalisés montrent qu'en présence de vanadium le saut de potentiel du titrage est déformé même pour un rapport V/Co = 1/3 mais le dosage reste possible jusqu'à un rapport de 1, à condition d'attendre suffisamment longtemps la stabilisation des potentiels au voisinage du point d'équivalence. La Fig. 5 reproduit deux courbes de titrages correspondant à un acier exempt de vanadium (courbe 1) et à un acier à 1,59% de vanadium et 5,70% de cobalt (courbe 2).

TABLEAU 1

## Etude des réactions d'autres cations métalliques

Metal	Rapport métal/cobalt	Interférence	Observations
Cu(II)	10	Nulle	Précipité de picolate de cuivre
	5	Nulle	Léger trouble
	1	Nulle	Solution limpide
Ni(II)	10	Nulle	Solution limpide
Cr(III)	10	Nulle	Solution limpide
Mn(II)	10	Nulle	Solution limpide
V(V) et V(IV)	1	Nulle	Solution limpide
	10	Importante	Solution limpide
Mo(VI)	4	Importante	Solution limpide
	1	Faible	Solution limpide
Ti(IV)	10	Nulle	Trouble très léger
	5	Nulle	Solution limpide
Cr(VI)	5	Légère	Précipité faible
	2	Nulle	Solution limpide
	1	Forte	Solution limpide

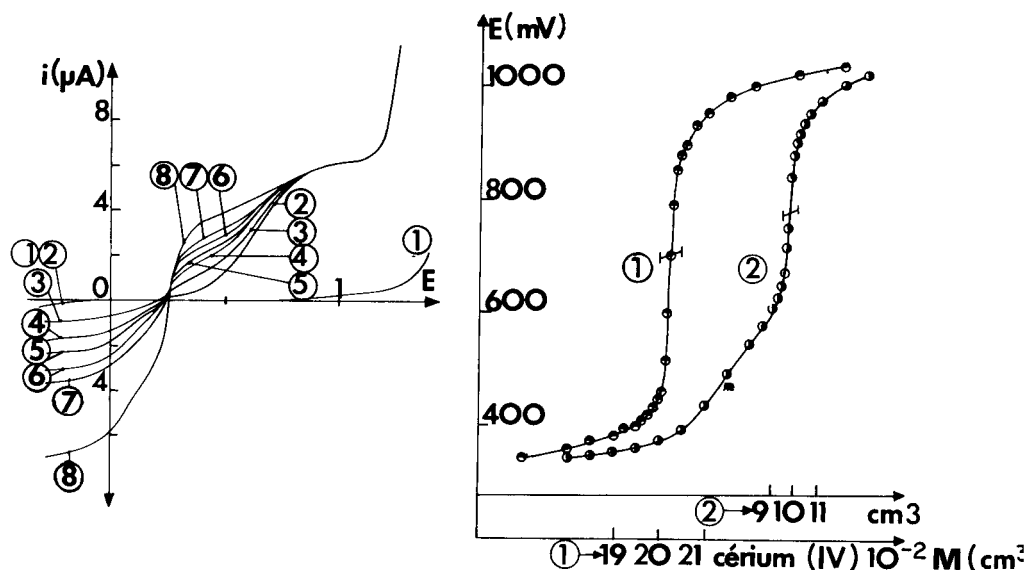


Fig. 4. Courbes intensité-potential relevées au cours de l'addition progressive de Fe(III) dans une solution de Co(II)  $1,828 \times 10^{-4}$  M: (1) électrolyte support (2 g HL + 25 ml  $\text{Na}_2\text{SO}_4$  M + 60 ml  $\text{H}_2\text{O}$ ); (2) solution de cobalt dans l'électrolyte de support; (3)–(8) additions de Fe(III): (3)  $2 \times 10^{-5}$  M; (4)  $4 \times 10^{-5}$  M; (5)  $6 \times 10^{-5}$  M; (6)  $8 \times 10^{-5}$  M; (7)  $10^{-4}$  M; (8)  $2 \times 10^{-4}$  M.

Fig. 5. Courbe de dosage du cobalt dans deux aciers: (1) acier BCS 233 sans vanadium; (2) acier BCS 241/2, rapport V/Co = 0,28.



## CONCLUSIONS

Cet ensemble de résultats montre que l'oxydation du cobalt(II) en cobalt(III) en milieu picolique, se fait par les ions ferriques et que dès lors le dosage du cobalt se ramène à celui du fer(II) formé. On peut donc prévoir qu'un dosage par addition d'un oxydant extérieur tel que le cérium(IV) ou par génération coulométrique d'un oxydant permettra de résoudre le problème dans une gamme étendue de concentrations [13].

## BIBLIOGRAPHIE

- 1 H. de la Roche-Govindaraju, *Bull. Soc. Fr. Ceram.*, 100 (1973) 49.
- 2 *Recueil des Normes des Produits Sidérurgiques*, Tome IV: Méthodes d'analyse et Matières Premières, Ed. AFNOR, Paris, 1972.
- 3 I. M. Kolthoff et P. J. Elving (Eds.), *Treatise on Analytical Chemistry*, Part II, Vol. 2, Interscience, New York, 1962.
- 4 G. Charlot, *Chimie Analytique Quantitative*, Tome II, Masson, Paris, 1974.
- 5 J. T. Stock, *Amperometric Titrations*, Wiley-Interscience, New York, 1965.
- 6 D. H. Brophy, *Ind. Eng. Chem., Anal. Ed.*, 3 (1931) 363.
- 7 L. Florant-Daltroff, *Bull. Soc. Chim. Fr.*, (1961) 823; (1962) 1039.
- 8 G. Thomas, Thèse, Lyon (1961).
- 9 L. G. Sillén et A. E. Martell, *Stability Constants (Supplement 1)*, Special Publ. 25, Chemical Society, London, 1971.
- 10 Chang Ma Nang Li, *J. Coord. Chem.*, 1 (1972) 33.
- 11 P. Livrozet, Thèse, Dijon (1975).
- 12 K. H. Pek-Choor, Thèse, Dijon (1978).
- 13 G. Clement et M. R. Pâris, *Anal. Chim. Acta*, 110 (1979) 227.
- 14 G. Clement, Thèse, Dijon (1976).

## DOSAGE ELECTROCHIMIQUE DU COBALT

### II. Applications aux Aciers à Faible ou à Moyenne Teneurs

G. CLEMENT

*Ecole Nationale Supérieure des Arts et Métiers, 71250 Cluny (France)*

M. R. PÂRIS\*

*Laboratoire de Chimie de Coordination, Université de Dijon, B.P. 138, 21004 Dijon Cédex (France)*

(Reçu le 1 mai 1979)

#### RESUME

Deux méthodes ont été mises au point pour le dosage du cobalt dans les aciers: une méthode potentiométrique, utilisable pour des teneurs supérieures à 500 ppm, qui n'exige que rarement des séparations lorsque la teneur dépasse 10 000 ppm; et une méthode de titrage coulométrique, avec fin potentiométrique lorsque la teneur est inférieure à 500 ppm, cas important pour les aciers destinés à la construction nucléaire. Le matériel utilisé est peu coûteux. La précision relative est meilleure que 2% dans ces d'un acier de composition très complexe contenant seulement 0,034% de cobalt.

#### SUMMARY

*Electrochemical determination of cobalt. Part II. Applications to steels with low and medium cobalt contents.*

Two methods are described for the determination of cobalt in steels; picolinic acid media are used in both cases. A potentiometric method is suitable for concentrations above 500 ppm, generally without separation at concentrations above 10,000 ppm. A coulometric titration with a potentiometric end-point is preferred when the cobalt content is less than 500 ppm. This case is very important for steels used in the nuclear industry. Sophisticated equipment is not required for these methods. The relative standard deviation is better than 2% for a steel with a very complex composition, containing only 0.034% of cobalt. The limit of determination is about 50 ppm.

Il a été montré précédemment [1], par étude du comportement oxydo-réducteur du cobalt en milieu complexant d'acide picolique, que l'ion cobalt(II) réduit le fer(III) en se transformant en ion cobaltique: le dosage du cobalt se ramène donc à celui du fer(II) formé.

Pour réaliser ce dosage deux solutions sont possibles suivant la teneur en cobalt: si celle-ci dépasse 500 ppm, on peut se contenter de doser le fer(II) formé par addition progressive d'un oxydant classique tel que le cérium(IV). Par contre, si la teneur en cobalt est inférieure à 500 ppm, on utilisera une génération coulométrique de l'oxydant. Cette dernière méthode s'avère particulièrement intéressante pour les aciers destinés à la construction

nucléaire, qui doivent titrer moins de 200 ppm de cet élément du fait de l'activation neutronique dans les réacteurs. La limite du dosage proposé se situerait au voisinage de 50 ppm.

#### CAS DES ACIERS A TENEUR EN COBALT > 10 000 ppm

L'attaque de l'acier se fera soit par l'acide chlorhydrique suivie d'une oxydation par quelques gouttes d'acide nitrique en fin de réaction, soit par l'eau régale. Pour le cas où l'acier contiendrait du tungstène, on l'éliminera sous forme d'acide tungstique en fin d'attaque par les procédés habituels.

#### *Mode opératoire*

Le dosage se fera sur des parties aliquotes de  $0,04$  à  $0,40 \times 10^{-3}$  mol de cobalt pour un volume de 100 ml environ. La prise d'essai est versée dans le récipient de titrage muni d'une électrode de platine, d'une électrode en verre et d'une électrode au calomel. Sous courant d'azote, on introduit 30 ml d'une solution 1 M de sulfate de sodium, puis 1,5 g d'acide picolique sublimé. Après 20 min de dégazage on amène le pH à 2 ( $\pm 0,05$ ) par addition de soude, et après 20 min (temps nécessaire pour la formation du complexe de Co(II)), on titre par du sulfate de cérium(IV)  $1 \times 10^{-2}$  M fraîchement préparé en maintenant le pH à 2. Au moment du virage, le saut de potentiel dépasse 200 mV.

#### *Résultats*

Ce protocole a été appliqué à deux aciers étalons; les résultats obtenus sont présentés dans le tableau 1.

*Acier BCS 233 (Permanent magnet alloy)*. Cet acier à forte teneur en cobalt présente la composition suivante résultant de la moyenne de plusieurs laboratoires d'analyse: Co 23,72%; Ni (11,22); Al (6,98); Cu (5,09); Ti (0,79); Mn (0,235); Si (0,57); C (0,042); Fe (51,35).

*Acier BCS 241/2 (Acier rapide au vanadium)*. Cet acier a été choisi pour sa teneur en tungstène (séparé après attaque) et en vanadium susceptible d'interférence [1]: Co 5,70%; V (1,59); W (19,9); Cr (5,35); C (0,84); Mo (0,53); Mn (0,27); Si (0,21); Ni (0,15); Cu (0,08); Sn (0,025); S (0,025); P (0,024); Fe (65,31).

*Séparations à effectuer (pouvant concerner tous les aciers dont la teneur en cobalt est supérieure à 500 ppm)*. En raison des interférences [1] il est nécessaire d'éliminer le vanadium, le fer et le chrome(VI): le vanadium lorsque sa teneur est supérieure au tiers de la teneur en cobalt, et le fer dans certains cas. Afin d'éviter des précipitations intempestives de picolates la teneur en fer doit rester inférieure à 400 mg pour 100 ml en solution. Il est nécessaire d'éliminer le chrome(VI) formé par oxydation en milieu nitrique, en particulier lors de l'élimination du tungstène et dans tous les cas où sa teneur est supérieure à 1%. On peut réduire Cr(VI) en Cr(III) (qui n'interfère pas) en opérant ainsi: après l'oxydation nitrique, refroidir, ajouter 1 g de nitrite de potassium, faire bouillir 5 min.

TABLEAU 1

Résultats obtenus pour deux aciers étalons

Acier	Valeurs trouvées (%)	Erreur absolue	Erreur relative (%)
BCS 233	23,81	0,09	0,4
	23,75	0,03	0,13
	23,78	0,06	0,25
BCS 241/2	5,73	0,03	0,5
	5,68	-0,02	-0,35
	5,68	-0,02	-0,35

Toutefois la méthode exposée ci-après élimine complètement la vanadium, le chrome et le fer, grâce à une précipitation par le benzoate d'ammonium suivie d'une concentration en cobalt sur résine Dowex A1 (60–100 mesh) sous forme ammonium. Il n'est pas nécessaire, si l'on opère ainsi, d'ajouter du nitrite de potassium. A noter toutefois, que si l'on élimine le fer, il est nécessaire juste avant le titrage d'introduire 5 cm<sup>3</sup> d'une solution de FeCl<sub>3</sub> 0,1 M fraîchement préparée et bouillie avec quelques gouttes d'acide nitrique concentré (pour les teneurs supérieures à 500 ppm en cobalt).

#### CAS DES ACIERS A FAIBLE TENEUR EN COBALT (<500 ppm)

Pour des teneurs faibles en cobalt, les solutions très diluées de cérium(IV) ne sont plus utilisables: on préfère alors produire le cérium(IV) par coulométrie à intensité constante, le point final du dosage étant toujours détecté par potentiométrie à intensité nulle. En outre étant donné la faible teneur en cobalt, il faut ici nécessairement éliminer l'excès de fer, le vanadium et éventuellement le nickel lorsqu'ils sont en quantité supérieure à 4% afin d'éviter la précipitation du picolate correspondant.

#### Modes opératoires et résultats

*Appareillage.* Le récipient de dosage est une cellule recevant sur son couvercle muni de rodages: une électrode de platine indicatrice, une électrode au calomel, une électrode en verre et les électrodes génératrices en platine (type EGD/Pt/Pt, Tacussel); ces dernières sont constituées d'une spirale centrale et d'une grille supportée par un tube de verre constituant l'anode; ces deux électrodes sont séparées par une pastille de verre fritté recouverte d'un gel d'agar-agar imprégné de chlorure de potassium. Un chronomètre électronique (CE, Tacussel) commande le passage du courant réglé à 1 mA au moyen d'une alimentation stabilisée en courant réalisée au laboratoire (Fig. 1). Les quantités d'électricité envoyées dans le circuit représentent le 1/20 de la quantité théorique correspondant au point d'équivalence, et l'on attend 1 min environ entre chaque nouvelle mise en route du circuit générateur. A proximité du point d'équivalence il est nécessaire d'attendre 3 min avant de lire le potentiel

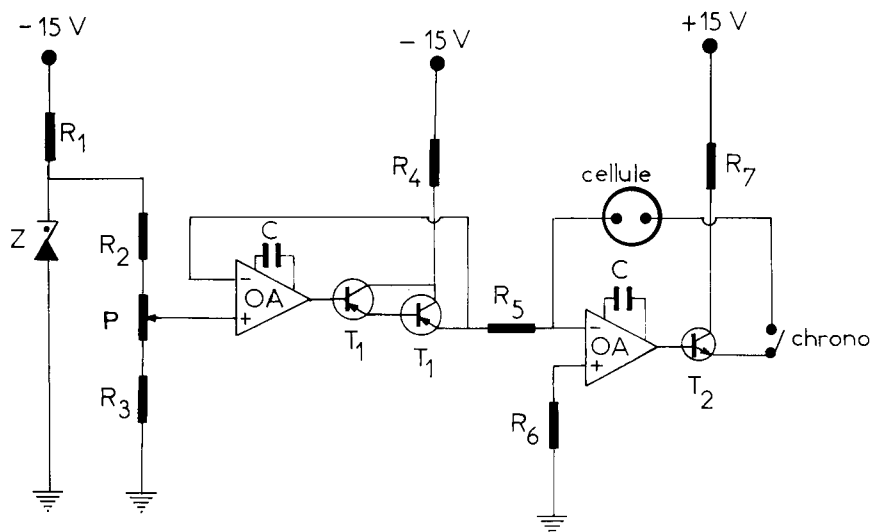


Fig. 1. Schéma électronique de la source de courant 1 mA.  $R_1 = 619 \Omega$ ;  $R_2 = 10 \text{ k}\Omega$ ;  $R_3 = 61 \Omega$ ;  $R_4 = R_5 = R_6 = R_7 = 100 \Omega$ .  $P = 100 \Omega$ ;  $T_1 = 2\text{N}2\ 905 \text{ A}$ ;  $T_2 = 2\text{N}1\ 711$ ; OA = SFC = 2 101 A; Z = 1N 939 A; C = 47 pF.

*Dosage du cobalt sur des solutions étalons.* Avant d'aborder le dosage du cobalt dans un acier, nous avons vérifié le bien fondé de la méthode sur des solutions étalons préparées à partir de cobalt de pureté spectroscopique. Les résultats (Tableau 2) ont été obtenus après correction sur des essais à blanc réalisés sur des solutions contenant tous les réactifs excepté le cobalt.

*Dosage d'un acier BCS 335.* Cet acier retenu pour sa complexité, présente la composition suivante résultant de la moyenne de plusieurs laboratoires: Co 0,034%; Cr (18,45); Ni (9,47); Mn (0,94); Si (0,67) Ti (0,46); Cu (0,11); V (0,040).

Après décapage à l'acide chlorhydrique, on traite 1,000 g d'acier sec par 20 ml d'HCl 6 M; en fin d'attaque on ajoute quelques gouttes d'acide nitrique 68% pour oxyder les ions  $\text{Fe}^{2+}$ . On précipite ensuite Fe(III) et Cr(III) (à teneur importante dans cet échantillon) par addition de 5 ml d'ammoniaque puis de 250 ml d'une solution bouillante de benzoate d'ammonium 0,6 M. Après filtration et lavage, le filtrat est traité par 25 ml d'ammoniaque 6 M puis passé sur colonne de Dowex A1 (50–100 mesh) sous forme ammonium sur laquelle sont retenus les cations Co(II), Ni(II) et Mn(II) en particulier.

Si l'acier est riche en nickel (>4%) il convient de procéder à son élimination: pour cela on élue la colonne Dowex A1 (10g) [2–4] avec 10 ml d'acide chlorhydrique 4 M puis par 40 ml d'eau. On évapore à sec, puis on reprend le résidu par 5 ml d'acide chlorhydrique 12 M et l'on fait passer la solution obtenue sur 1 g de résine Dowex 1-X4 (50–100 mesh) sous forme

TABLEAU 2

Dosage du cobalt sur les solutions étalons

Co introduite ( $\times 10^{-3}$ mol)	<i>i</i> (mA)	Quantité d'électricité (mC)	Co trouvée ( $\times 10^{-3}$ mol)	Erreur relative (%)
0,914	1,010	88,9	0,921	+0,8
0,914	1,010	89,9	0,932	+2
1,828	1,010	178,8	1,852	+1,3
1,828	1,010	176,7	1,832	+0,2
3,656	1,010	365,5	3,695	+1
3,656	1,010	350,5	3,632	-0,7

de chlorure qui ne retient pas le nickel. On élue ensuite les autres ions dont le cobalt par  $4 \times 5$  ml d'eau et on élimine la forte acidité chlorhydrique par évaporation à sec et reprise par 10 ml d'eau.

Si l'acier contient peu de nickel (<4%), l'élution de la colonne Dowex A1 (5 g) se fait simplement avec 5 ml d'acide chlorhydrique 4 M et  $3 \times 10$  ml d'eau.

La prise d'essai résultant de l'un ou l'autre des traitements suivant la teneur en nickel est soumise à une courte ébullition en présence de quelques gouttes d'acide nitrique concentré et après refroidissement introduite dans la cellule de dosage. Le volume de solution doit être voisin de 40 ml. Après 10 min sous barbotage d'azote, on ajoute 5 ml de solution d'acide picolique 1,2 M fraîchement préparée et on amène le pH à 2,2 par addition de hydrogènocarbonate de potassium. On attend 20 min, puis on verse 5 ml de nitrate de cérium 0,25 M en enfin 5 gouttes de solution de fer(III)  $10^{-1}$  M fraîchement préparée et bouillie en présence de quelques gouttes d'acide nitrique. Après avoir fixé les électrodes comme il est indiqué plus haut, on procède au dosage coulométrique du cobalt. Les résultats obtenus après correction de l'essai à blanc, sont présentés dans le Tableau 3 et l'allure des courbes de titrage sur la Fig. 2.

## CONCLUSIONS

Les résultats obtenus, aussi bien pour des solutions synthétiques de cobalt que pour des aciers vérifient les conclusions de la première étude [1] qui laissait présager la possibilité de dosages potentiométriques ou coulométriques du cobalt, grâce à l'oxydation en milieu picolique de Co(II). Les dosages sont réalisables avec une précision dans une gamme élevée de teneurs.

Au-dessus de 10 000 ppm, la précision atteint 0.1% et il n'est pas toujours nécessaire d'effectuer des séparations. Celles-ci sont le plus souvent nécessaires pour les moyennes teneurs et dans tous les cas pour les basses teneurs (<500 ppm) où le titrage coulométrique est alors indispensable. Les résultats sont encore satisfaisants dans ce dernier cas surtout si l'on considère la composition complexe de l'acier choisi.

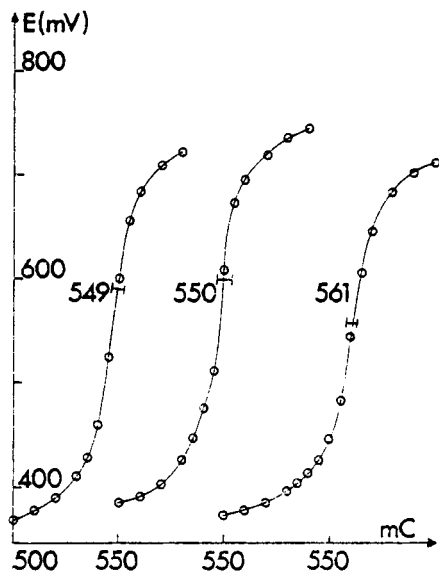


Fig. 2. Courbes de titrage coulométrique de l'acier BCS 335.

TABLEAU 3

Dosage de l'acier BCS 335

Essai	$i$ (mA)	Quantité d'électricité (mC)	Co trouvé (%)
1	1,007	547,8	0,0334
2	1,007	549,8	0,0335
3	1,007	557,9	0,0340

#### BIBLIOGRAPHIE

- 1 G. Clement et M. R. Pâris, *Anal. Chim. Acta*, 110 (1979) 219.
- 2 L. Savidan, *La Chromatographie*, Dunod, Paris, 1970, p. 101.
- 3 B. Trémillon *Les Séparations par les Résines Echangeuses d'Ions*, Gauthier-Villars, Paris, 1965, pp. 230, 231.
- 4 J. J. Kirkland, *Chromatographie en Phase Liquide*, Gauthier-Villars, Paris, 1973, p. 252.

## DETERMINATION OF THE WATER CONTENT IN MUSCOVITES CONTAINING LARGE AMOUNTS OF FLUORINE BY KARL FISCHER TITRATION AFTER FUSION WITH SILICON DIOXIDE

KAZUHISA YAMAYA

*Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Meguro-ku, Tokyo 152 (Japan)*

(Received 19th April 1979)

### SUMMARY

Complete release of water (or of hydrogen in the lattice which is finally released as water) from muscovite containing a large amount of fluorine, requires heating above 1500°C, or addition of an appropriate flux. Experimental data from differential thermal analysis, x-ray diffraction patterns and dehydration curves showed that silicon dioxide is a useful flux. Samples are mixed with a 3 : 1 (weight) ratio of silicon dioxide in a platinum crucible and heated inductively in a nitrogen stream at 1200°C. The water released is absorbed in anhydrous (1 + 1) methanol–1,2-ethanediol and titrated by the Karl Fischer method. For a representative muscovite sample, the water contents were  $4.26 \pm 0.03\%$  at 1300–1400°C and  $4.35 \pm 0.08\%$  above 1500°C in the absence of silicon dioxide. When silicon dioxide was added as described, the mean result was  $4.33 \pm 0.01\%$  at 1200°C (95% confidence level) with a standard deviation of 0.015 and a coefficient of variation of 0.35%.

Determination of the water content of minerals is important, with a variety of implications in mineralogy and geology. The term “water” is here used in the sense that the result of the determination is represented as H<sub>2</sub>O, without reference to the manner in which the hydrogen is incorporated in the crystal lattice. The conventional methods [1–9] for the determination of water in rocks and minerals are not satisfactory with respect to accuracy and precision. The determination of water with high accuracy is difficult and the process is sometimes very complicated compared with analytical methods for other chemical components. Several methods have been proposed for the determination of the water content in rocks and minerals with high accuracy and precision by using Karl Fischer titrations [10–14]. The methods have been applied to determine trace amounts of water in volcanic rocks released during mechanical grinding [10], small amounts of water in volcanic rocks [11], water in highly hydrated glassy rocks and rocks including so-called “residual magmatic water” and “zeolitic water” [12], and water in fluorine-bearing minerals [13, 14].

It was found in earlier work [14] that the higher the fluorine content, the higher was the heating temperature required for complete release of



water from micas such as muscovite, biotite and phlogopite. The water in two muscovite samples containing 0.06% and 0.47% fluorine was released at 1100°C and above 1300°C, respectively. However, it is not practical to heat the samples above 1300°C for long time, and it is desirable to reduce the heating temperature by adding an appropriate flux to the sample. Common fluxes, such as lead oxide and sodium tungstate, contain small amounts of adsorbed water and so cause error to the determination of water.

Several workers [15–17] have reported the reaction between muscovite and quartz at high temperatures: appropriate heating of muscovite and quartz gives K-feldspar, aluminum silicate and water. In this study, particular attention was given to preparation of a quartz powder which is substantially non-hygroscopic, and the feasibility of quartz powder as a flux was checked.

## EXPERIMENTAL

### *Apparatus for the determination of water in minerals*

The apparatus consists of four main parts; a purification train, a heating system, a conversion system and the measurement system. These parts were connected by glass and copper pipes, as shown in Fig. 1(a).

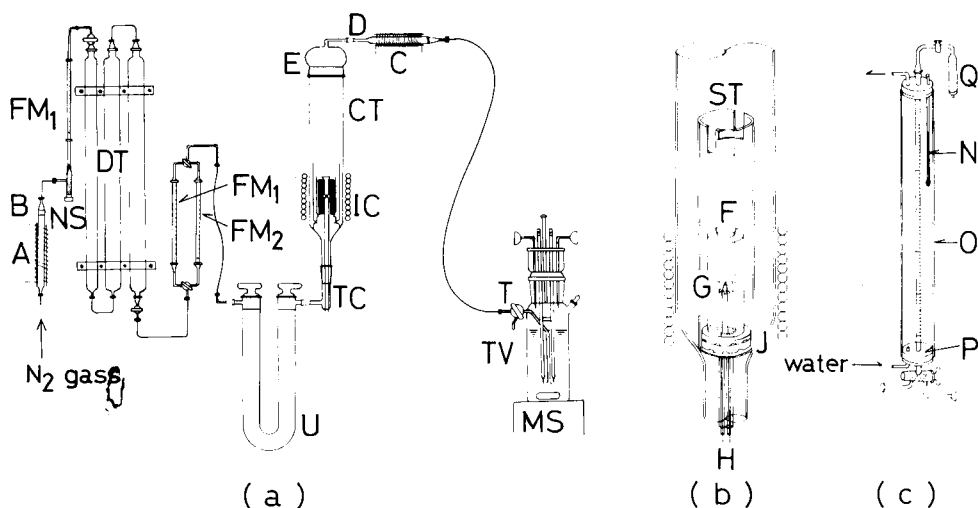


Fig. 1. Schematic diagram of the apparatus for determination of water in muscovite. (a) apparatus for determining water: (A) and (C) electric furnaces; (B) and (D) conversion tubes; (DT) and (U) drying tubes; (FM) gas flow meters (FM<sub>1</sub>, 100–2500 ml min<sup>-1</sup>, FM<sub>2</sub>, 1–250 ml min<sup>-1</sup>); (TC) adapter (side-arm type) holding a Pt/Rh thermocouple; (E) adapter; (CT) combustion tube; (IC) induction coil; (TV) titration vessel; (MS) magnetic stirrer; (NS) Teflon needle valve; (T) three-way stopcock. (b) Heating system: (ST) supporting tube; (F) platinum crucible; (G) platinum cylinder; (J) silica rings; (H) thermocouple. (c) Buret at constant temperature: (N) thermometer; (O) glass tube (50 mm diameter); (P) rubber stopper; (Q) silica gel drying tube.

*Purification train.* Cylinder nitrogen was passed continuously through the whole apparatus. For purification, it was passed through tube B (see Fig. 1a) packed with copper(II) oxide and palladium asbestos maintained at about 700°C by electric furnace A, and then through large drying tubes (DT and U) packed with silica gel—anhydrous magnesium perchlorate—phosphorus pentoxide, and phosphorus pentoxide, respectively.

*Heating system.* The combustion tube (CT) was made of transparent silica with ground joints at both ends; the wider part was 470 mm long (57 mm i.d.) and the lower tube was 150 mm long (25 mm i.d.), the total length being 660 mm. The tube (CT) was held vertically in the induction coil (IC). The h.f. induction furnace was a Touro SRF-433 model (3 kW, 400 kHz, 6.5 kVA; Tokyo High Frequency Induction Furnace Co.). The temperature in tube CT was measured with a Pt—Rh thermocouple sealed in an adapter with a side arm (TC), and controlled within a few degrees by a temperature controller (type ET—1530, Tokyo High Frequency Induction Furnace Co.). Two mica condensers (Cap. 0.005  $\mu$ F, T.V. 3 K, V d.c.) were connected with the thermocouple leads and earthed.

A platinum tube (21 mm o.d., 10 mm i.d., 55 mm long) was inserted in tube CT as the pyrogen (Fig. 1b). The sample powder was placed in a platinum crucible (9.5 mm diameter, 30 mm high). A supporting tube (ST) made of fused silica (32 mm o.d., 130 mm long) was used to set the crucible into the combustion tube. The position of the platinum column in the support was adjusted by using silica rings (26 mm o.d., 12 mm i.d., 3 mm thick). A T-shaped insertion rod (5  $\times$  40  $\times$  600 mm) was used for insertion of the assembled system into the combustion tube.

*Conversion system.* Hydrogen and hydrogen fluoride released from the sample can be quantitatively converted to water by using a tube packed with palladium and copper(II) oxide [13]. Tube D (Fig. 1a) was made of fused silica (20 mm i.d., 500 mm long) and was packed with alternate layers of palladized asbestos (10 mm), copper(II) oxide wire (20 mm) and their 1 + 10 mixture (50 mm) held in place by silica wool plugs. This tube was heated at about 400°C by an electric furnace (C). The copper(II) oxide wire was of 0.5 mm diameter in 1.5 mm lengths (Merck); the palladized asbestos contained 20% palladium (Kozima Kagaku Co.).

*Measuring system.* The released water was absorbed in anhydrous methanol—1,2-ethanediol and determined with a Karl Fischer titration apparatus (Tsutsui Rikagaku Kikai Co. model KFD-8) based on the dead-stop end-point technique. This titration apparatus has three burets connected to an enclosed titration vessel (TV) with a magnetic stirrer (MS) (see Fig. 1a). The burets were used for Karl Fischer reagents at two different concentrations and for pure methanol. One of the burets is held at constant temperature (Fig. 1c), because the Karl Fischer reagent has a fairly large coefficient of thermal expansion.

#### *Other instruments*

Differential thermal analyses were done with a Rigaku Denki type TG—

DTA apparatus. About 30 mg of sample was used and the heating rate was  $10^{\circ}\text{C min}^{-1}$ . The x-ray diffraction patterns were obtained with a Toshiba model ADG-301E x-ray diffractometer; the experimental conditions were Cu(Ni), 40 kV, 20 mA and 2000 cps.

### Reagents

*Karl Fischer reagent.* The Karl Fischer reagent used was SS "Mitsubishi" [18] (Mitsubishi Kasei Co.) which has two different indicated strengths equivalent to 0.7–1.0 and 2.5–3.0 mg of water per ml, respectively. The former is hereafter denoted as K. F. reagent (L) and the latter as K. F. reagent (H). K. F. reagent (L) was standardized against known amounts of distilled water [18], or against disodium tartrate dihydrate (analytical-reagent grade) [18]. The titres of the K. F. reagent by the two different methods agreed within experimental error, e.g.,  $0.947 \pm 0.002$  mg of water per ml.

*Water absorbent.* Mix 200 ml of methanol with 200 ml of 1,2-ethanediol (both analytical-reagent grade) in a 500-ml Erlenmeyer flask with a ground-glass stopper. Add about 50 g of molecular sieve 4A to the mixture. Insert the stopper and allow to stand overnight at room temperature. Use the supernatant solution as the absorbent for water in the titration vessel.

*Anhydrous silicon dioxide.* Pulverize transparent silica until it passes through a 0.044 mm (325 mesh) sieve. Ignite the powder above  $1200^{\circ}\text{C}$  for 2–3 h. Grind the slightly sintered cake in an agate mortar, and ignite again. Repeat this process two or three times. Finally, heat the powder at about  $900^{\circ}\text{C}$  and store in a desiccator over anhydrous magnesium perchlorate.

### Samples

The muscovite samples used were from (A) Ishikawa-chō, Fukushima Pref., Japan; (B) Nishishunkin, Ina-shi, Nagano Pref., Japan; (C) an unknown locality in India; (D) an unknown locality in Japan. The fluorine contents of samples A and D were 0.060 and 0.47%, respectively. Samples A, B and C were large flat hexagonal crystals. Sample D was composed of small crystals separated from pegmatite. The x-ray diffraction patterns of all samples were almost the same as that described in the ASTM card 7-42. Kuroda et al. [19] determined the water released from sample D on heating above  $1500^{\circ}\text{C}$  by a hydrogen volume method similar to that described by Friedman and Smith [20] and Godfrey [21], and the mean result was  $4.35 \pm 0.06\%$ .

*Preparation of samples.* Very thin films were peeled from the large crystal using a razor blade and cut with steel scissors to pass through a 100-mesh sieve.

### Procedure for the determination of water

Weigh accurately 100–250 mg of the sample and an amount of silicon

dioxide powder about 3 times the sample weight into the platinum crucible. (Weigh the crucible containing about half the silicon dioxide required, then weigh in the sample and finally add the rest of the silicon dioxide.) Mix the powders well with a platinum wire. Dry the crucible and contents at 110°C for 3 h.

Disconnect adapter E from the conversion tube at D and the top of the combustion tube CT (see Fig. 1a). Place the crucible into the platinum column held by support ST. Hang the support ST on the T-shaped insertion rod, and place it at the center of the induction coil (see Fig. 1b).

Replace adapter E, wind heating tape around the combustion tube (CT) and the copper piping, and heat the tubes. Pass purified nitrogen at a flow rate of 200 ml min<sup>-1</sup> through the whole apparatus except the titration vessel, discharging the gas from a three-way stopcock (T). Transfer 80–100 ml of the water absorbent (previously roughly dehydrated by molecular sieve 4A) into the titration vessel, and titrate with K.F. reagent (H) to the end-point, so that the absorbent is completely anhydrous.

*Blank test.* After passing the purified nitrogen to remove all adsorbed water, turn stopcock T so that the gas passes into the titration vessel. Regulate the flow rate at a constant value in the range 120–180 ml min<sup>-1</sup>. Add a small excess (0.05 or 0.10 ml) of the standardized K.F. reagent (L) to the anhydrous absorbent, and pass nitrogen until this excess has reacted completely with residual water in the nitrogen; measure the time required for the end-point. Repeat this procedure until the time measured remains almost constant. Calculate the amount of water in the carrier gas. Although the water contents in the gas are very low, the volumes of the carrier gas required are very large. The blank test must therefore be done before every measurement for accurate analysis.

Immediately after the blank test, operate the high-frequency induction furnace and heat the sample to 1200°C for 120–150 min at the same flow rate of carrier gas as in the blank test. Titrate the absorbed water with K.F. reagent (L). In order to absorb the water completely, add a few ml of titrant to the anhydrous absorbent before introducing the carrier gas. Measure the time required for the end-point to appear. Repeat this procedure continuously as the reactions proceed, reducing the amount of titrant gradually. Finally, add 0.05 or 0.10 ml of titrant and stop the titration when the time required becomes almost the same as that measured for the blank test. Correct for the blank of the total amount of carrier gas passed.

## RESULTS AND DISCUSSION

### *Dehydration curves*

The effect of heating temperature on water release was examined for the samples of muscovite alone and for mixtures of 150 mg of the muscovite with 500 mg of silicon dioxide. The samples were heated for 120–150 min at various temperatures from 450 to 1400°C. The dehydration curves for

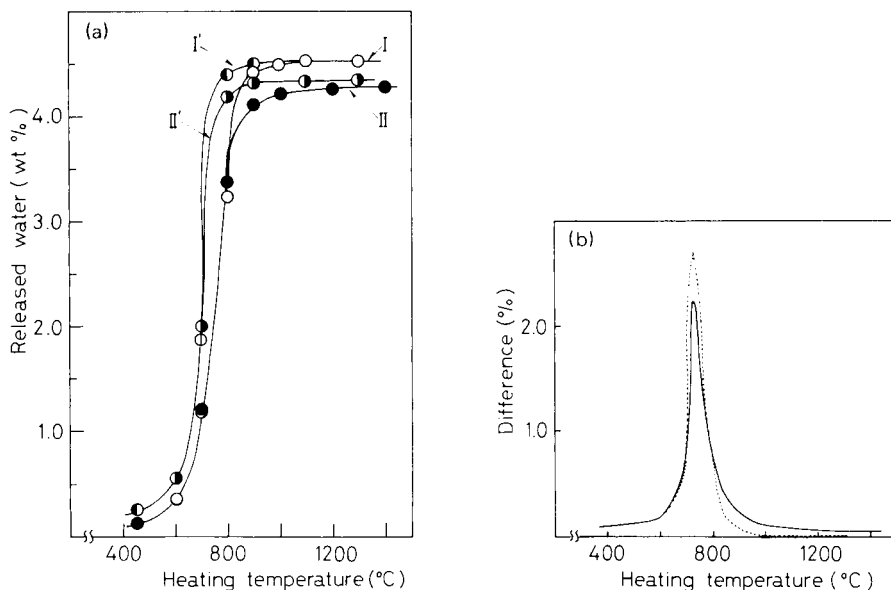


Fig. 2. Effect of heating temperature on water release. (A) Curves I, I', sample A; curves II, II', sample D. (○) and (●) Samples A and D heated without flux (○) and (●) samples A and D (150 mg) heated with 500 mg of silicon dioxide. (B) Differential dehydration curves: (—) sample A; (....) sample D.

samples A and D (Fig. 2a) show the amount of water released at 100–200°C intervals under non- or near-equilibrium conditions. The form of dehydration curve I for sample A is very similar to that for sample D up to 800°C. The amount of water released is almost negligible below 400°C, but increases sharply above 600°C and amounts to 97% of the total water in the samples at 900°C; curves I and II show no further release of water above 1100°C and 1300°C, respectively. The dehydration patterns I' and II'' for samples A and D with silicon dioxide added are very similar up to 730°C, then there is an abrupt increase but this occurs at a lower temperature than that for curves I and II, and the final plateaux are also reached at a lower temperature (1000°C). The curves for sample A overlap completely at temperatures above 1100°C, whereas the curves for sample B fail to overlap even at 1400°C.

Differential dehydration curves obtained by subtracting curve I from curve I', and curve II from curve II'' are shown in Fig 2(b). The effect of silicon dioxide on the water release was large in the temperature range 700–800°C, and was maximal at 730°C. The water in muscovite was released smoothly by the addition of silicon dioxide, and the temperature needed to release all the water was reduced to about 1000°C from above 1300°C. In sample D containing a large amount of fluorine, the amount of water released from the mixed sample at 1000°C was 0.06% higher than

that from the muscovite sample alone at 1300°C. The effectiveness of the silicon dioxide flux was thus confirmed for the determination of water in fluorine-rich muscovite. For security, the heating temperature for the sample with this flux was fixed at 1200°C.

#### *Differential thermal analysis and x-ray diffraction patterns*

The dehydroxylation path of muscovite was studied by using d.t.a. and x-ray diffractometry. The d.t.a. curves of the muscovite samples are shown in Fig. 3 (solid lines); the differences between these curves are slight. The main endothermic peak at 770–840°C corresponds to the dehydroxylation of muscovite; in the range 840–900°C, the curves change only slightly, but exothermic effects start at 900°C, showing a small broad peak at ca. 930°C. Grim and Rowland [22] suggested that the peak at about 940°C is due to re-arrangement of muscovite to leucite. It seems unlikely that the hollow between 1100 and 1130°C can properly be attributed to an endothermic effect. The second exothermic peak appears at about 1130–1150°C.

The d.t.a. curves for mixtures (1:5) of muscovite and silicon dioxide are shown by dotted lines in Fig. 3. The endothermic effect now occurs uniformly in the region 550–900°C, and a small exothermic peak appears at 910°C. The second exothermic effect observed at 1130–1150°C in absence of the flux, however, is hardly visible.

As the x-ray diffraction patterns of the original samples and the heated samples (900 and 1130°C, at heating rates of 10°C min<sup>-1</sup>) were almost identical for all four samples, only the patterns of sample A are shown in Fig. 4 (a). The patterns of this sample heated at 900°C and 1130°C are substantially the same; most of the dehydroxylated muscovite crystal remains even after heating to 1130°C, and peaks of spinel oxide, mullite or

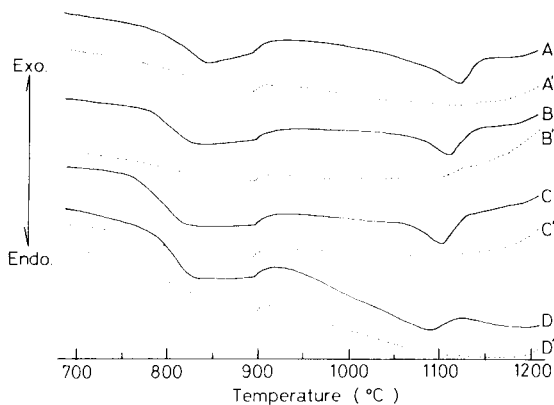


Fig. 3. D.t.a. curves for muscovites (samples A–D as indicated): (—) samples heated alone; (....) samples heated after mixing with 5 times their weight of silicon dioxide.

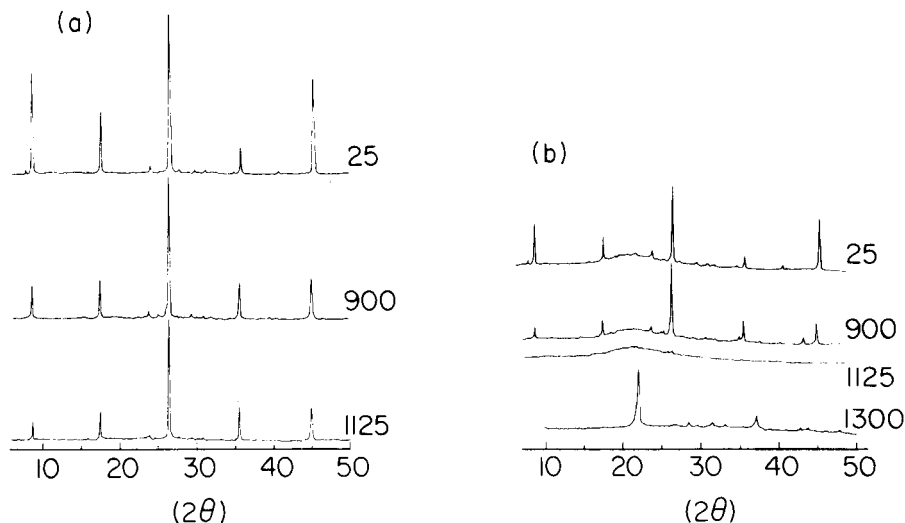


Fig. 4. X-ray diffraction patterns of muscovite A. (a) The muscovite sample alone; (b) 1:5 mixtures of muscovite and silicon dioxide. The numbers on the curves are the temperatures to which the samples had been heated.

leucite are not recognizable. The peaks of the dehydroxylated muscovite disappear on heating at about 1200°C. The patterns of mixtures of sample A and silicon dioxide are shown in Fig. 4 (b). The peaks of the mixture heated at 900°C pertain to dehydroxylated muscovite, and disappear when samples are heated at 1130°C. On further heating at 1300°C for 120 min with silicon dioxide, silicon dioxide in the sample is converted to (low)  $\alpha$ -cristobalite.

#### *Water contamination from the silicon dioxide flux*

The water in sample A was completely released at 1200°C; therefore, this sample was used as a reference sample. The water contents found by the recommended procedure in mixtures of sample A with silicon dioxide at various ratios are listed in Table 1. As can be seen, these water contents are not significantly affected by the amount of silicon dioxide. At the 95% confidence level, the mean water contents found were  $4.55 \pm 0.04\%$  and  $4.56 \pm 0.02\%$  for the muscovite alone and the mixed sample, respectively. These results show that there is no significant water contamination when the recommended method is followed.

#### *Effect of amounts of silicon dioxide added*

The d.t.a. curves for mixtures of muscovite sample D with silicon dioxide at various ratios are shown in Fig. 5; these curves are typical of those found for all samples. When the amount of silicon dioxide added exceeds 4 times the amount of muscovite, the second exothermal peak disappears completely, demonstrating the utility of the flux.

TABLE 1

Determination of water in mixtures of muscovite sample A and silicon dioxide

SiO <sub>2</sub> : Muscovite (w/w)	Sample		Water content of muscovite (%)
	Muscovite taken (mg)	SiO <sub>2</sub> added (mg)	
0.3	151.35	50.10	4.55
0.7	150.60	100.85	4.55
1.0	156.10	150.30	4.58
2.0	152.10	303.50	4.56
		Mean	4.56
0.0	150—250	—	4.55 <sup>a</sup>

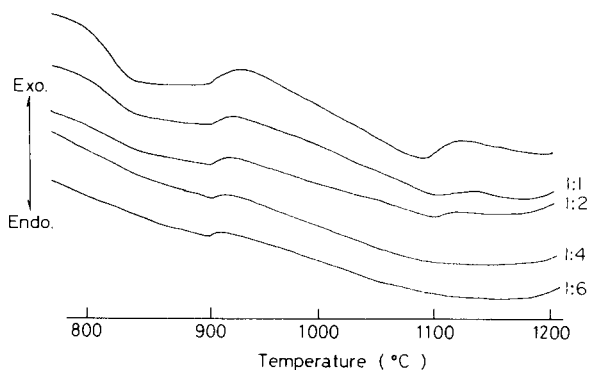
<sup>a</sup>Reported previously [13].

Fig. 5. D.t.a. curves for mixtures of muscovite D and silicon dioxide in different ratios. The top curve corresponds to the original sample; the numbers on the curves indicate the weight ratio of sample to flux.

Results for the water content in mixtures of sample D with silicon dioxide at various ratios are given in Table 2. The results for the water content of sample D in the absence of silicon dioxide were low even at 1300—1400°C, the mean result being  $4.26 \pm 0.03\%$  [14]. The addition of silicon dioxide is clearly effective. Even when the weight ratio of flux to sample varied in the range 2.0—5.0, the scatter in the measured values was very small, the standard deviation and relative standard deviation being 0.015 and 0.35%, respectively. For a 95% confidence level, the mean was  $4.33 \pm 0.01\%$ , which is higher than that obtained without the flux. The most suitable ratio of flux to muscovite is about 2—5:1; for general use, about 3-fold amounts of flux are appropriate.



TABLE 2

Determination of water in muscovite sample D with silicon dioxide at 1200°C

SiO <sub>2</sub> : Muscovite (w/w)	Muscovite taken (mg)	SiO <sub>2</sub> added (mg)	Water found (%)	Statistical analysis <sup>a</sup>
0.5	99.90	50.00	4.36	$\bar{x} = 4.30$
	189.55	102.50	4.33	$s = 0.044$
	99.90	56.00	4.26	$s_r = 1.02$
	99.40	52.90	4.26	$\mu = 4.30 \pm 0.06$
	202.35	101.10	4.31	
1.0	98.05	97.80	4.29	$\bar{x} = 4.31$
	103.00	100.00	4.31	$s = 0.017$
	101.30	100.00	4.32	$s_r = 0.39$
	99.90	100.35	4.33	$\mu = 4.31 \pm 0.03$
2.0	102.30	200.00	4.34	$\bar{x} = 4.33$
	101.10	202.25	4.31	$s = 0.016$
	100.80	200.60	4.33	$s_r = 0.37$ $\mu = 4.33 \pm 0.04$
≈ 3.0	152.50	505.25	4.33	$\bar{x} = 4.34$
	152.80	501.85	4.36	$s = 0.017$
	152.80	501.90	4.33	$s_r = 0.39$
	100.35	300.70	4.32	$\mu = 4.34 \pm 0.02$
	197.85	549.55	4.35	
5.0	99.80	488.35	4.35	$\bar{x} = 4.33$
	101.25	493.50	4.33	$s = 0.015$
	101.85	491.75	4.33	$s_r = 0.35$
	99.90	491.00	4.31	$\mu = 4.33 \pm 0.02$
	100.30	489.25	4.32	

<sup>a</sup> $\bar{x}$  = mean,  $s$  = standard deviation,  $s_r$  = relative standard deviation,  $\mu$  = for 95% confidence level of the mean ( $\bar{x}$ ) ( $\bar{x} \pm t \cdot s/n$  %).

#### *Precision of the proposed method*

The precision of the proposed method is satisfactory. The 95% confidence levels of the water contents found were  $4.56 \pm 0.02\%$  for sample A and  $4.33 \pm 0.01\%$  for sample D.

The proposed method and the hydrogen volume method of Kuroda et al. [19] were compared for sample D; the results obtained by the two different methods ( $4.33 \pm 0.01\%$  by the proposed method and  $4.35 \pm 0.06\%$  by the hydrogen volume method) are in good agreement. The result of  $4.26 \pm 0.03\%$  obtained for sample D without silicon dioxide is significantly different from the others. These results prove that the water in sample D was not completely released in the absence of silicon dioxide even at 1300–1400°C, whereas with the flux, heating at 1200°C was entirely adequate.

The author is grateful to Professor Sadao Matsuo for providing sample D and to his co-workers for the data by the hydrogen volume method; to

Associate Professor Mitsuo Abe for the use of the d.t.a. apparatus; to Professor Jōyo Ossaka for the use of the x-ray diffractometer; and to Professor Takashi Katsura, Professor Takejino Ozawa (Saitama Univ.) and Dr. Minoru Yoshida for helpful discussions. This work was partly supported by a grant from the Ministry of Education.

#### REFERENCES

- 1 L. C. Peck, U.S. Geol. Surv. Bull., 1170 (1964) pp. 17, 61, 83.
- 2 L. Shapiro and W. W. Brannock, U.S. Geol. Surv. Bull., 1144-A (1962) p. 46.
- 3 J. P. Riley, *Analyst*, 83 (1958) 42; J. P. Riley and H. P. Williams, *Mikrochim. Acta*, (1959) 525.
- 4 M. Cremer and H. N. Elsheimer, *Anal. Chim. Acta*, 60 (1972) 183.
- 5 K. Sato, H. Higashikuse and M. Matsui, *Bunseki Kagaku*, 18 (1969) 1003; H. Higashikuse and J. Takagi, *Bunseki Kagaku*, 19 (1970) 554.
- 6 C. S. Ross and R. L. Smith, *Am. Mineral.*, 40 (1955) 1071.
- 7 J. W. Aucott and M. Marshall, *Mineral. Mag.*, 37 (no. 286) (1969) 256.
- 8 R. W. T. Wilkins and W. Sabine, *Am. Mineral.*, 58 (1973) 508.
- 9 A. Quesada and W. H. Dennen, *Appl. Spectrosc.*, 21 (1967) 155.
- 10 K. Yamaya, M. Yoshida, T. Ozawa and I. Iwasaki, *Nippon Kagaku Kaishi*, (1972) 893.
- 11 K. Yamaya, M. Yoshida and T. Ozawa, *Nippon Kagaku Kaishi*, (1974) 2111.
- 12 K. Yamaya, *Nippon Kagaku Kaishi*, (1975) 1203.
- 13 K. Yamaya, *Nippon Kagaku Kaishi*, (1978) 967.
- 14 K. Yamaya, *Nippon Kagaku Kaishi*, (1978) 1492.
- 15 H. W. Day, *Am. Mineral.*, 58 (1973) 255.
- 16 E. Althaus, E. Karotke, K. H. Nitsch and H. G. F. Winkler, *Neues Jahrb. Mineral. Monatsh.*, 7 (1970) 325.
- 17 B. W. Evans, *Am. J. Sci.*, 263 (1965) 647.
- 18 W. Funasaka and K. Muroi, *The Determination of Water*, Tokyo Kagaku Dōjin, 1969, pp. 90, 104.
- 19 Y. Kuroda, T. Suzuoki, S. Matsuo and S. Kanisawa, *J. Jpn. Assoc. Min. Petr. Econ. Geol.*, 69 (1974) 95.
- 20 I. Friedman and R. L. Smith, *Geochim. Cosmochim. Acta*, 15 (1958) 218.
- 21 J. D. Godfrey, *Geochim. Cosmochim. Acta*, 26 (1962) 1215.
- 22 R. E. Grim and R. A. Rowland, *Am. Mineral.*, 27 (1942) 746, 801.

## CHARACTERIZATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SHALE OIL BY CHROMATOGRAPHY AND FLUORESCENCE DENSITOMETRY

R. J. HURTUBISE\* and J. D. PHILLIP

*Department of Chemistry, The University of Wyoming, Laramie, Wyoming 82071 (U.S.A.)*

(Received 2nd May 1979)

### SUMMARY

Polycyclic aromatic hydrocarbons (6-, 5-, 4- and 3-ring) were characterized in several shale oil samples. Open-column, dry-column and thin-layer chromatography were used in the separation steps. Visible fluorescence from the separated components on chromatoplates was measured directly to obtain fluorescence profiles of the distribution on the chromatoplates. The methods developed are inexpensive, reproducible, and allow rapid characterization of polycyclic aromatic hydrocarbons in shale oil samples.

Many polycyclic aromatic hydrocarbons (PAH) are carcinogenic to animals and probably to man [1]. Because of their occurrence in automobile exhaust, coal tars, processed foods, high-boiling petroleum, and other samples, PAH have been investigated extensively in recent years. Several reports have been published on the separation, characterization, identification and determination of PAH in complex samples [2–11]. Methods for separation, characterization and identification of PAH in shale oil, and the determination of benzo(a)pyrene in shale oil and filtered retort water have been reported from this laboratory [12–14]. This paper reports on an expanded PAH characterization method for 6-, 5-, 4- and 3-ring PAH in shale oil samples that should be applicable to a variety of fossil-fuel samples.

### EXPERIMENTAL

#### *Apparatus, reagents and materials*

All fluorimetric measurements were made with a Schoeffel SD3000 spectrodensitometer in the reflection mode. Only an ultraviolet cutoff filter was employed in the reflection mode so that fluorescence emitted throughout the visible region was detected.

Individual PAH and other samples were obtained from commercial sources and were recrystallized when needed. The shale-oil samples were obtained from the Laramie Energy Technology Center, Laramie, Wyoming.

The 30%-acetylated cellulose thin-layer chromatoplates were Brinkmann

precoated Cel 300 AC/30-20 plates. The aluminum oxide (activity II–III) for dry-column chromatography was obtained from ICN Life Science Group, Cleveland, Ohio. The silica gel 60 (MN-Kieselgel 60 0.1-0.2 mm/70–140 mesh ASTM) was obtained from Brinkmann. Nylon lay-flat tubing was obtained from Hall Manufacturing Corp., Mahwah, New Jersey. A 10- $\mu$ l Hamilton syringe was used in spotting the chromatoplates. A Buchi Rotavapor-M was used for evaporation of solvents.

### *Procedures*

*Characterization without acid treatment.* A 28-cm section of nylon lay-flat tubing (i.d., 6.62 mm) plugged with glass wool at one end was packed with 8.50 g of aluminum oxide. The height of the aluminum oxide was ca. 17.5 cm. Aluminum oxide (0.5 g) was added to a 30-ml evaporating flask. Then a 0.0500-g sample of shale oil was weighed accurately in the flask and 1 ml of n-hexane added. The mixture was heated to 30°C in the flask while stirring under vacuum with a rotary evaporator. This step assured that the shale oil sample was distributed evenly on the aluminum oxide. The dried aluminum oxide with shale oil adsorbed on it was transferred quantitatively to the top of the aluminum oxide already in the column. The mobile phase (1 ml), n-hexane–ether (19:1), was used to rinse the evaporating flask and the rinsings were quantitatively transferred to the column. After this volume had absorbed into the aluminum oxide, 6 ml more of n-hexane–ether (19:1) was added to the column. After development of the column, it was cut into four sections. The lengths of each successive section starting from the interface of the aluminum oxide that had shale oil initially adsorbed and fresh aluminum oxide were 0.0–6.5 cm, 6.5–11.5 cm, 11.5–15.0 cm, and 15.0–20.0 cm. Later work with nylon tubing of 7.18-mm i.d. gave section lengths of 0–4 cm, 4–8 cm, 8–12.5 cm, and 12.5–17 cm. The sections contained maximum concentrations of 6-, 5-, 4- and 3-ring PAH, respectively, though fluoranthene overlapped into the 3-ring fraction. With a given diameter of tubing and alumina activity, migration rates were very reproducible. When these factors changed, a standard column was run to establish new migration distances. An identical standard aluminum oxide column was prepared that had coronene, benzo(a)pyrene, triphenylene, fluoranthene, phenanthrene, and fluorene adsorbed on the top of the column. This column was developed in an identical manner as the sample column and then the sample column was cut into sections based on the migration distances of the standards. The aluminum oxide sections were stirred separately in beakers for 20 min with 10 ml of 1,2-dichloroethane and then the 1,2-dichloroethane was decanted. The aluminum oxide sections were washed with 5 ml of 1,2-dichloroethane, and the combined extracts from each section were evaporated individually to dryness by directing air into beakers heated at 30°C. A small amount of n-hexane was added to each beaker and then the n-hexane aliquots were transferred quantitatively to a 1-ml volumetric flask. The beakers were rinsed with additional aliquots of n-hexane, the rinsings were added to the appropriate volumetric flask, and the final volume was adjusted to 1 ml.

Each solution was spotted (5  $\mu$ l) 2.0 cm from the bottom edge of a 30% acetylated cellulose chromatoplate that had been cleaned previously by development with methanol-n-hexane-acetone (7:3:2). The spotted chromatoplate was developed to 10 cm in a rectangular tank containing 155 ml of methanol-water-acetic acid-acetone (20:5:3:3) which had been allowed to equilibrate for 1 h before development of the chromatoplate. After development, the chromatoplate was dried in air and then positioned on the stage of the spectrodensitometer. The excitation monochromator was set at 310 nm. The stage of the spectrodensitometer was started and the visible fluorescence of the components distributed on the chromatoplate recorded. Scans were made from 1 cm above the solvent front to the spot origin.

*Characterization with acid treatment.* A 0.25-g quantity of silica gel was added to a 30-ml evaporating flask. Then an accurately weighed 0.0500-g sample of shale oil was weighed in the flask and 1 ml of diethyl ether added. The mixture was heated to 30°C in the flask while stirring under vacuum with a rotary evaporator. After evaporation of the diethyl ether, the silica gel with shale oil absorbed on it was transferred quantitatively to a previously prepared acid-treated silica gel column. Chloroform (1 ml) was used to rinse the evaporating flask and the rinsings were added to the column. The acid-treated silica gel column was prepared by slurry-packing 3.30 g of silica gel in distilled chloroform into a 15 cm  $\times$  1.05-cm i.d. glass column. Then 0.2 ml of concentrated hydrochloric acid was allowed to absorb into the silica gel at the top of the column [15]. The acid-treated silica gel with shale oil was eluted with 9 ml of chloroform, and the chloroform was collected in a 30-ml evaporating flask that contained 0.5 g of aluminum oxide. This sample was then heated to 30°C in a rotary evaporator and transferred to the aluminum oxide column as described above.

## RESULTS AND DISCUSSION

### *General characterization of PAH*

Snyder [16] has shown that PAH can be separated according to ring size by using an aluminum oxide stationary phase and a relatively weak mobile phase. These concepts were applied in developing separation methods for PAH in shale oil samples [12]. That work has been expanded further, as described here. In the initial dry-column chromatography, aluminum oxide (activity II-III) was the stationary phase and n-hexane-ether (19:1) was the mobile phase. Data from several PAH standards with different ring sizes again indicated that PAH would be separated by ring size with limited overlap of bands. After the particular ring band had been sliced out, the second separation step with t.l.c. was used. The 30% acetylated cellulose was employed because it is useful in separating PAH ring isomers [5], and many PAH give intense fluorescence signals on 30% acetylated cellulose [12, 13]. The mobile phase used gave smaller spots, better separation of shale oil components, and distributed the components over a greater distance on the chromatoplate than the mobile phase reported previously [13]. The final characterization step involved

measurement of reflected fluorescence from the chromatoplates, thus a fluorescence profile of the separated components was obtained.

In this work, nine different shale oil samples were characterized for PAH. Different sample sizes for the dry-column step and different amounts spotted on the chromatoplates for the t.l.c. step were tested so that maximum response and reproducible data could be obtained. Five shale oil samples were run through the entire procedure at least twice. The  $R_f$  values corresponding to the major fluorescence peaks in the scans of the chromatoplates were reproducible ( $\pm 0.02$ ) and the overall shapes of the fluorescence profiles of components separated on chromatoplates were reproducible. The relative fluorescence intensity values for the major peaks in the profiles could be used as a semi-quantitative measure of various components. It is not surprising that relative intensity values were not highly reproducible; the large number of components in each ring fraction would increase the probability of quenching interactions and of components migrating at somewhat variable rates.

Figure 1 (A, B) compares the fluorescence profiles of the 4-ring PAH fractions from samples 13 and 14, respectively. The general shapes of the fluorescence profiles for the 4-ring PAH fractions are similar, suggesting a similar composition for the two fractions. However, the relative intensity (peak height) for the 4-ring fraction from sample 13 is greater than that for sample 14, indicating a higher concentration of 4-ring PAH in sample 13. Analogous reasoning can be applied to the 3-ring PAH fractions for samples 13 and 14 (Fig. 1, C and D). The fluorescence profiles are very similar for the 3-ring fractions, and it appears that there is a higher concentration of 3-ring PAH in sample 13 than in sample 14. In Fig. 1, the fluorescence band at  $R_f$  values of about 0.95 was due to fluorescent impurities in the chromatographic system.

The  $R_f$  values determined at the fluorescence maxima for the major fluorescence peaks and the relative fluorescence intensity values for the major peaks obtained from the fluorescence profiles for samples 13 and 14 are compared in Table 1. For all the ring fractions, sample 13 yielded greater relative fluorescence intensity values than sample 14. This indicates that sample 13 contains a higher concentration of 6-, 5-, 4- and 3-ring PAH than sample 14. Comparison of  $R_f$  values for given ring fractions for the two samples shows that within a given fraction the  $R_f$  values are similar except for the 6-ring fraction. Also, except for the 6-ring fraction, each given ring fraction contains the same number of  $R_f$  values. These results suggest a general similarity of the composition of the various ring fractions. For the 6-ring fractions in Table 1, sample 14 gave a greater number of major peaks than sample 13, indicating a compositional difference between these two fractions. Similar comparisons were made with the other shale oil samples investigated. The relative fluorescence intensities for the major fluorescence peaks in the 5-ring PAH fractions for four shale oil samples are compared in Fig. 2; also shown are  $R_f$  ranges for fluorescence peaks, and possible compound types and their  $R_f$  values. Sample 18 shows the highest concentration of 5-ring PAH.

Table 2 lists the  $R_f$  values for the PAH standards obtained with the t.l.c. system employed. For the 6-, 5-, and 4-ring PAH, no  $R_f$  values exceed 0.33;

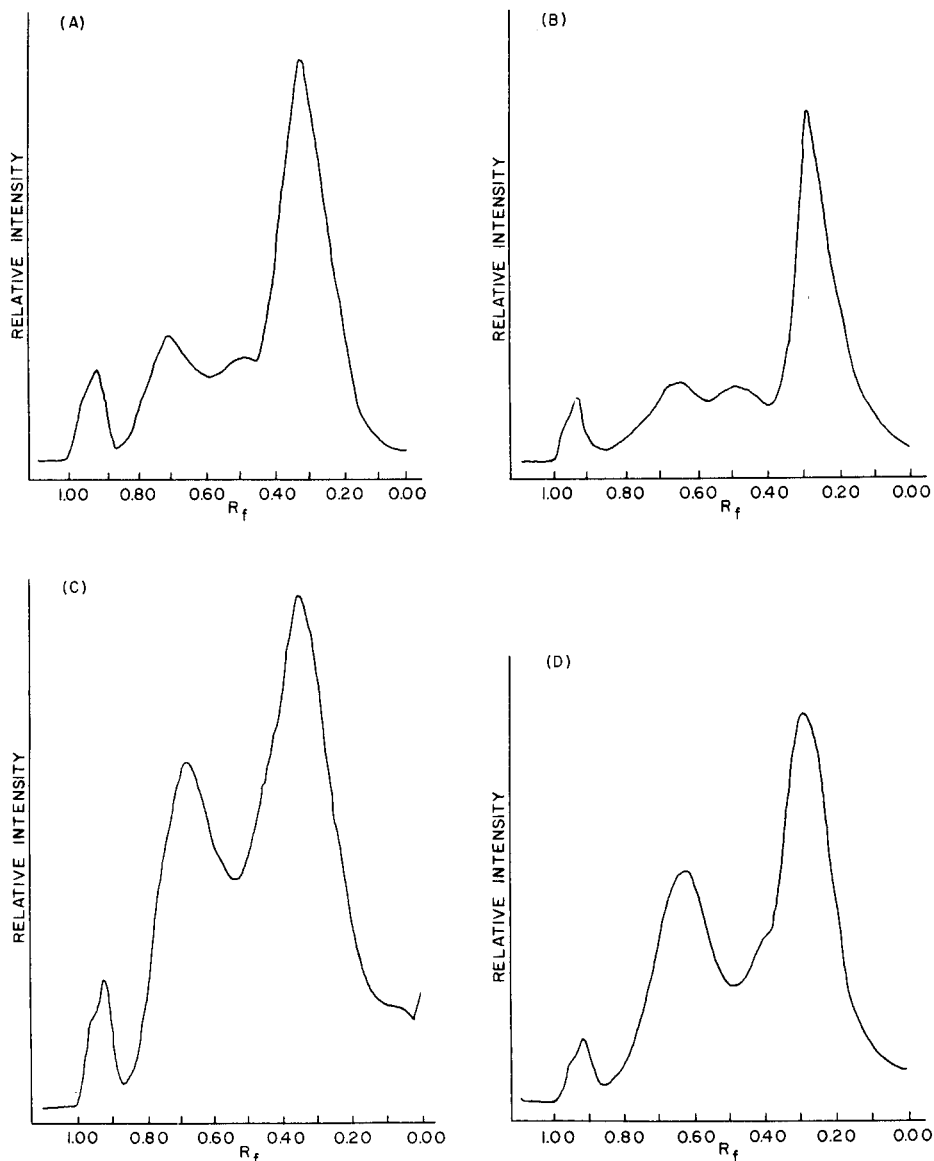


Fig. 1. Fluorescence profiles of: (A) The 4-ring fractions from sample 13; (B) the 4-ring fraction from sample 14; (C) the 3-ring fraction from sample 13; (D) the 3-ring fraction from sample 14; all without acid treatment.

for the 3-ring PAH, no  $R_f$  values exceed 0.43. All the fluorescence profiles obtained for the different ring fractions indicated fluorescence components beyond these  $R_f$  limits (Table 1). This suggested that the fluorescence beyond the  $R_f$  limits was not due to PAH but mainly to nitrogen heterocycles.

TABLE 1

Comparison of  $R_f$  and relative fluorescence intensity values

Sample	Ring fraction	$R_f$	Relative intensity	Sample	Ring fraction	$R_f$	Relative intensity
13	6	0.21	128	13	4	0.31	125
		0.96	26			0.51	36
						0.69	48
14	6	0.13	97	14	4	0.94	42
		0.31	64			0.25	60
		0.47	47			0.49	14
		0.64	19			0.64	18
		0.92	25			0.94	15
13	5	0.26	120	13	3	0.35	107
		0.51	30			0.67	61
		0.70	21			0.94	24
		0.93	27				
14	5	0.19	34	14	3	0.29	62
		0.48	12			0.61	39
		0.65	12			0.92	16
		0.95	14				

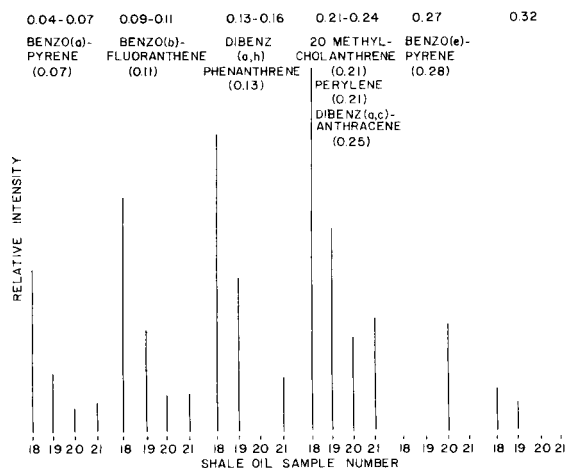


Fig. 2. Comparison of 5-ring PAH in four shale oil samples, with the  $R_f$  ranges for fluorescence peaks, possible compounds and their  $R_f$  values.

### Nitrogen heterocycles

Aluminum oxide dry-column experiments with carbazole-type and pyridine-type standards and n-hexane-ether (19:1) as the mobile phase showed that some of these compounds migrated on the column. Carbazole and 1,2-benzocarbazole did not migrate, but 9-methylcarbazole (distance  $\approx 8.5$  cm), 9-ethylcarbazole ( $\approx 9.2$  cm), and 9-n-butylcarbazole ( $\approx 10.8$  cm) did migrate.



TABLE 2

 $R_f$  values for polycyclic aromatic hydrocarbons

Compounds	$R_f$	Compounds	$R_f$
<i>6-Ring systems</i>		<i>4-Ring systems</i>	
3,4,8,9-Dibenzpyrene	0.02	Chrysene	0.11
3,3,9,10-Dibenzpyrene	0.10	9,10-Dimethyl-1,2-benzanthracene	0.21
2,3- <i>o</i> -Phenylene-pyrene	0.10	1,2-Benzofluorene	0.25
1,2,4,5-Dibenzpyrene	0.19	Pyrene	0.24
1,2,7,8-Dibenzchrysene	0.22	Triphenylene	0.29
Coronene	0.22	2,3-Benzofluorene	0.31
1,2,3,4-Dibenzpyrene	0.31	Fluoranthene	0.33
<i>5-Ring systems</i>		<i>3-Ring systems</i>	
Benzo(a)pyrene	0.07	Phenanthrene	0.34
1,2,6,7-Dibenzphenanthrene	0.13	9,10-Diphenylanthracene	0.34
3,4-Benzofluoranthene	0.11	1-Methylphenanthrene	0.40
20-Methylcholanthrene	0.21	2-Methylphenanthrene	0.40
Perylene	0.21	2-Methylanthracene	0.36
1,2,3,4-Dibenzanthracene	0.25	9-Methylanthracene	0.33
Benzo(e)pyrene	0.28	9,10-Dimethylanthracene	0.36
		Anthracene	0.38
		Fluorene	0.43
		3,6-Dimethylphenanthrene	0.43

Benzo(c)cinnoline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline and 1,10-phenanthroline monohydrate did not migrate. 2,2'-Biquinoline ( $\approx 1$  cm), acridine ( $\approx 1$  cm), phenazine ( $\approx 0.7$  cm), 5,6-benzoquinoline ( $\approx 0.5$  cm), phenanthridine ( $\approx 0.5$  cm), and quinoline ( $\approx 0.5$  cm) migrated slightly. Bender and Elbert [17] have indicated the  $R_f$  values of several pyridines in an aluminum oxide-pentane-ether (19:1) system; they commented that compounds with a non-sterically-hindered aza nitrogen are attracted more strongly to aluminum oxide than compounds with a sterically-hindered aza nitrogen and thus have low  $R_f$  values. Sterically-hindered pyridines can migrate at rates similar to PAH. From some experiments done here with  $Al_2O_3$ -*n*-pentane-ether (19:1) and the results given by Bender and Elbert, it can be concluded that carbazoles substituted in the 9-position, and sterically-hindered pyridines, can migrate with PAH. It appears that the fluorescence beyond the  $R_f$  limits for PAH discussed above could be due to such compounds. The migration distances of compounds such as 2,2'-biquinoline and acridine on an alumina column indicated that these compounds could appear in the 6-ring PAH fraction. The migration distances on alumina columns for the 9-alkyl-substituted carbazoles indicated that they could appear in the 3-, 4-, or 5-ring PAH fractions. Table 3 gives the  $R_f$  values for several carbazole and pyridine types on the acetylated-cellulose t.l.c. system employed. The  $R_f$  values show that compounds of these types can migrate readily. All the compounds in Table 3 except 2,2'-biquinoline and 9-methylcarbazole have  $R_f$  values greater than the  $R_f$  limit for 6-, 5-, and 4-ring PAH, namely, 0.33. Also, several of the com-

TABLE 3

 $R_f$  values for nitrogen heterocycles

Compound	$R_f$	Compound	$R_f$
3-Methylcarbazole	0.42	1,10-Phenanthroline monohydrate	0.77
9-Methylcarbazole	0.33	Phenazine	0.69
9-Ethylcarbazole	0.41	2,9-Dimethyl-4,7-diphenyl-1,- 10-phenanthroline	0.55
9-n-Butylcarbazole	0.38	4-Azafluorene	0.62
1,2,3,4-Tetrahydrocarbazole	0.76	5,6-Benzoquinoline	0.61
1,2,7,8,-Dibenzocarbazole	0.36	Acridine	0.65
7H-Dibenzo(c, g)carbazole	0.23	Dibenz(a, j)acridine	0.39
Carbazole	0.39		
2,2'-Biquinoline	0.24		

pounds in Table 3 have  $R_f$  values greater than 0.43, the  $R_f$  limit of 3-ring PAH. No spectral work was done to identify the components beyond the  $R_f$  limits mentioned above.

#### Removal of pyridine types

Results obtained in this work and previous work showed that many pyridine compounds did not migrate with a chloroform mobile phase on a silica gel column that had concentrated hydrochloric acid absorbed at the top of the column [15]. The exact mechanism for the inhibition of migration of the pyridine compounds is not known; presumably the compounds are protonated at the ring nitrogen and are thus strongly adsorbed onto silica gel. In this work it was shown that acridine, 4-azafuorene, benz(c)acridine, 2,2'-biquinoline and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline did not migrate or migrated only slightly on the acidified silica gel column with chloroform as a mobile phase. Carbazole compounds migrated readily on the acid silica gel column. Another separation step was added to remove pyridine compounds from the shale oil samples. With this additional separation step, the overall separation scheme involved an acid silica gel step, a dry-column aluminum oxide step, and finally an acetylated-cellulose t.l.c. step.

Shale oil samples 13 and 14 were investigated further with the additional separation step. This was done by carrying out the separation procedure twice, once with the acid silica gel step and the other without this step. In this way, two fluorescent profiles were obtained. One profile represented PAH and some nitrogen heterocycles, and the other PAH with most pyridine compounds removed. Additional work is needed to define other classes of compounds in the fractions, but the results reported here indicate that mainly nitrogen heterocycles and PAH are found in the fractions without the acid silica gel step included.

The fluorescence profiles obtained for the 4- and 3-ring PAH fractions from sample 14 with the acid silica gel step included are compared in Fig. 3; the fluorescence beyond the  $R_f$  limits discussed earlier is absent. Without the

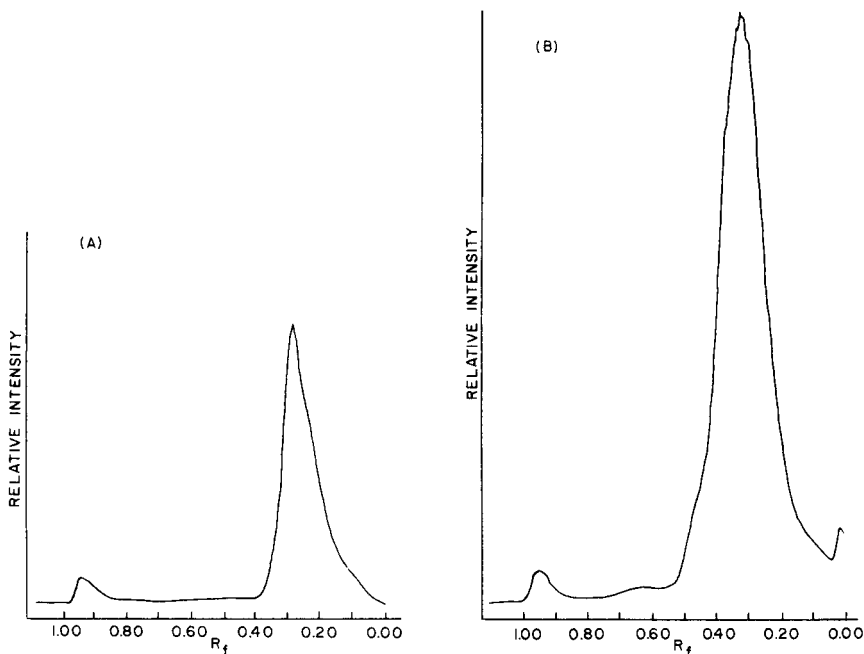


Fig. 3. Fluorescence profile of fractions from sample 14 with acid treatment: (A) 4-ring fraction; (B) 3-ring fraction.

acid silica gel step, the fluorescence remains beyond the  $R_f$  limits, as shown in Fig. 1 (B, D). These results and the results in Tables 2 and 3 indicate that some nitrogen heterocycles are responsible for the fluorescence beyond the  $R_f$  limits for PAH. The fluorescence beyond these limits is probably due to carbazole types and sterically-hindered pyridine compounds. More work is needed to characterize and identify these nitrogen heterocycles.

#### *Percentage recovery*

As a general check on the percentage recovery of PAH for the characterization procedures with and without the acid silica gel step, the percentage recovery benzo(a)pyrene (BaP) was determined by a method developed previously [13]. Samples (4  $\mu\text{g}$ ) of BaP were added separately to an acidified silica gel column, an alumina column and a shale oil sample. The acidified silica gel column was eluted with chloroform, the alumina column was eluted with n-hexane—ether (19:1), and the spiked shale oil sample was run through both an acidified silica gel—chloroform system and alumina—n-hexane-ether (19:1) system. Finally, the BaP was determined by measuring the fluorescence reflected from the acetylated cellulose as described earlier [13]. For the acidified silica gel column, the recovery was 102%, for the alumina column the recovery was 98%, and for the shale oil sample the recovery was 103%. BaP

TABLE 4

## Determination of benzo(a)pyrene

Sample	Concentration of benzo(a)pyrene (ppm) <sup>a</sup>	
	Without acid silica gel step	With acid silica gel step
13	28	31
14	64	66
15	7.2	8.9
16	11	9.2
17	14	15

<sup>a</sup>Duplicate determinations.

was also determined in several shale oil samples with and without the acid silica gel step; the results are listed in Table 4. All the results indicated that BaP can be determined accurately with the acid silica gel step included.

This work was supported by the Department of Energy's Laramie Energy Technology Center under Contract No. DE-AS20-79-LC01761 to the Rocky Mountain Institute of Energy and Environment.

## REFERENCES

- 1 J. B. Andelman and J. E. Snodgrass, *CRC Critical Reviews in Environmental Control*, 4 (1974) 69.
- 2 G. F. Kirbright and C. G. de Lima, *Analyst*, 99 (1974) 338.
- 3 W. Giger and M. Blumer, *Anal. Chem.*, 46 (1974) 1663.
- 4 G. M. Janini, K. Johnston and W. L. Zielinki, *Anal. Chem.*, 47 (1975) 670.
- 5 R. C. Pierce and M. Katz, *Anal. Chem.*, 47 (1975) 1743.
- 6 K. Potthast and G. Eigner, *J. Chromatogr.*, 103 (1975) 173.
- 7 M. L. Lee, M. Novotny and K. D. Bartle, *Anal. Chem.*, 48 (1976) 405.
- 8 R. E. Tentoft and T. H. Gouw, *Anal. Chem.*, 48 (1976) 2195.
- 9 R. F. Severson, M. E. Snook, R. F. Arrendale and O. T. Chortyk, *Anal. Chem.*, 48 (1976) 1866.
- 10 D. K. Basu and J. Saxena, *Environ. Sci. Technol.*, 12 (1978) 791.
- 11 K. Ogan, E. Katz and W. Slavin, *J. Chromatogr. Sci.*, 16 (1978) 517.
- 12 R. J. Hurtubise, J. F. Schabron, J. D. Feaster, D. H. Therkildsen and R. E. Poulson, *Anal. Chim. Acta*, 89 (1977) 377.
- 13 R. J. Hurtubise, G. T. Skar and R. E. Poulson, *Anal. Chim. Acta*, 97 (1978) 13.
- 14 R. J. Hurtubise, J. D. Phillip and G. T. Skar, *Anal. Chim. Acta*, 101 (1978) 333.
- 15 J. F. Schabron, R. J. Hurtubise and H. F. Silver, *Anal. Chem.*, in press (August).
- 16 L. R. Snyder, *Principles of Adsorption Chromatography*, M. Dekker, New York, 1968.
- 17 D. F. Bender and W. C. Elbert in *Chromatographic Analysis of the Environment*, R. L. Grob (Ed.), M. Dekker, New York, 1975, Ch. 5.

## RAPID ANALYSIS FOR POLYNUCLEAR AROMATIC HYDROCARBONS BY LINEAR-SWEEP DIFFERENTIAL PULSE VOLTAMMETRY

KERILYN C. BURROWS\*\* and MICHAEL C. HUGHES\*

*Department of Chemistry, Lehigh University, Bethlehem, PA 18015 (U.S.A.)*

(Received 23rd April 1979)

### SUMMARY

Rapid-scan linear-sweep differential pulse voltammetry at scan rates of up to 200 mV s<sup>-1</sup> is evaluated for the rapid analysis of polynuclear aromatic hydrocarbon mixtures in acetonitrile at a platinum working electrode. Three- and four-component mixtures with appropriate peak potential separation between the components can be readily separated and quantified at the 1–5-ppm concentration level. A major advantage of the method is the short time requirement. A four-component mixture which requires a 1.2-V range to cover all peaks can be scanned in only 6 s instead of the 5–10 min required by conventional differential pulse voltammetry.

Concern over pollution from polynuclear aromatic hydrocarbons (PAH) has grown with increasing evidence of their carcinogenic properties and studies showing PAH to be common environmental contaminants, particularly in airborne particulate matter. The literature on analyses for PAH is now very large: the most widely used analytical methods are gas chromatography, gas chromatography—mass spectrometry and high-performance liquid chromatography. Preliminary isolation of the PAH fraction is usually necessary, and numerous procedures have been reported.

The present work was undertaken to evaluate the applicability of rapid-scanning linear sweep differential pulse voltammetry (l.s.d.p.v.) to the analysis of PAH mixtures. Coetzee et al. [1] have reported the conventional l.s.d.p.v. of a number of PAH in acetonitrile and sulfolane solvents at platinum and glassy carbon electrodes. They found sensitivities similar to those of the chromatographic methods under normal conditions, and the data presented indicated a definite possibility that the redox potential selectivity of voltammetry would allow for multicomponent analysis. The technique of rapid-scan l.s.d.p.v. has been developed here as a variation of the square-wave voltammetry (s.w.v.) first reported by Barker [2] and recently described as a trace analytical method at stationary electrodes by Rifkin and Evans [3, 4]. At the present time the advantages of l.s.d.p.v. vs. s.w.v. lie largely

---

\*\*Present address: Department of Chemistry, Madonna College, 36600 Schoolcraft Rd., Livonia, Michigan, U.S.A.

in cost and the ease with which rapid scan rates ( $>50 \text{ mV s}^{-1}$ ) may be used with small applied pulse heights. With respect to cost, an easily-built inexpensive digital function generator has been developed which allows a readily available commercial electrochemical analyzer to be used for l.s.d.p.v. at scan rates up to  $500 \text{ mV s}^{-1}$  [5, 6]. Further, although rapid scan s.w.v. has been reported [7], very sophisticated computerized instrumentation had to be used and no analytical applications were described.

The anodic electrochemistry of PAH in non-aqueous solvents has been extensively studied; two excellent reviews are available [8, 9]. It appears likely that all PAH undergo an initial 1-e oxidation to the radical cation, the stability of which depends on the structure of the PAH and, to some extent, on the solvent employed. In all but a few cases, even very rapid voltammetric measurements show evidence of e.c.e. mechanisms caused by instability of the radical cation. The presence of this type of electrode reaction mechanism does not at all preclude the use of d.p.v. measurements, but a decrease in sensitivity relative to a species undergoing a reversible oxidation is expected in any case where an apparently "irreversible" oxidation occurs [1, 10].

## EXPERIMENTAL

### *Instrumentation*

The instrumentation used has been described in detail elsewhere [5, 6], or the detailed circuit diagrams may be obtained from the authors. Briefly, a digital function generator is used to replace the signal-generating section of a Princeton Applied Research Model 174 Polarographic Analyzer (PAR 174). Drop times (really pseudo-drop times,  $t_{pd}$ , since a stationary electrode is used), pulse widths ( $\delta$ ) and sample windows ( $t_s$ ) may be set in increments of 1 ms up to 1 s for  $\delta$  and  $t_s$  and up to 10 s for  $t_{pd}$ . The generator also controls the opening and closing of the four gates on the PAR 174 which apply the pulses to the electrochemical cell, sample the current, and process and read out the differential currents. The PAR 174 potentiostat is used unmodified; the sample processing circuits are very simply modified to decrease their effective RC time constants to values more compatible with rapid scanning [10]. Pulse-height and scanning parameters are set with the PAR 174 front panel controls. In this work the standard working parameters were:  $t_{pd} = 20$  ms,  $\delta = 10$  ms,  $t_s = 8$  ms, RC time constant = 10 or 25 ms. Scan rates of 100 and  $200 \text{ mV s}^{-1}$  were used, since only recorder readout (Hewlett-Packard Moseley 7001-A) was available for making accurate current measurements. The working electrode was made by sealing platinum wire into the end of a borosilicate glass tube and polishing a flat surface with a nominal electrode area of about  $0.01 \text{ cm}^2$ . Effective electrochemical area was not measured. Electrical contact was made through mercury to a platinum wire. The counter electrode was a 16-gauge platinum wire. The cell used was a conventional polarographic H-cell (Sargent). The reference electrode was a poised silver-silver chloride made by oxidizing a cleaned silver wire in 10% KCl for a few seconds.

## Chemicals

Acetonitrile (Eastman Spectrograde) was used as received. The supporting electrolyte was polarographic-grade tetraethylammonium tetrafluoroborate ( $\text{TEABF}_4$ ; Southwestern Analytical Chemicals) which was used as received, stored over  $\text{P}_2\text{O}_5$ . Solutions measured were 0.10 M in  $\text{TEABF}_4$ . Samples of various PAH compounds (Aldrich Chemical Company; Gold Label purity where possible) were used as received. Stock solutions of naphthalene and anthracene contained about  $0.14 \text{ mg ml}^{-1}$  in acetonitrile. All other compounds were dissolved in benzene to give concentrations of  $0.14\text{--}0.15 \text{ mg ml}^{-1}$ , except for perylene, which was  $0.075 \text{ mg ml}^{-1}$ . Runs were made at ambient temperature ( $22 \pm 2^\circ\text{C}$ ).

## RESULTS AND DISCUSSION

Figure 1 shows typical background current and current for a mixture of anthracene and chrysene, 1.4 ppm each ( $7.9 \times 10^{-6} \text{ M}$  and  $6.1 \times 10^{-6} \text{ M}$ , respectively) scanned at  $200 \text{ mV s}^{-1}$  under the operating parameters previously given, and an applied pulse height ( $E_a$ ) of +5 mV. The peaks from the two compounds are defined well enough that even the chrysene peak, located on a steeply sloping baseline, can be quantified with reasonable precision by measuring peak height from an interpolated baseline. Figure 2 shows current vs. concentration plots for chrysene over a 10-fold concentration range (0.70–7.0 ppm) at scan rates of 100 and  $200 \text{ mV s}^{-1}$ ; each point on the graph is the average of eight consecutive runs and the lines shown were calculated by linear least squares. The non-zero intercepts are apparently

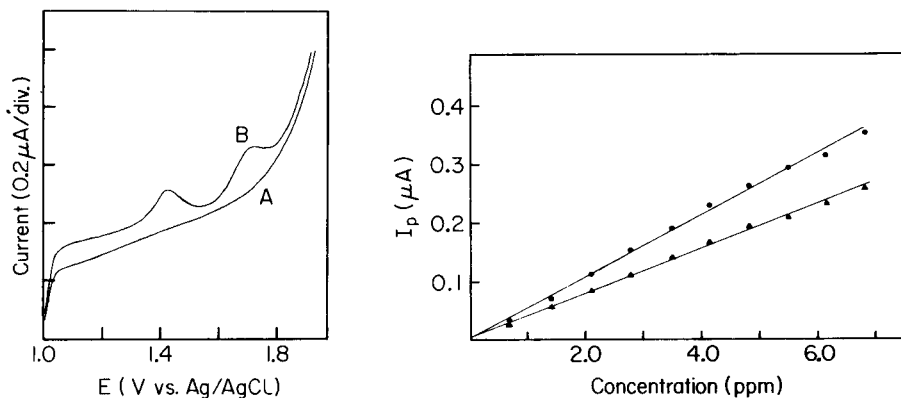


Fig. 1. l.s.d.p.v. in acetonitrile—0.10 M  $\text{TEABF}_4$ . (A) Background current; (B) mixture of 1.4 ppm anthracene (first peak) and 1.4 ppm chrysene (second peak). Scan rate,  $200 \text{ mV s}^{-1}$ ; applied pulse height, +5 mV. Other experimental parameters are given in the text.

Fig. 2. Current vs. concentration for chrysene.  $E_a$ , +5 mV; scan rates  $100 \text{ mV s}^{-1}$  ( $\blacktriangle$ ) and  $200 \text{ mV s}^{-1}$  ( $\bullet$ ). Other experimental parameters are given in the text.

a consequence of using baseline interpolation. The current enhancement obtained at the  $200 \text{ mV s}^{-1}$  scan rate is obvious and there is no loss in reproducibility. The average relative standard deviation at the 95% confidence level for all points in the series was 6% at  $200 \text{ mV s}^{-1}$  and 7% at  $100 \text{ mV s}^{-1}$ . An analogous set of measurements made on anthracene gave relative standard deviations of 6% at both 200 and  $100 \text{ mV s}^{-1}$ .

Increasing  $E_a$  has two deleterious effects. The slope of the background current increases at a rate which is not offset by increasing peak current and the peaks become broader with increasing pulse height so that at an  $E_a$  value of +25 mV the anthracene and chrysene peaks from a mixture begin to merge at the baseline. Both of these situations decrease the accuracy with which the peak current can be read. The ability to utilize  $E_a$  values of only +5 mV at scan rates of  $200 \text{ mV s}^{-1}$  (or higher) is a major advantage of l.s.d.p.v. over s.w.v. It would be possible to use s.w.v. under these conditions but the instrumentation required would be very sophisticated. (It should also be noted, however, that under comparable conditions, s.w.v. would be expected to give better charging current discrimination than l.s.d.p.v., although it is difficult to predict how much the difference would be.)

Table 1 gives the analytical parameters found for single PAH compounds with an  $E_a$  value of +5 mV at scan rates of 100 and  $200 \text{ mV s}^{-1}$ . The non-zero intercepts for several of the PAH are again ascribed to the interpolation of a sloping baseline to obtain the peak currents. The effect is especially noticeable for naphthalene with its extremely positive peak potential.

Figures 3 and 4 show the results of rapid-scan l.s.d.p.v. of PAH mixtures. Eight consecutive scans were run for each mixture at a scan rate of  $200 \text{ mV s}^{-1}$  and an  $E_a$  of +5 mV. Each point in Fig. 4 is the average of all current values obtained; none were dropped. The scans shown in Fig. 3 are for mixtures of perylene, anthracene, chrysene and sometimes naphthalene. Although only a few concentrations were run, Fig. 4 clearly shows the potential for accurate analysis of multicomponent PAH mixtures at ppm levels with a very short analysis time. Each scan took only 6 s to run; conventional d.p.v. would have required 6–10 min per scan.

Coetzee et al. [1] reported detection limits approaching  $1 \times 10^{-8} \text{ M}$  at the glassy carbon electrode for  $E_a$  values of +10 to +50 mV and a scan rate of  $2 \text{ mV s}^{-1}$ . Under the conditions employed in this work, realistic accurate limits of determination for all of the compounds except naphthalene are about 0.5 ppm, corresponding to  $2\text{--}3 \times 10^{-6} \text{ M}$ , depending on the compound being measured. Since the purpose of this work was to evaluate the application of rapid-scan l.s.d.p.v. to the analysis of mixtures, no attempt was made to determine a minimum detection limit for single compounds at the slow scan rates and higher  $E_a$  values which would optimize detection limits at the expense of analysis time. It should also be noted that no special data treatment was used to determine the peak currents. The results given were taken directly from recorder traces. Working on instrumentation improvements which will permit more sophisticated data treatment is in



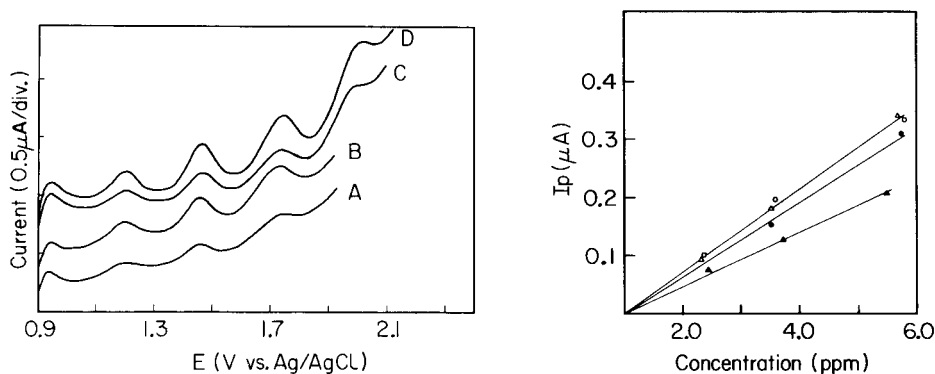


Fig. 3. PAH mixtures scanned at 200 mV s<sup>-1</sup> ( $E_a = +5$  mV); all other experimental conditions as in text. Concentrations (compounds listed in order of increasing peak potential): (A) perylene (1.47 ppm), anthracene (1.38 ppm), chrysene (1.35 ppm); (B) perylene (2.84 ppm), anthracene (2.67 ppm), chrysene (2.62 ppm); (C) perylene (2.79 ppm), anthracene (2.62 ppm), chrysene (2.57 ppm), naphthalene (2.57 ppm); (D) perylene (4.55 ppm), anthracene (4.89 ppm), chrysene (4.79 ppm), naphthalene (4.79 ppm). (The "peak" at ca. +0.95 V is an artifact produced by the response time of the sample—hold circuit.)

Fig. 4. Current vs. concentration plots for multicomponent PAH analysis. (○) Anthracene; (△) chrysene; (●) naphthalene; (▲) perylene. See text for explanation and discussion.

TABLE 1

Electrochemical parameters observed for PAH compounds in 0.10 M TEABF<sub>4</sub>—acetonitrile at a platinum working electrode

Compounds	Scan rate (mV s <sup>-1</sup> )	$\Delta E_{p/2}$ (mV) <sup>a</sup>	$E_p^b$	Slope (nA μM <sup>-1</sup> )	Intercept (nA)
Anthracene	200	116	+1.40	43	-1.7
	100	116	+1.40	32	0.0
Chrysene	200	140	+1.67	23	0.0
	100	140	+1.67	17	0.0
Perylene	100	120	+1.15	11	-1.0
Benzo(a)pyrene	100	108	+1.35	14	-1.0
Naphthalene	100	128	+1.93	30	+4.4
Pyrene <sup>c</sup>	100	140	+1.45	16	+1.5

<sup>a</sup>Half-peak width.

<sup>b</sup>vs. poised Ag—AgCl. Day-to-day reproducibility of this electrode was approximately ± 50 mV, so that the values given should only be used as an indication of the expected peak potential differences between the compounds, and not absolute electrode potential measurements.

<sup>c</sup>Pyrene appears to interact with the Pt surface at concentrations above about 3 ppm ( $1.5 \times 10^{-5}$  M). The peak potential does not change, but the wave shape becomes quite asymmetric with the background current increasing sharply on the anodic side of the wave.

progress, and this can be expected to enhance sensitivity considerably. The present results clearly demonstrate the potential of rapid-scan l.s.d.p.v. as a rapid and accurate method for the determination of PAH alone and in mixtures. The great decrease in analysis time while still preserving good sensitivity is especially important.

The authors acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

#### REFERENCES

- 1 J. F. Coetzee, G. H. Kazi and J. C. Spurgeon, *Anal. Chem.*, 48 (1976) 2170.
- 2 G. C. Barker, R. L. Faircloth and A. W. Gardner, *Nature*, 181 (1959) 247.
- 3 S. C. Rifkin and D. H. Evans, *Anal. Chem.*, 48 (1976) 1616.
- 4 S. C. Rifkin and D. H. Evans, *Anal. Chem.*, 48 (1976) 2174.
- 5 B. D. Yeakel, K. C. Burrows and M. C. Hughes, *Chem. Biomed. Environ. Instrum.*, in press.
- 6 K. C. Burrows, Ph. D. Thesis, Lehigh University, 1979.
- 7 K. Drake, R. Van Duyne and A. M. Bond, *J. Electroanal. Chem.*, 89 (1978) 231.
- 8 C. K. Mann and K. K. Barnes, *Electrochemical Reactions in Nonaqueous Systems*, M. Dekker, New York, 1970.
- 9 R. N. Adams, *Electrochemistry at Solid Electrodes*, M. Dekker, New York, 1969.
- 10 K. C. Burrows, M. P. Brindle and M. C. Hughes, *Anal. Chem.*, 49 (1977) 1459.

## FLUORESCENCE PROPERTIES OF DOMPERIDONE AND ITS DETERMINATION IN PHARMACEUTICAL PREPARATIONS

W. BAEYENS\* and P. DE MOERLOOSE

*State University of Ghent, Faculty of Pharmaceutical Sciences, Department of Pharmaceutical Chemistry and Drug Quality Control, Akademisch Ziekenhuis, De Pintelaan 135, B-9000 Ghent (Belgium)*

(Received 21st February 1979)

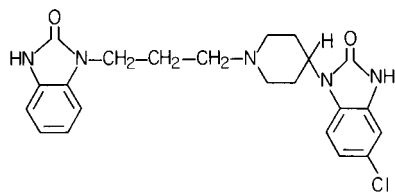
### SUMMARY

The native fluorescence characteristics of domperidone in various solvents and at different pH values are reported. The fluorophore is the benzo-1,3-diazolin-2-one group which is also present in the analogous benperidol, droperidol and pimozone molecules from which domperidone is derived; the substituent may therefore be considered as a relatively strong fluorophore; its excitation and emission maxima are little influenced by pH variation. Domperidone can be determined in pharmaceutical preparations by its native fluorescence in ethanol ( $\lambda_{\text{ex}} = 283 \text{ nm}$ ;  $\lambda_{\text{em}} = 324 \text{ nm}$ ) and in 0.01 M HCl ( $\lambda_{\text{ex}} = 284 \text{ nm}$ ;  $\lambda_{\text{em}} = 329 \text{ nm}$ ) with a detection limit of  $0.01 \mu\text{g ml}^{-1}$ .

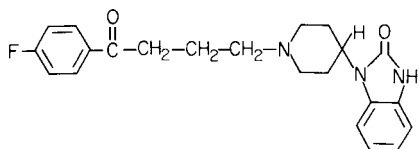
Domperidone (5-chloro-1-[1-[3-(2,3-dihydro-2-oxo-1H-benzimidazol-1-yl)propyl]-4-piperidinyl]-1,3-dihydro-2H-benzimidazol-2-one; I) is a chemically novel gastrokinetic anti-nauseant for the treatment of dyspepsia and vomiting [1]. It shares several pharmacological properties with the anti-emetic metoclopramide and several potent neuroleptic drugs, e.g. haloperidol, with anti-emetic properties. However, it differs from these as it does not penetrate the blood-brain barrier and, therefore, is not expected to produce psychotropic effects or extrapyramidal side-effects [2]. Its effects on the motor function of the stomach and small intestine [3] and a double-blind comparison with placebo and metoclopramide on the effects of oral domperidone on gastric emptying and motility have been described [4]. Domperidone is not related chemically to known anti-dyspeptic agents. In contrast to existing neuroleptic anti-emetics, its potent anti-emetic properties are observed at much lower dosages than those inducing cerebral or cardiovascular effects [5].

As a result of an extensive and systematic investigation of the fluorescence properties of various chemically homologous drugs, the fluorescence properties of some butyrophenones [6, 7], the influence of nitric oxide formation [8] and the oxidative determination of some of these substances involving fluorophore isolation and identification [9] were worked out. The correlation between molecular structure, electron transitions and the fluorescence emission of benperidol and pimozone, a structurally related 4,4-di-

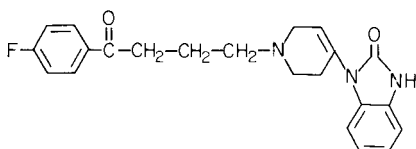
phenylbutylpiperidine antipsychotic, was discussed [10] and a similar examination was described for the anti-emetic metoclopramide [11].



(I)



(II)



(III)

Chemically, domperidone resembles the butyrophenones benperidol(II) and droperidol(III), which show remarkable fluorescence emission [6]; the benzo-1,3-diazolin-2-one moiety responsible occurs twice in domperidone, with the substitutional effects of fluorine and chlorine compensating each other.

As fluorescence generally occurs if the lowest excited singlet state is of the  $\pi, \pi^*$  type, i.e. when the excitation transition of the extensively  $\pi$ -conjugated system is  $\pi \rightarrow \pi^*$ , the influence of the carbonyl groups in which the lowest excited singlet is of  $n, \pi^*$  type, causing intersystem crossing to the triplet state [12], might be significant.

The luminescence properties were investigated qualitatively and quantitatively to increase knowledge of the native fluorescent characteristics of substituted benzimidazoles and to provide a rapid, selective and sensitive method for determining domperidone in pharmaceutical preparations.

## EXPERIMENTAL

### Chemicals

Domperidone (R 33812), benperidol (R 4584) and droperidol (R 4749) (gifts from Janssen Pharmaceutica, Beerse, Belgium) were used without further purification. The Motilium formulations were obtained from the same manufacturer.

Thallium(I) acetate, lead tetraacetate (Fluka) and mercury(II) nitrate (Merck), all "purum" quality, were satisfactory. All other reagents were of analytical grade (Merck or J. T. Baker) and were checked before use for any fluorescent background signal. Deionized water was used throughout after a rapid scan for contaminating fluorescers.

A series of buffer solutions (pH 1–13) having the composition described previously [11] was prepared.

### *Apparatus*

Fluorescence spectra and readings were measured with an Aminco-Bowman spectrofluorimeter (American Instrument Co., Silver Spring, Md.) fitted with a Hanovia 150-W xenon arc lamp, excitation and emission monochromators with gratings,  $1 \times 1$ -cm quartz sample cells, a photomultiplier (R 446S) operated at 700–800 V and an X-Y recorder; the slits varied between 1 and 4 mm; spectral bandpass of  $5.5 \text{ nm mm}^{-1}$  of slit width (Aminco off-axis ellipsoidal condensing system). Lamp stabilization was achieved with a magnetic arc stabilizer (Aminco). Control readings to ascertain that lamp intensity did not fluctuate were done with the fluorescence standards anthracene, naphthalene and *p*-terphenyl (ISA Belgium Groupe Instruments S.A., no. 16.156.139). Corrections were not made for variations in source radiance, monochromator transmission, or photomultiplier sensitivity with wavelength. The wavelength maxima reported were averages of at least five experimental values. The detection limit was defined as the concentration yielding a signal exceeding the background signal for pure solvent by 5% full scale deflection at maximum photomultiplier setting.

Ultraviolet absorption spectra were recorded on a Zeiss recording spectrophotometer, Model DMR 21, equipped with hydrogen light source, 1-cm quartz cuvette, and photomultiplier.

### *Motilium formulations*

Tablets contained domperidone (10 mg/tablet) with adjuvants lactose, starch, povidone, sodium lauryl sulfate, microcrystalline cellulose, magnesium stearate, hydrogenated oil, hydroxypropylmethylcellulose, polyethylene glycol 6000, ethylcellulose, glycerol.

Oral solution contained domperidone ( $1 \text{ mg ml}^{-1}$ ) with tartaric acid, oil of currant, oil of peppermint and sorbitol solution (70%). Oral drops contained domperidone ( $10 \text{ mg ml}^{-1}$ ) with saccharin, polyethylene glycol 400, oil of peppermint, oil of banana and propylene glycol.

Injection ampoules were of two types:  $2 \text{ mg ml}^{-1}$  containing domperidone (2 mg) with tartaric acid and water for injection; and  $5 \text{ mg ml}^{-1}$  containing domperidone (10 mg) with acetic acid and water for injection per 2 ml.

Suppositories were of three strengths: for adults, each suppository contained 60 mg of domperidone; for children, each contained 30 mg; and for infants, 10 mg. The suppositories also contained tartaric acid, sorbitan monostearate, polyethylene glycol 400, polyethylene glycol 1000 and *adepts solidus*.

### *Preliminary investigations*

As there was no significant influence of oxygen on the fluorescence properties of domperidone, precautions to exclude oxygen were not necessary.

Excitation and emission spectra were recorded and relative intensity measurements made at room temperature for fluorophore solutions in different solvents at concentrations of  $1 \times 10^{-3}$ – $10^2 \mu\text{g ml}^{-1}$ . The pH-dependence was established by mixing equal volumes of a methanolic solution ( $20 \mu\text{g ml}^{-1}$ )

of the compound of interest with buffer solutions in the range pH 1–13, directly followed by the scanning of excitation and emission spectra. Blank solutions were subsequently scanned at the wavelength maxima of the fluorophore under investigation to compensate for contaminating substances. From the curves obtained, suitable excitation and emission maxima were chosen to determine the pH-dependence of the fluorescence emission intensities; the same mixing ratio was maintained. Analytical calibration graphs were then obtained under analogous mixing conditions at the wavelength maxima and pH values giving optimum emission intensity and stability. From these curves the linear range of the graphs was established and detection limits were calculated.

#### *Determination of domperidone in pharmaceutical preparations*

*Tablets.* Twenty tablets, weighed accurately, were reduced to a homogeneous, fine powder in a mortar and an amount equal to the calculated average tablet mass was extracted for 30 min in a 250-ml calibrated flask by shaking with ca. 150 ml of ethanol. The mixture was made up to volume with ethanol and filtered (Schleicher and Schüll No. 604, 11-cm diameter). At least 20 ml of the filtrate was discarded and the remainder, diluted with ethanol to a final domperidone concentration of about  $4 \mu\text{g ml}^{-1}$ , was measured fluorimetrically.

For other pharmaceutical preparations, the solutions for fluorimetric measurement were obtained as follows.

*Oral solution.* Direct dilution with 0.01 M hydrochloric acid to a final domperidone concentration of about  $3 \mu\text{g ml}^{-1}$ .

*Oral drops, and injection ampoules.* Direct dilution in ethanol to a final domperidone concentration of about  $4 \mu\text{g ml}^{-1}$ .

*Suppositories.* To one suppository (for adults), weighed accurately in a 100-ml calibrated flask, about 80 ml of a chloroform–methanol mixture (1 + 1) was added. After dissolution, the solution was made up to volume with this mixture and filtered (Schleicher and Schüll No. 604, 11-cm diameter). At least 10 ml of the filtrate was discarded. Of the remaining filtrate, 2.0 ml was pipetted into a 250-ml separating funnel containing 20 ml of 0.05 M sulfuric acid and 20 ml of diethyl ether. After extraction, the aqueous layer was collected in a second 250-ml separating funnel. The ether phase was extracted with two 10-ml portions of 0.05 M sulfuric acid, which were added to the second separating funnel. This acidic aqueous phase was made alkaline with 2.5 ml of 10% (w/v) ammonia solution, and extracted with 50 ml of diethyl ether. The aqueous layer was quantitatively transferred to a third 250-ml separating funnel and extracted with 50 ml of diethyl ether. After separation, the aqueous layer was discarded and the two ether phases were each washed with 10 ml of water which was discarded. Both ether phases were collected in a 500-ml calibrated flask and the solvent was expelled on a boiling water bath with the aid of a gentle air current. The residue was dissolved in 0.01 M hydrochloric acid and made up to volume; this solution (theoretical domperidone concentration =  $2.4 \mu\text{g ml}^{-1}$ ) was measured fluorimetrically.

Suppositories (paediatric) were treated as for the suppositories (adults), but 4.0 ml of the original filtrate was pipetted instead of 2.0 ml. Suppositories for infants were treated in the same way except that 6.0 ml of the original filtrate was pipetted instead of 2.0 ml and the 500-ml calibrated flask was replaced by a 250-ml flask.

*Standard solutions.* For the tablets, oral drops and injection ampoules, a standard solution was prepared by dissolving domperidone in ethanol and diluting with ethanol to a final concentration of ca.  $4 \mu\text{g ml}^{-1}$ .

For the oral solution, domperidone was dissolved in 0.01 M hydrochloric acid and diluted with this solvent to a final concentration of ca.  $3 \mu\text{g ml}^{-1}$ .

For the suppositories, ca. 30 mg of pure domperidone, accurately weighed, was dissolved in 50.0 ml of a chloroform—methanol mixture (1 + 1) and 2.0 ml of this solution was pipetted into a 250-ml separating funnel containing 20 ml of 0.05 M sulfuric acid and 20 ml of diethyl ether. The preparation was continued as described under *Suppositories (adults)* from "... After extraction the aqueous layer was collected in a second 250-ml ...". The final concentration was ca.  $2.4 \mu\text{g ml}^{-1}$ .

*Blank solutions.* For the tablets, oral drops and injection ampoules, pure ethanol was used. For the oral solution and for the suppositories, 0.01 M hydrochloric acid was used.

*Wavelength maxima for the fluorescence intensity readings.* Average excitation and emission wavelengths of 285 nm and 325 nm, respectively, were used for measuring the fluorescence intensities of the final, standard, and blank solutions. As these values are uncorrected, it is advisable to run excitation and emission spectra to establish the appropriate maxima given by the instrument available. These values remained unchanged during the intensity readings of unknown, standard, and blank solutions.

## RESULTS AND DISCUSSION

### *Fluorescence properties of domperidone, benperidol and droperidol*

Preliminary experiments showed that domperidone possessed relatively strong native fluorescence, as expected from its structural similarity to benperidol [6]. Pure 1-(*p*-fluorophenyl)-butan-1-one does not fluoresce, and pimozide shows the wavelength maxima typical of benzimidazoles [10].

Data for the native fluorescence of domperidone in various solvents are given in Table 1. The diluted acids used are based on the solubility data of the substance at room temperature. The optimum fluorescence signals are obtained in ethanol (Fig. 1); fluorescence intensities decrease markedly in less polar solvents. The excitation spectrum is — in theory — identical with the absorption spectrum and differs only as a result of instrumental artifacts [13]; Table 1 shows that the only fluorescence band is associated with the absorption band of longest wavelength.

The fluorescence data for benperidol and droperidol are shown in Table 2. Intensity measurements were made at the wavelength maxima of domperidone

TABLE 1

Excitation and emission maxima and fluorescence intensities<sup>a</sup> of domperidone in various solvents (10  $\mu\text{g ml}^{-1}$ )

Solvent	$\lambda_{\text{ex}}$ <sup>b</sup> (nm)	$\lambda_{\text{em}}$ (nm)	Fluorescence intensity <sup>c</sup>	U.v. absorption maxima (nm) <sup>d</sup>
0.01 M HCl	(235), 284	329	56	205-(227 sh.)-283 <sup>e</sup>
0.01 M Citric acid	(235), 284	329	56	213-(228 sh.)-284 <sup>f</sup>
Methanol	(240), 287	328	64	207-(230 sh.)-286 <sup>e</sup>
Ethanol	(240), 283	324	73	207-231-287 <sup>g</sup>
2-Propanol	(240), 286	325	70	210-(232 sh.)-289 <sup>e</sup>
Chloroform	295	329	7	240-290 <sup>f</sup>
<i>N,N</i> -Dimethylformamide	292	335	31	254-291 <sup>f</sup>

<sup>a</sup>Data are averages of 6 independent experiments. U.v. absorption maxima are given for comparison. <sup>b</sup>Weaker, secondary excitation maxima in brackets. <sup>c</sup>Average wavelength maxima are used: measurements with emission monochromator set on 329 nm and excitation monochromator set on 287 nm. The intensity readings against the blank signals are arbitrary units, calculated with respect to the anthracene polymer fluorescence standard sample (No. 1) = 100. <sup>d</sup>sh. = shoulder. <sup>e</sup>2  $\mu\text{g ml}^{-1}$ . <sup>f</sup>20  $\mu\text{g ml}^{-1}$ . <sup>g</sup>1  $\mu\text{g ml}^{-1}$ .

TABLE 2

Excitation and emission maxima and fluorescence intensities<sup>a</sup> of benperidol and droperidol in various solvents (10  $\mu\text{g ml}^{-1}$ )

Drug	Solvent	$\lambda_{\text{ex}}$ <sup>b</sup> (nm)	$\lambda_{\text{em}}$ (nm)	Fluorescence intensity <sup>c</sup>	
				a	b
Benperidol	0.01 M HCl	(230), 281	318	45	110
	0.01 M Citric acid	(235), 280	315	44	111
	Methanol	(236), 285	320	43	115
	Ethanol	(234), 284	315	54	127
	2-Propanol	(236), 283	315	33	91
	Chloroform	293	315	1	2
	<i>N,N</i> -dimethylformamide	290	322	31	76
Droperidol	0.01 M HCl	280	318	23	37
	0.01 M Citric acid	280	318	20	39
	Methanol	281	319	174	398
	Ethanol	(235), 282	317	150	416
	2-Propanol	282	320	136	313
	Chloroform	292	316	33	10
	<i>N,N</i> -dimethylformamide	290	319	171	341

<sup>a</sup>Data are averages of 6 independent experiments. <sup>b</sup>Weaker, secondary excitation maximum in brackets. <sup>c</sup>Measurements (a) at the domperidone average maxima:  $\lambda_{\text{ex}} = 287$  nm,  $\lambda_{\text{em}} = 329$  nm; (b) at the benperidol average maxima:  $\lambda_{\text{ex}} = 285$  nm,  $\lambda_{\text{em}} = 317$  nm (for benperidol); at the droperidol average maxima:  $\lambda_{\text{ex}} = 284$  nm,  $\lambda_{\text{em}} = 318$  nm (for droperidol). The intensity readings against the blank signals are in arbitrary units, calculated with respect to the anthracene polymer fluorescence standard sample (No. 1) as 100.



to correlate with the domperidone emission intensities and at the average wavelength maxima of the compound of interest representing the true native fluorescence properties. Tables 1 and 2 show that there are only minor changes in the excitation or emission wavelengths for domperidone, benperidol and droperidol. Pimozide exhibits analogous spectral behaviour (in methanol  $\lambda_{\text{ex}} = 230$  nm (weak), 284 nm;  $\lambda_{\text{em}} = 321$  nm [10]). From these data, substituted benzo-1,3-diazolin-2-one derivatives appear to have distinct fluorescence characteristics, especially in methanol, ethanol and 2-propanol, with average excitation and emission wavelengths of 285 nm and 320 nm, respectively. However, there is a slight bathochromic shift in the excitation spectra in less polar solvents, e.g. dimethylformamide and chloroform, indicating a less polar excited state than the ground state [14]. Benperidol behaves similarly to domperidone regarding the influence of solvent. Droperidol differs, apart from the pH effect discussed below, in that unexpected high emission intensities are obtained in dimethylformamide.

The external heavy-atom effect on the fluorescence characteristics of domperidone, benperidol and droperidol was investigated with potassium iodide, thallium(I) acetate, lead tetraacetate (0.01 N in methanol) and mercury(II) nitrate (0.01 N in 0.1 M hydrochloric acid). Only minor influences occurred: the excitation wavelengths increased slightly and the emission wavelengths remained nearly unchanged. Quantitatively, domperidone was not influenced by the ions tested; benperidol showed decreased fluorescence intensity and droperidol exhibited rather unstable emission signals, which presumably originated from (oxidative) attack on the piperidine double bond by the heavy metal ions.

Data for the native fluorescence characteristics of domperidone in some solvents are given in Table 3; the detection limits quoted obviously depend on solvent purity, power and age of the lamp and of the photomultiplier, etc.

The dependence of the fluorescence on pH was studied to establish the optimum pH values for analytical work. After mixing equal volumes of methanolic domperidone solution ( $20 \mu\text{g ml}^{-1}$ ) and a buffer solution of known pH, the spectra and intensity were measured. Table 4 shows that the excitation and emission maxima are largely pH-independent with average values of  $\lambda_{\text{ex}} = 285$  nm and  $\lambda_{\text{em}} = 327$  nm. This quasi pH-independence also occurs with benperidol ( $\lambda_{\text{ex}} = 281$  nm,  $\lambda_{\text{em}} = 317$  nm) and with droperidol ( $\lambda_{\text{ex}} = 286$  nm,  $\lambda_{\text{em}} = 314$  nm). The influence of pH on the fluorescence intensity of domperidone, benperidol and droperidol is represented in Fig. 2. Domperidone and benperidol show optimum fluorescence intensities up to ca. pH 10 and pH 12, respectively. The  $n \rightarrow \pi^*$  transitions associated with the carbonyl groups of the imidazole side-chains and of the phenylbutanone part in benperidol may be responsible for the quenching above pH 11; protonation of the non-bonding electrons may explain the maximum fluorescence at lower pH ranges. Droperidol differs in that quenching also occurs below pH 7; this can be attributed to the double bond in the piperidine ring; although there may be a different stereochemical configuration in droperidol (this

TABLE 3

Data for domperidone fluorescence measurements<sup>a</sup>

Solvent	Upper limit of linear range ( $\mu\text{g ml}^{-1}$ ) <sup>b</sup>	Limit of detection <sup>c</sup> ( $\mu\text{g ml}^{-1}$ )	Maxima used (nm)		Coefficient of variation (%)
			$\lambda_{\text{ex}}$	$\lambda_{\text{em}}$	
0.01 M HCl	4	0.01	284	329	0.8
Methanol	6	0.01	287	328	1.0
Ethanol	6	0.01	283	324	1.0
2-Propanol	0.5	0.02	286	325	1.1

<sup>a</sup>Mean of 6 individual experiments for relative intensity vs. concentration graphs. All slits 4 mm (spectral bandpass 5.5 nm mm<sup>-1</sup>); photomultiplier voltage, 0.8 kV. <sup>b</sup>Concentration-quenching causing a negative curvature occurs at concentrations above ca. 40  $\mu\text{g ml}^{-1}$ . <sup>c</sup>Concentration yielding a signal exceeding the background signal for pure solvent by 5% full scale deflection at maximum photomultiplier setting.

TABLE 4

Influence of pH on domperidone excitation and emission wavelengths<sup>a</sup>

pH (22°C)	$\lambda_{\text{ex}}^{\text{b}}$ (nm)	$\lambda_{\text{em}}$ (nm)	pH (22°C)	$\lambda_{\text{ex}}^{\text{b}}$ (nm)	$\lambda_{\text{em}}$ (nm)
0.25	(235), 282	322	6.95	(245), 284	326
1.00	(235), 283	325	8.15	(243), 285	327
2.05	(235), 284	327	8.90	(245), 283	327
3.00	(245), 285	327	9.85	(245), 284	325
3.90	285	325	10.95	(245), 283	325
4.90	284	326	12.00	(250), 285	328
5.95	285	325	12.75	(255), 290	337

<sup>a</sup>Equal volumes of methanolic solution (20  $\mu\text{g ml}^{-1}$ ) and buffer solution are mixed.

<sup>b</sup>Weaker, secondary excitation maxima in brackets. All results are average of two experiments.

part of the molecule becoming flatter) an interaction of the  $\pi$ -electrons of the double bond with the lone electron pair of the neighbouring nitrogen atom may also occur. The double bond can be a source of electrons, i.e. may act as a base [15]; quenching of molecular luminescence may then occur in acidic medium through deactivation of the excited state responsible for fluorescence by interaction of either the ground or excited states with the species in solution. Quenching by interaction with the solvent or by interaction with hydrogen bonding solvent molecules may proceed by a vibrational mechanism [16]; vibrational coupling may favor efficient internal conversion. The reduced fluorescence emission of droperidol in acidic medium is, however, not completely understood.

For domperidone, the fluorescence intensity values obtained below pH 7 (Fig. 2) were of the same magnitude as those shown for the dilute acid solutions

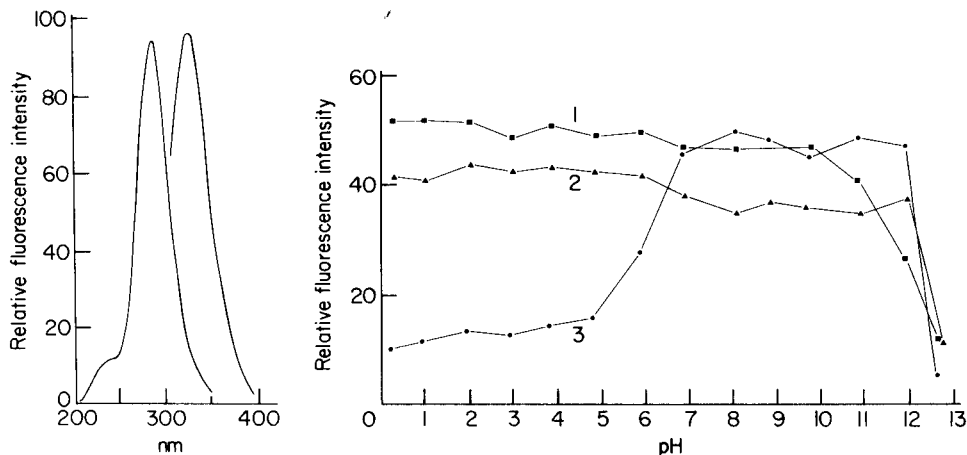


Fig. 1. Excitation and emission spectra of domperidone ( $20 \mu\text{g ml}^{-1}$ ) in ethanol ( $\lambda_{\text{ex}} = 240 \text{ nm}$  (weak),  $283 \text{ nm}$ ;  $\lambda_{\text{em}} = 324 \text{ nm}$ ).

Fig. 2. Fluorescence intensity versus pH for equal volumes of methanolic solution ( $10-20 \mu\text{g ml}^{-1}$ ) and buffer solution at the average excitation and emission wavelengths given in the text. Blank corrections are included. (■) Domperidone; (▲) benperidol; (●) droperidol.

in Table 1; ethanol and 0.01 M hydrochloric acid are suitable solvents for fluorimetric domperidone determinations. Direct determinations based on extraction and successive dilution in ethanol were possible for Motilium tablets, oral drops and injection ampoules, but not for the oral solution; sorbitol precipitated on mixing with ethanol and caused low results through coprecipitation of the active material. Good results were obtained when 0.01 M hydrochloric acid was used in place of ethanol.

Because the suppositories contained sorbitan monostearate emulsifier attempted extractions with diethyl ether in the presence of 0.01 M HCl or buffer solutions (pH 2.0) gave stable emulsions. Dissolution in chloroform-methanol mixture (1 + 1) and successive extractions with 0.05 M sulfuric acid in the presence of diethyl ether, and with diethyl ether in the presence of 10% (w/v) ammonia solution, followed by dissolution of the evaporated residue in 0.01 M hydrochloric acid and fluorimetric measurement gave a reliable method for these pharmaceutical products. Table 5 shows the results obtained from fluorimetric determinations of some of these commercial preparations. Under the conditions mentioned, no significant influence of the excipients on the domperidone luminescence behaviour was observed. It should be noted, however, that the proposed direct fluorescence methods were not tested on degradation products of domperidone as these were not available. To obtain reliable stability-indicating results, chromatographic separation methods should be applied followed by fluorescence measurements. Degradation products and contaminants containing the benzimidazole fluoro-

TABLE 5

Fluorimetric determination<sup>a</sup> of domperidone in pharmaceutical products

Formulation <sup>b</sup>	Approximate concn. measured ( $\mu\text{g ml}^{-1}$ )	Solvent	Recovery <sup>c</sup> against the appropriate standard (%)	Coefficient of variation (%)
Tablets (10 mg)	4	ethanol	98.5	1.2
Oral solution (1 mg ml <sup>-1</sup> )	3	0.01 M HCl	99.7	1.4
Oral drops (10 mg ml <sup>-1</sup> )	4	ethanol	98.5	2.7
Injection ampoules (2 mg ml <sup>-1</sup> )	4	ethanol	101.4	1.3
(5 mg ml <sup>-1</sup> )	4	ethanol	98.8	2.7
Suppositories (adults: 60 mg)	2.4	0.01 M HCl	98.0	1.8
(paediatric: 30 mg)	2.4	0.01 M HCl	97.8	1.5
(infants: 10 mg)	2.4	0.01 M HCl	99.2	2.2

<sup>a</sup> $\lambda_{\text{ex}} = 285 \text{ nm}$ ,  $\lambda_{\text{em}} = 325 \text{ nm}$ . <sup>b</sup>Motilium. <sup>c</sup>Average recovery in ten experiments with individual standard solutions.

phore fraction are likely to produce intense fluorescence emission. For routine analyses, t.l.c. experiments for identifying the active material may suffice prior to fluorescence measurements in order to establish the absence of potential interferents.

The fluorescence method has not been applied to the determination of trace drug levels in body fluids; it should be useful for domperidone and its metabolites containing the benzo-1,3-diazolin-2-one moiety.

## REFERENCES

- 1 A. J. Reyntjens, C. J. E. Niemegeers, J. M. Van Nueten, P. Laduron, J. Heykants, K. H. L. Schellekens, R. Marsboom, A. Jageneau, A. Broekaert and P. A. J. Janssen, *Arzneim. Forsch.*, 28 (II), 7 (1978) 1194.
- 2 Janssen Pharmaceutica, Beerse (Belgium), unpublished data.
- 3 R. Baeyens, A. Reyntjens and E. Van de Velde, *Arzneim. Forsch.*, 28 (I), 4 (1978) 682.
- 4 A. De Schepper, F. Wollaert and A. Reyntjens, *Arzneim. Forsch.*, 28 (II), 7 (1978) 1196.
- 5 C. J. E. Niemegeers and P. A. J. Janssen, Paper presented at the 7th International Congress of Pharmacology, Paris, July 16–21, 1978.
- 6 W. Baeyens, *Analyst*, 102 (1977) 525.
- 7 W. Baeyens, *Pharm. Weekbl.*, 112 (1977) 681.
- 8 W. Baeyens, P. De Moerloose and L. De Taeye, *J. Pharm. Sci.*, 66 (1977) 1787.
- 9 W. Baeyens and P. De Moerloose, *Pharmazie*, 32, 12 (1977) 764.
- 10 W. Baeyens, *Talanta*, 24 (1977) 579.
- 11 W. Baeyens and P. De Moerloose, *Analyst*, 103 (1978) 359.
- 12 J. E. Crooks, *The Spectrum in Chemistry*, Academic Press, London, 1978, pp. 126–7.
- 13 S. Udenfriend, *Fluorescence Assay in Biology and Medicine*, Academic Press, London, 1962, p. 20.
- 14 G. G. Guilbault, *Practical Fluorescence, Theory, Methods and Techniques*, M. Dekker, New York, 1973, p. 101.
- 15 R. T. Morrison and R. N. Boyd, *Organic Chemistry*, 2nd edn., Allyn and Bacon, Boston, 1972, pp. 145, 146, 176.
- 16 S. G. Schulman, *Fluorescence and Phosphorescence Spectroscopy: Physicochemical Principles and Practice*, Pergamon Press, Oxford, 1977, p. 102.

## DOSAGE DU BARYUM DANS L'EAU ET LES LIQUIDES BIOLOGIQUES PAR SPECTROMETRIE D'EMISSION AVEC SOURCE PLASMA HAUTE FREQUENCE

Y. MAURAS et P. ALLAIN\*

*Laboratoire de Pharmacologie, Centre Hospitalier Universitaire, 49036 Angers Cedex (France)*

(Reçu le 23 mars 1979)

### SUMMARY

*Determination of barium in water and biological fluids by emission spectrometry with an inductively-coupled plasma*

An emission spectrometric method is described for the determination of barium in water, urine and blood with an inductively-coupled plasma. The method is highly selective, reproducible, and sensitive. The limits of detection are  $0.06 \mu\text{g l}^{-1}$  in water,  $0.25 \mu\text{g l}^{-1}$  in urine,  $0.6 \mu\text{g l}^{-1}$  in blood. For thirteen healthy subjects, the barium content was  $4.3 \mu\text{g l}^{-1}$  ( $s = 1.4$ ) in urine and less than  $1 \mu\text{g l}^{-1}$  in blood. For a case of accidental poisoning, the content was  $260 \mu\text{g Ba l}^{-1}$  in blood and  $280 \mu\text{g Ba l}^{-1}$  in urine.

### RESUME

Une technique de dosage du baryum par spectrométrie d'émission avec une source plasma, par induction haute fréquence, est décrite. Elle est appliquée à la détermination du baryum dans l'eau, l'urine et le sang. C'est une technique spécifique, reproductible et sensible, dont la limite de détection est de  $0,06 \mu\text{g l}^{-1}$  dans l'eau, de  $0,25 \mu\text{g l}^{-1}$  dans l'urine et de  $0,6 \mu\text{g l}^{-1}$  dans le sang. Les dosages, effectués chez treize sujets en bonne santé, ont montré que l'urine contient en moyenne  $4,3 \mu\text{g Ba l}^{-1}$  ( $s = 1,4$ ) et que le sang n'en contenait pas ou en quantité inférieure au  $1 \mu\text{g l}^{-1}$ . Après intoxication accidentelle chez un malade, elle a permis de révéler  $260 \mu\text{g Ba l}^{-1}$  dans le sang et  $280 \mu\text{g Ba l}^{-1}$  dans l'urine.

Les méthodes récentes de dosage du baryum font appel soit à l'absorption atomique en flamme [1–3] ou au four [4, 5] soit à l'émission atomique obtenue par excitation thermique dans une flamme [6] ou dans un four graphite [7, 8]. Ces techniques sont très largement appliquées au dosage du baryum dans les eaux et dans les matériaux géologiques, mais on ne rencontre pratiquement pas dans la littérature d'applications aux liquides biologiques. La technique que nous proposons ici permet le dosage du baryum dans l'eau, l'urine et le sang par spectrophotométrie d'émission à l'aide d'un plasma induit par haute fréquence comme source d'excitation.

## PARTIE EXPERIMENTALE

### *Appareillage et réactifs*

L'appareil utilisé est un spectroanalyseur séquentiel Jobin-Yvon JY 38 P. Il se compose d'une source PlasmaTherm à induction par haute fréquence de 27,12 MHz dont la puissance disponible est de 1,5 kW, d'un monochromateur thermostaté HR 1000 de résolution 0,01 nm et d'une console électronique de mesure. Le gas plasmogène est l'argon. L'introduction des échantillons dans le plasma est effectuée par un nébuliseur pneumatique de type concentrique. Les spectres d'émission sont obtenus sur un enregistreur Linséis par défilement automatique de la longueur d'onde. Les différents paramètres de réglage font l'objet d'une étude systématique afin d'obtenir les meilleures conditions de travail qui sont celles donnant le rapport signal/fond le plus élevé.

### *Réactifs*

L'étalonnage en baryum est effectué grâce à une solution standard à  $1 \text{ g l}^{-1}$  (Titrisol, Merck). Toutes les dilutions sont effectuées dans des récipients en matière plastique avec de l'eau osmosée puis déminéralisée. Les solutions à  $1 \text{ g l}^{-1}$  des autres métaux sont obtenues soit à partir d'un standard (Titrisol, Merck) soit par dissolution dans l'eau d'un sel p.a.

### *Préparation des échantillons*

Les urines et les sangs sont systématiquement dilués (1 + 3 et 1 + 9, respectivement). Les eaux sont dosées pures. L'étalonnage est effectué par une technique d'ajouts. Chaque échantillon est surchargé par des solutions de concentrations convenables pour obtenir des ajouts de  $6,25 \mu\text{g l}^{-1}$ ,  $25 \mu\text{g l}^{-1}$  et  $100 \mu\text{g l}^{-1}$ . Cinq mesures de 5 s sont effectuées sur chaque tube, après centrifugation pour éliminer les éventuelles particules en suspension susceptibles d'obstruer le nébuliseur. Le fond, déterminé après décalage manuel de la longueur d'onde 0,06 nm vers les bases longueurs d'ondes, est retranché de chaque mesure. La droite d'ajouts est calculée par la méthode des moindres carrés et la concentration dans l'échantillon obtenue par calcul de son point d'intersection avec l'axe des concentrations.

### *Conditions opératoires*

La recherche systématique des raies d'émission du baryum nous a conduit à sélectionner la raie 455,40 nm pour le dosage. Il est cependant possible d'utiliser la raie 493,41 nm dont la sensibilité est légèrement inférieure.

La meilleure sensibilité est obtenue pour les réglages suivants: puissance 1 kW, hauteur d'observation de 20 mm au-dessus de la spire d'induction, débit de refroidisseur  $15 \text{ l min}^{-1}$ , nébulisation sous une pression de 20 psi avec un débit d'argon de  $0,8 \text{ l min}^{-1}$ . Ces conditions permettent d'obtenir, avec une solution de baryum à  $1 \text{ mg l}^{-1}$ , un rapport signal/fond de 300:1 à 455,40 nm et de 200:1 à 493,41 nm.

## RESULTATS

*Etude des interactions dues à la matrice*

*Etude des interférences spectrales.* L'étude des interférences spectrales permet de déceler l'existence soit des raies d'émission d'un autre élément, soit des lumières parasites pouvant chevaucher l'émission du baryum ou s'y superposer. Elle est conduite en enregistrant les spectres d'émission entre 455,10 nm et 455,70 nm d'une part, et 493,10 nm et 493,70 nm d'autre part, en nébulisant des solutions à  $1 \text{ g l}^{-1}$  de différents métaux et notamment ceux rencontrés en biologie. Nous n'avons observé aucune raie se détachant du fond spectral avec le Na, K, Li, Rb, Al. Avec d'autres métaux (Zn, La, Ca, Mg, Hg, Fe, Cd, Pb, Cu, Sr, Si) nous obtenons des émissions plus ou moins importantes attribuées à des impuretés ou des contaminations en baryum car elles sont situées exactement aux longueurs d'onde de ce métal (455,40 et 493,41 nm), et qu'à chacune de ces longueurs d'onde leur intensité en  $\mu\text{g l}^{-1}$  de baryum est identique soit  $1 \mu\text{g l}^{-1}$  pour Zn, La, Ca;  $8 \mu\text{g l}^{-1}$  pour Mg et Hg;  $4 \mu\text{g l}^{-1}$  pour Fe;  $12 \mu\text{g l}^{-1}$  pour Cd;  $20 \mu\text{g l}^{-1}$  pour Pb;  $60 \mu\text{g l}^{-1}$  pour Cu et Sr;  $140 \mu\text{g l}^{-1}$  pour Si.

Par ailleurs, dans le voisinage des longueurs d'ondes du baryum, plusieurs raies peuvent être observées (Tableau 1). Etant donné la haute résolution du monochromateur, elles sont aisément séparées et n'interfèrent ni dans le dosage du baryum proprement dit, ni dans la mesure du fond décalé de 0,06 nm. Une exception doit toutefois être faite avec les fortes concentrations en fer où la longueur d'onde 493,34 nm apporterait une erreur dans la mesure du fond lors d'un dosage du baryum à 493,40 nm.

L'acide borique ou le borate de sodium à concentration supérieure à  $100 \text{ mg B l}^{-1}$  donne un spectre très accidenté avec des pics recouvrant partiellement ceux du baryum.

TABLEAU 1

Etude des interférences spectrales. Différentes raies observées dans le voisinage des longueurs d'onde de dosage du baryum, 455,40 et 493,41 nm.

Métal <sup>a</sup>	Raies observées (nm)	Rapport signal/fond
Fe	455,19	4,5
	455,61	2
	493,34	2
Cu	455,24	21
La	455,26	6
	455,94	400
	455,85	2 700
	493,50	550
	493,60	75

<sup>a</sup>Concentration,  $1 \text{ g l}^{-1}$ .

*Modification du fond spectral.* Indépendamment des émissions de raies, certains métaux provoquent une augmentation générale du fond spectral (Fig. 1).

La Fig. 2 montre l'influence de concentrations variables de différents métaux sur le fond mesuré à 455,34 nm. Le calcium, silicium et strontium à  $1 \text{ g l}^{-1}$  peuvent le doubler, tandis que le Li, Al, Na et Cu ont une action plus faible, l'augmentant de 20–30%. Les autres métaux (K, Mg, Fe, Rb, Pb, Hg, Zn, Cd) ne sont pas représentés car leur influence, à la concentration de  $1 \text{ g l}^{-1}$ , est inférieure à 15%.

Nous avons également mesuré le fond en présence d'anions divers (chlorure, sulfate, phosphate, nitrate, éthylènediaminetétracétate) sans observer aucune différence.

Les modifications du fond autour de la raie 493,41 nm du baryum sont identiques. Cette dernière longueur d'onde, moins sensible pour le dosage, est également plus difficile à utiliser pour la mesure du fond par décalage de la longueur d'onde car la ligne de base du spectre de fond est moins linéaire.

*Action sur le signal.* Nous avons comparé le signal net donné par  $100 \mu\text{g l}^{-1}$  de baryum dans l'eau distillée et dans les solutions à  $1 \text{ g l}^{-1}$  des éléments suivants: Na, K, Ca, Mg, Sr, Fe, La, Rb, Pb, Hg, Li, Cu, Zn, Cd, Al, B. Aucune

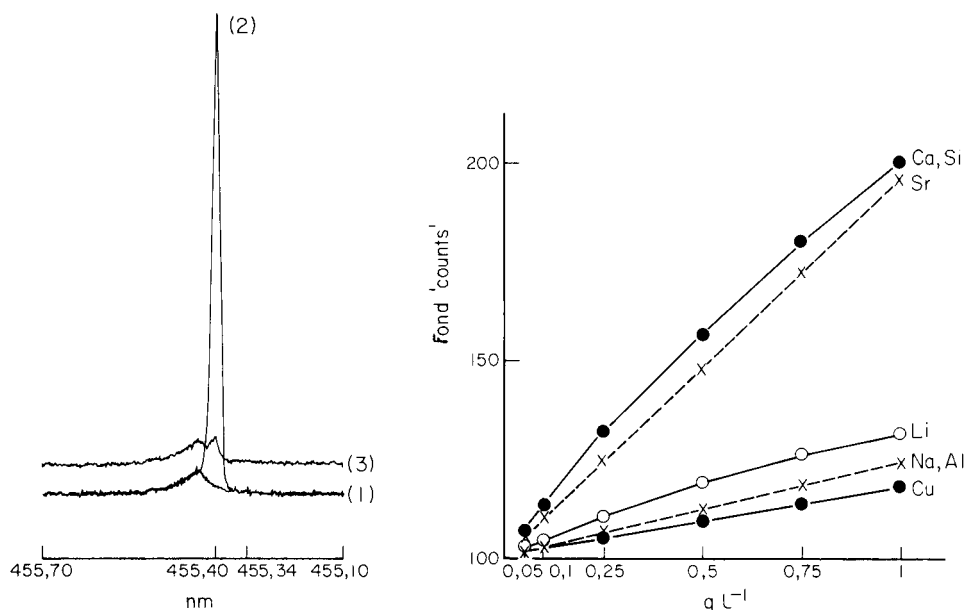


Fig. 1. Spectres d'émissions obtenus par défilement de longueur d'onde entre 455,10 et 455,70 nm, avec: (1) de l'eau pure; (2) de l'eau contenant  $20 \mu\text{g Ba l}^{-1}$ ; (3) une solution contenant Na, K, Ca, Mg à concentrations égales de  $0,25 \text{ g l}^{-1}$ .

Fig. 2. Action de quelques métaux sur le fond mesuré au pied de la raie du baryum à 455,34 nm. La valeur 100 est attribuée au fond donné par l'eau déminéralisée.



modification du signal supérieure à 10% n'a été relevée. De même, la nature de l'anion (chlorure, nitrate, phosphate, éthylènediaminetétracétate) n'influe pas sur le signal. Seul le silicium à  $1 \text{ g l}^{-1}$  a provoqué une augmentation du signal de 35%.

*Dosage du baryum.* Les courbes d'étalonnage pour des concentrations en baryum de 0–400  $\mu\text{g l}^{-1}$  montrent une linéarité parfaite aussi bien dans l'eau, que dans l'urine ou le sang. Les équations des courbes d'étalonnage (pour un coefficient de régression linéaire  $r = 1,000$ ) sont  $y = 25,39x - 2,6$  (l'eau),  $y = 6,324x - 24,5$  (l'urine) et  $y = 2,536x + 1$  (le sang).

Les limites de détection sont calculées comme étant l'équivalent en concentration de deux fois la déviation standard du fond [9, 10]. Dans les conditions de dilutions utilisées, elles sont de 0,06  $\mu\text{g l}^{-1}$  en solution pure, 0,25  $\mu\text{g l}^{-1}$  dans l'urine et 0,6  $\mu\text{g l}^{-1}$  dans le sang.

Les reproductibilités obtenues en effectuant dix dosages dans la même série, et en effectuant le même dosage pendant vingt jours sont données dans le Tableau 2. Dans la même série, le coefficient de variation est de 1–4% suivant la concentration. Dans la reproductibilité d'un jour à l'autre, les coefficients de variation sont de 3–7% pour les concentrations de l'ordre de 100  $\mu\text{g l}^{-1}$  en baryum et de 15–25% pour les très faibles concentrations.

Chez treize sujets des deux sexes, en bonne santé, nous n'avons pas trouvé de baryum dans le sang. Par contre, les urines contiennent toutes du baryum en quantité aisément dosable, allant de 1,8  $\mu\text{g l}^{-1}$  à 7  $\mu\text{g l}^{-1}$ , avec en moyenne 4,3  $\mu\text{g l}^{-1}$  ( $s = 1,4$ ). Chez un malade au cours d'une intoxication, nous avons trouvé 260  $\mu\text{g Ba l}^{-1}$  dans le sang et 280  $\mu\text{g Ba l}^{-1}$  dans l'urine.

Des dosages dans l'eau de la ville d'Angers nous ont donné en moyenne 60  $\mu\text{g Ba l}^{-1}$  ( $s = 6$ ,  $n = 8$ ). L'eau a été prélevée au robinet d'arrivée après 5 mins d'écoulement, des jours différents et dans des endroits différents.

TABLEAU 2

Reproductibilités obtenues

	Moyenne $\bar{x}$ ( $\mu\text{g l}^{-1}$ )	Ecart type, $s$	Coefficient variation ( $s/\bar{x}$ ) $\times 100$
<i>Dix dosages dans la même série</i>			
Eau	24	0,4	1,7
	125	1,5	1,2
Urine	5,2	0,2	3,8
	105,4	3,1	2,95
<i>Le même dosage une fois par jour pendant 20 jours</i>			
Eau	0,83	0,21	25,3
	111,7	4,5	4
Urine	5,5	1,25	22,7
	82,1	2,9	3,5
Sang	9,3	1,45	15,6
	127,8	8,6	6,7

## DISCUSSION

La recherche des interférences ne révèle aucune raie due à un autre métal ni aucune lumière parasite recouvrant l'émission du baryum. Seul le bore, à concentration supérieure à  $100 \text{ mg l}^{-1}$ , pourrait interférer. Une telle éventualité ne se présentant pas en biologie, la spécificité du dosage du baryum dans les milieux biologiques est largement assurée.

La limite de détection de  $0,06 \text{ } \mu\text{g l}^{-1}$  en solution aqueuse est plus basse que toutes celles qui sont citées pour les autres méthodes de dosage: absorption atomique en flamme  $90 \text{ } \mu\text{g l}^{-1}$  [2], absorption atomique au four  $1 \text{ } \mu\text{g l}^{-1}$  [4] ou  $4 \text{ } \mu\text{g l}^{-1}$  [5], émission avec flamme  $2 \text{ } \mu\text{g l}^{-1}$  [6] et émission au four graphite  $0,4 \text{ } \mu\text{g l}^{-1}$  [7] ou  $0,8 \text{ } \mu\text{g l}^{-1}$  [8]. La linéarité est toujours excellente, s'étend à des zones de concentrations extrêmement larges et n'est pas affectée par la composition de la matrice: eau, urine ou sang. La reproductibilité est aussi bonne que celle de toute autre technique et le coefficient de variation ne s'élève qu'au voisinage des limites de détection.

Spécifique, linéaire, reproductible, d'une grande sensibilité, et s'appliquant aussi bien aux dosages dans les liquides biologiques que dans l'eau, la spectrophotométrie d'émission avec source plasma est donc une technique de choix pour le dosage du baryum. Cependant, pour obtenir de bons résultats, notamment dans les milieux biologiques, il faut tenir compte à la fois de la composition de la matrice modifiant le fond et des différences de nébulisation entre les solutions minérales et les solutions organiques complexes comme le sang dilué. C'est pourquoi la mesure du fond spectral au pied de la raie et l'étalonnage par ajouts dosés sont nécessaires.

Les variations normales de la ligne de base en l'absence de baryum entraînent une légère différence entre les mesures effectuées à  $455,40$  et  $455,34 \text{ nm}$  (Fig. 1, courbe 1). Cette différence qui ne doit pas être comptée comme étant du baryum est mesurée sur l'eau distillée et ajoutée à la mesure du fond de chaque échantillon.

Le métabolisme du baryum chez l'homme n'est pas bien connu et il n'existe que de très rares données concernant le baryum sanguin et urinaire. Olehy et al. en 1966 [11], utilisant l'analyse par activation neutronique, donnent  $7 \text{ } \mu\text{g Ba l}^{-1}$  dans les globules rouges et  $66 \text{ } \mu\text{g Ba l}^{-1}$  dans le plasma. Schroeder et al. en 1972 [1], utilisant l'absorption atomique en flamme, ont trouvé  $79 \text{ } \mu\text{g Ba l}^{-1}$  dans le plasma humain et  $22 \text{ } \mu\text{g Ba l}^{-1}$  dans l'urine. Pour notre part, chez treize sujets en bonne santé, nous n'avons pas trouvé de baryum dans le sang total. Cependant, les urines en contenaient toujours des quantités allant de  $1,8$  à  $7 \text{ } \mu\text{g l}^{-1}$  soit en moyenne cinq fois moins que celles citées par Schroeder et al. [1]. On sait que l'eau et les aliments apportent quotidiennement du baryum à l'organisme. L'excrétion urinaire bien que faible, montre qu'une partie de ce baryum passe nécessairement par le sang, mais en quantité inférieure aux quantités dosables, c'est-à-dire inférieure au microgramme par litre.

Nous remercions Madame Jouglard, du Centre Anti-Poisons de Marseille, pour les prélèvements de sang et d'urine d'un malade intoxiqué qu'elle nous a fait parvenir.

#### BIBLIOGRAPHIE

- 1 H. A. Schroeder, I. H. Tipton and A. P. Nason, *J. Chronic Dis.*, 25 (1972) 491.
- 2 H. Kawamura and G. Tanaka, *Spectrochim. Acta, Part B*, 28 (1973) 309.
- 3 R. Frache and A. Mazzucotelli, *Talanta*, 23 (1976) 389.
- 4 G. D. Renshaw, *At. Absorpt. Newsl.*, 12 (1973) 158.
- 5 R. Cioni, A. Mazzucotelli and G. Ottonello, *Anal. Chim. Acta*, 82 (1976) 415.
- 6 E. E. Pickett and S. R. Koirtzohann, *Spectrochim. Acta, Part B*, 23 (1968) 235.
- 7 R. C. Hutton, J. M. Ottaway, T. C. Rains and M. S. Epstein, *Analyst*, 102 (1977) 429.
- 8 L. Ebdon, R. C. Hutton and J. M. Ottaway, *Anal. Chim. Acta*, 96 (1978) 63.
- 9 P. W. J. H. Boumans and F. J. de Boer, *Spectrochim. Acta, Part B*, 32 (1977) 365.
- 10 S. Greenfield, *ICP Inf. Newsl.*, 4 (1978) 199.
- 11 D. A. Olehy, R. A. Schmitt and W. F. Bethard, *J. Nucl. Med.*, 7 (1966) 917.

## FLAME ATOMIC ABSORPTION ANALYSIS FOR SELENIUM AFTER ELECTROCHEMICAL PRECONCENTRATION

WALTER LUND\* and RAGNAR BYE

*Department of Chemistry, University of Oslo, Box 1033 Blindern, Oslo 3 (Norway)*

(Received 18th May 1979)

### SUMMARY

Selenium(IV) is determined in the presence of 3.5% sodium chloride by electrochemical preconcentration on a platinum spiral, prior to flame atomic absorption analysis. The electrodeposition is carried out in the presence of hydrazine dihydrochloride to prevent the generation of chlorine at the counter electrode; chlorine oxidizes selenium(IV) to the non-reducible selenium(VI) ion. A detection limit of 5 ppb and an electrolysis efficiency of 10% were obtained for a 25-ml sample and a 5-min electrolysis time. The absolute detection limit was 10 ng.

The electrochemical preconcentration of metals is used in atomic absorption analysis to eliminate interferences from high concentrations of salts which would otherwise give rise to unspecific light losses. The method involves the electrodeposition of metals onto a metal wire or carbon rod, and atomization either in a normal flame [1], or by electrothermal heating [2–5]. Recently it was brought to our attention [6] that the electrochemical preconcentration method did not give satisfactory results for selenium(IV) when the sample contained a high concentration of chloride. The interference from chloride arises from the generation of chlorine at the counter electrode (anode). The chlorine oxidizes selenium(IV) to selenium(VI), and thus renders it electrochemically inactive. The problem is of practical importance, because many of the typical samples analyzed in environmental control programs will contain relatively high concentrations of chloride (e.g. sea water, urine).

In this work various procedures for handling the interference from chloride are discussed. A platinum spiral was used for the preconcentration of selenium, and the deposited selenium was determined by flame atomic absorption analysis, by using a quartz absorption tube above the filament [1]. All samples analyzed contained 3.5% sodium chloride.

### EXPERIMENTAL

A Perkin-Elmer 303 atomic absorption spectrometer and a Perkin-Elmer 159 recorder were used. The instrument was equipped with a deuterium background corrector. For atomization, an air-acetylene flame and a three-

slot burner were used. A quartz absorption tube (length 10 cm, outer diameter 15 mm) was placed in the optical path 16 mm above the burner.

Atomization was done from a spiral-wound platinum wire (0.5 mm diameter; 99.999%, Koch-Light) as described previously [1]. It was mounted in a holder similar to that used for the Delves cup technique; the spiral was positioned just below the circular opening in the absorption tube. The diameter of the opening was slightly larger than that of the spiral filament.

The electrochemical preconcentration was done by controlled-potential electrolysis with a home-made potentiostat. The platinum filament served as the working electrode, a silver/silver chloride electrode was used as the reference electrode and a platinum coil was used as the counter electrode; the counter electrode was placed in a glass tube equipped with a porosity G1 glass sinter. A Metrohm EA 880 vessel was used as the electrolytic cell. The samples were stirred with a constant-rate (500 rpm) magnetic stirrer during the electrolysis.

The selenium(IV) solutions were prepared by diluting analytical-grade selenous acid. All solutions to be analyzed were made 3.5% in sodium chloride.

### *Procedure*

Add 0.3 g of hydrazine dihydrochloride and 25  $\mu$ l of a 0.5 g l<sup>-1</sup> copper sulphate solution to each 25-ml aliquot and electrolyze with stirring for 5 min at -0.8 V vs. Ag/AgCl. At the end of the deposition period, remove the filament electrode from the electrolytic cell, rinse the electrode with distilled water, and disconnect the electrical circuit. Wash the electrode with acetone, and let it dry in air before placing it in the holder, which has been adjusted to give the best position of the spiral filament relative to the burner head and the opening in the quartz absorption tube. Move the filament into its pre-adjusted position in a lean air-acetylene flame, and record the atomic absorption signal at 196.1 nm. To a new aliquot, add the same amounts of hydrazine dihydrochloride and copper(II) solution as before, and 25-50  $\mu$ l of a standard solution of selenium(IV); repeat the deposition and atomization steps, and finally calculate the concentration of selenium according to the standard addition procedure. Extinguish the flame between the measurements to avoid overheating the burner.

## RESULTS AND DISCUSSION

### *Electrodeposition of selenium*

The electrochemical behaviour of selenium(IV) has been studied mainly at mercury electrodes [7-9]. Based on this work, various polarographic and stripping voltammetric procedures have recently been developed [10-14]. The electrochemical reactions of selenium(IV) at graphite [15, 16] and gold electrodes [17] have also been described. The electroanalytical procedures are complicated by the formation of selenides; deposited selenium may react

with the electrode material, and also with co-deposited elements. This may give rise to interfering polarographic waves and stripping peaks. The interferences can be overcome by solvent extraction [12], chemical generation of hydrogen selenide [13], and separation by ion-exchange [18].

The deposition of selenium(IV) at solid electrodes is preferably carried out from acidic solutions, at a moderately negative potential. At highly negative potentials and in alkaline solutions the deposited selenium can be further reduced to hydrogen selenide, resulting in a loss of selenium from the electrode.

In the above-mentioned electroanalytical procedures, the total current through the cell is normally small, owing to the small area of the working electrode. Consequently the generation of chlorine, which will take place at the counter electrode in chloride media, will be insignificant. However, in this work currents of the order of 1 mA were obtained, owing to the relatively large surface area of the working electrode and the simultaneous reduction of hydrogen ions. Therefore, a marked evolution of chlorine was noticed at the counter electrode in chloride media unless special precautions were taken. The reaction prevented the deposition of selenium, because chlorine oxidized selenium(IV) to selenium(VI), and thus rendered the element electrochemically inactive. A qualitative test [19] confirmed the presence of selenium(VI) in the sample solutions when the electrolysis had been carried out for some time.

There are various ways of avoiding the interference from chlorine in the deposition of selenium. Firstly, the counter electrode should be placed in a separate anode compartment. A classical H-cell with a glass frit in the middle should serve the purpose well; however, in this work the counter electrode was placed inside a glass tube with a sintered disc at the end. A disc with a low porosity was first used to prevent the chlorine from leaking into the sample solution, but a large IR drop, which the potentiostat did not fully compensate, was noted in this case. Therefore, the physical separation of the counter electrode with a high-porosity (G1) disc was combined with the use of hydrazine for preventing chlorine evolution. Hydrazine has long been used as a depolarizer in electroanalysis [20] and was found to serve the purpose well in the present work, provided that a glass sinter was also used. Experiments with only hydrazine showed a marked decrease in the selenium deposition, similar to the results obtained with the glass sinter in the absence of hydrazine.

When hydrazine dihydrochloride was used as the depolarizer a strongly acidic solution was obtained (pH 1.0). The salt prevented any pH change at the working and counter electrodes. Such changes would have been observed in the absence of a buffer, because the reactions at both electrodes involve hydrogen ions. In this work an acidic medium was preferred also because selenium(IV) is more easily reduced in such solutions [7]. The optimal amount of hydrazine dihydrochloride was found to be 0.3 g per 25 ml. A decrease in the atomic absorption signal, and thus in the amount of sel-

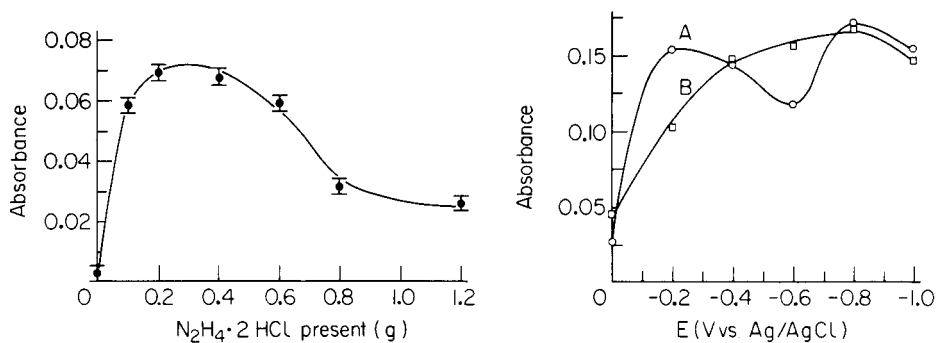


Fig. 1. Effect of concentration of hydrazine dihydrochloride (given as g/25 ml) on the amount of selenium deposited. 100 ppb selenium(IV) in 3.5% NaCl; deposition potential  $-1.0$  V vs. Ag/AgCl; deposition time 5 min.

Fig. 2. Effect of deposition potential on the amount of selenium deposited. (A) 100 ppb selenium(IV) in 3.5% NaCl with 0.3 g  $N_2H_4 \cdot 2HCl$ ; (B) as in (A) with 0.5 ppm copper(II) added.

enium deposited, was observed for both higher and lower concentrations of the hydrazine salt, as illustrated in Fig. 1. However, because the amount of chlorine generated is proportional to the electrolysis time, the optimal concentration of hydrazine will probably depend on this parameter.

The effect of deposition potential is shown in Fig. 2 (curve A). The variation in the atomic absorption signal, and thus in the amount of selenium deposited, is quite marked. Two maxima are observed, at  $-0.2$  and  $-0.8$  V respectively. The deposition of selenium is also affected by the presence of other metals. Copper is of particular concern here because it is present in a relatively high concentration in many types of samples and its deposition potential is close to that of selenium(IV). The effect of copper is also illustrated in Fig. 2 (curve B). At potentials more positive than  $-0.4$  V, a decrease in the atomic absorption signal was noticed on addition of 0.5 ppm copper, whereas at more negative potentials the presence of copper made the signals almost independent of deposition potential. The formation of copper selenide probably prevented the generation of hydrogen selenide at the more negative potentials. The actual excess of copper was not critical; no significant change in peak height was observed for concentrations of copper lower or higher than 0.5 ppm.

The addition of copper to the sample solution is recommended, to make the measurements less dependent on the deposition potential.

#### Determination of selenium

The deposited selenium was atomized in an air-acetylene flame, by using a three-slot burner head and a quartz absorption tube [1]. A sharp atomic absorption signal was obtained, as shown in Fig. 3. A shift in the baseline occurred as the spiral was moved into the flame because this

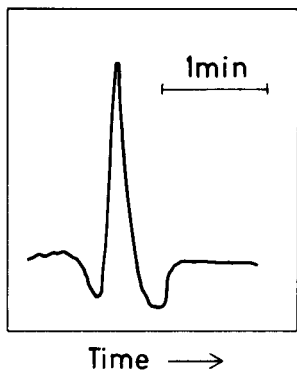


Fig. 3. Atomic absorption signal from 75 ppb selenium(IV) in 3.5% NaCl; deposition potential  $-0.8$  V; deposition time 5 min.

altered the gas flow within the absorption tube. The peak height was always measured from the lower baseline.

The height of the absorption signal was markedly influenced by the position of the spiral relative to the flame and the opening in the absorption tube. To obtain an optimal peak height the spiral should be placed as close as possible to the opening in the absorption tube.

When electrochemical preconcentration is used, there is normally no need to use background correction. However, background correction was used in the analysis for selenium because the flame gases also absorb at 196 nm.

The detection limit (signal to noise, 2:1) was 5 ppb selenium for a 5-min electrolysis. If a longer electrolysis time is used, an improved detection limit is obtained. The absolute detection limit was determined in the following way. A 25- $\mu$ l aliquot of a 1-ppm standard selenium(IV) solution (without added sodium chloride) was placed directly on the platinum spiral with a micropipette. The electrode was dried at 80°C for 5 min and the atomization was then carried out in the usual way. An absolute detection limit of 10 ng was found from this experiment. In comparison, Kerber and Fernandez [21] found a detection limit of 100 ng for selenium with the Delves cup. The poor sensitivity obtained by these authors is probably explained by the formation of nickel selenide in the cup and tube, which were both made from nickel.

The electrolysis efficiency was determined by comparing the absorption signal obtained after an electrochemical deposition with the signal obtained by the direct application of selenium(IV) to the spiral. It was found that ca. 10% of the selenium was deposited on the spiral during a 5-min electrolysis, when a 25-ml aliquot was analyzed.

For the determination of selenium the standard addition technique should be used. The standard should be added to a separate aliquot of the sample, because of the 10% depletion of the sample during the electrolysis. Before



using the standard addition technique the linearity of the calibration curve should be checked. For concentrations above 100 ppb selenium, marked curvature was noticed.

For optimal reproducibility the stirring rate and the position of the electrodes in the cell should be kept constant, and so should the position of the spiral relative to the flame and the opening in the absorption tube.

#### REFERENCES

- 1 W. Lund, Y. Thomassen and P. Døvlø, *Anal. Chim. Acta*, 93 (1977) 53.
- 2 W. Lund and B. V. Larsen, *Anal. Chim. Acta*, 70 (1974) 299.
- 3 W. Lund and B. V. Larsen, *Anal. Chim. Acta*, 72 (1974) 57.
- 4 W. Lund, B. V. Larsen and N. Gundersen, *Anal. Chim. Acta*, 81 (1976) 319.
- 5 Y. Thomassen, B. V. Larsen, F. J. Langmyhr and W. Lund, *Anal. Chim. Acta*, 83 (1976) 103.
- 6 S. Forbes, personal communication.
- 7 J. J. Lingane and L. W. Niedrach, *J. Am. Chem. Soc.*, 71 (1949) 196.
- 8 G. D. Christian, E. C. Knoblock and W. C. Purdy, *Anal. Chem.*, 35 (1963) 1128.
- 9 F. Vajda, *Acta Chim. Acad. Sci. Hung.*, 63 (1970) 257.
- 10 A. M. Shafiqul Alam, O. Vittori and M. Porthault, *Anal. Chim. Acta*, 87 (1976) 437.
- 11 C. Arlt and R. Naumann, *Fresenius Z. Anal. Chem.*, 282 (1976) 463.
- 12 M. W. Blades, J. A. Dalziel and C. M. Elson, *J. Assoc. Off. Anal. Chem.*, 59 (1976) 1234.
- 13 B. L. Dennis, J. L. Moyers and G. S. Wilson, *Anal. Chem.*, 48 (1976) 1611.
- 14 G. P. Bound and S. Forbes, *Analyst*, 103 (1978) 176.
- 15 T. A. Krapirina, E. M. Roizenblat and G. A. Kalambet, *Zavod. Lab.*, 41 (1975) 263.
- 16 E. Ya. Neiman and G. B. Ponomarenko, *J. Anal. Chem. USSR (Engl. Transl.)*, 30 (1975) 952.
- 17 R. W. Andrews and D. C. Johnson, *Anal. Chem.*, 47 (1975) 294.
- 18 R. W. Andrews and D. C. Johnson, *Anal. Chem.*, 48 (1976) 1056.
- 19 A. I. Vogel, *Macro and Semimicro Qualitative Inorganic Analysis*, 4th edn., Longmans, London, 1955, p. 586.
- 20 J. J. Lingane and S. L. Jones, *Anal. Chem.*, 23 (1951) 1798.
- 21 J. D. Kerber and F. J. Fernandez, *At. Absorpt. Newsl.*, 10 (1971) 78.

## DIRECT ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF SELENIUM IN SERUM

K. SAEED and Y. THOMASSEN\*

*Institute of Occupational Health, Gydas vei 8, Oslo 3 (Norway)*

F. J. LANGMYHR

*Department of Chemistry, University of Oslo, Oslo 3 (Norway)*

(Received 16th May 1979)

### SUMMARY

The effect of copper, iron, nickel and silver ions on the thermal stability of inorganic and metabolized forms of selenium in serum was studied with radioactive  $^{75}\text{Se}$ . Copper and iron had no stabilizing effect but in the presence of nickel or silver the temperature could be raised to 1050°C or 1250°C, respectively, without loss of selenium. On this basis an electrothermal atomic absorption spectrometric method was developed for the direct determination of selenium in human serum; selenium is stabilized with nickel during ashing. In 12 samples of sera from unexposed individuals, the concentrations ranged from 92 ppb to 140 ppb. The relative standard deviation of the method is 4%, and the detection limit is 5 ppb.

Selenium is an essential trace element which is found in minute amounts in nearly all substances. In most human organs and fluids the concentration is below 1 ppm; whole human blood normally contains 0.1–0.3 ppm, but in serum the content is somewhat lower. When administered to humans or animals, the inorganic forms of the element are readily converted to various organo-selenium compounds. In living systems selenium is found, either as low-molecular-weight compounds, e.g. dimethylselenide, or bound to proteins e.g. glutathione peroxidase. A circumstance contributing to the increasing interest in the biological role of selenium is the evidence that the element protects human beings and animals from the toxic effects of certain heavy metals.

The small amounts of selenium present in biological materials and the volatility of the element complicate its determination. Selenium is lost during conventional dry ashing, and most methods are therefore based on an oxidizing wet ashing of sample followed by tedious separation and/or concentration steps. The methods mostly employed for the determination of selenium are absorptiometry, fluorimetry, neutron activation analysis and atomic absorption spectrometry (a.a.s.).

This paper presents studies of the volatility of selenium from inorganic and metabolized forms of the element in the absence or presence of stabil-

izing metals, and a direct electrothermal a.a.s. method for the determination of the element in serum.

## EXPERIMENTAL

### *Apparatus*

A Perkin-Elmer model 300 atomic absorption spectrometer equipped with selenium electrodeless and deuterium arc lamps, an HGA-76 graphite tube furnace, an AS-1 automatic sampler and a Perkin-Elmer model 56 recorder were used. The  $\gamma$ -radiation was measured with a Packard Auto-Gamma scintillation spectrometer equipped with a Teletype recorder. Biological materials were ashed in a TracerLab LTA-505 plasma asher.

Liquids were transferred to the graphite furnace with plastic-tipped micropipettes.

### *Reagents and standard solutions*

The chemicals employed were of reagent-grade quality. The solution of sodium selenite labelled with  $^{75}\text{Se}$  (half-life 120 d) was delivered by the Radiochemical Centre, Amersham, U.K. Before use, the solution was diluted with an aqueous 5.0 mM inactive solution of sodium selenite until a suitable activity was obtained.

A 1000 ppm solution of selenium was prepared by dissolving the appropriate amount of sodium selenate decahydrate in water, adding 10 ml of concentrated nitric acid and diluting the solution to 1 l. From this solution, two diluted solutions containing 100 ppb and 200 ppb selenium and 0.5% (w/v) in nickel(II), were prepared.

Solutions of copper, iron and nickel (0.1% metal ion as nitrates) were obtained from BDH Chemicals. A 5.0% (w/v) solution of nickel(II) and 5.0 and 0.1% solutions of silver(I) were prepared by dissolving the nitrates in water.

The *in vivo* preparation of organoselenium compounds labelled with  $^{75}\text{Se}$  was achieved by injecting radioactive solutions of suitable activities intravenously into rats, and after 1 h withdrawing about 10 ml of blood from the vena cava.

### *Determination of selenium in serum (standard addition procedure)*

Of the serum sample to be analyzed, 0.2-ml portions were transferred to 6 of the cups on the automatic sampler. Into two cups 0.2 ml of the 0.5% nickel solution were added, into the next two cups 0.2 ml of the combined 100 ppb selenium and 0.5% nickel solution were added, and into the remaining two cups 0.2 ml of the 200 ppb selenium/0.5% nickel solution were transferred. With the use of the automatic sampler 20- $\mu\text{l}$  portions were pipetted into the furnace, and selenium was determined by electrothermal a.a.s. by using the following program: heating by ramp rate 2 (50 s) to 150°C, drying at 150°C for 90 s, heating by ramp rate 2 (70 s) to 1050°C, heating at 1050°C

for 30 s, and finally, with the purging gas at miniflow, atomization for 3 s at maximum power and for 5 s at 2200°C. Two aliquots were atomized from each cup.

## RESULTS

### *Studies of the volatility of selenium*

Several new, pyrolytically-coated graphite tubes were cleaned by heating; into each tube were injected 20  $\mu\text{l}$  of whole blood labelled in vivo with  $^{75}\text{Se}$ , and 20  $\mu\text{l}$  of a 0.1% metal ion solution. The mixtures were dried by ramp heating to 150°C, and were kept at this temperature for 40 s. The residues were then ashed for 30 s at different preselected temperatures and the activities were measured. A series of samples without added metal ion solution was also dried and ashed in the same way.

Figure 1 shows the activities of the residues after ashing at different temperatures. It is clear that the addition of copper and iron had no stabilizing effect, whereas in the presence of nickel and silver ions, the ashing temperatures could be raised to 1050°C and 1250°C, respectively, without losing selenium. A series of similar measurements was made to find the best ratio of nickel or silver to selenium. In order to stabilize the metabolized selenium present in 20- $\mu\text{l}$  samples of whole rat blood (ca.  $10^{-8}$  g of selenium), it was necessary to add 20  $\mu\text{l}$  of a 0.5% nickel(II) solution (0.1 mg of Ni) or 20  $\mu\text{l}$  of a 0.1% silver solution (20  $\mu\text{g}$  of Ag).

The above experiments were repeated with unmetabolized radioactive selenium. Portions of whole rat blood and a sodium selenite solution of suitable activity were mixed; 20  $\mu\text{l}$  of this mixture and 20  $\mu\text{l}$  of 0.1% metal solution were transferred to a graphite tube, the further procedure being as described above. The measurements confirmed the results obtained with metabolized selenium, and demonstrated that the inorganic forms of the

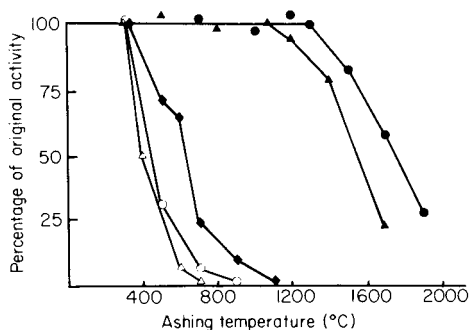


Fig. 1. Selenium radioactivity (as % of original activity) as a function of ashing temperature for samples of whole rat blood labelled with  $^{75}\text{Se}$ , with and without added metals: (●) silver; (▲) nickel; (◆) copper; (○) iron; (△) no metal added.

element are also stabilized by nickel or silver ions. In order to study the volatility of selenium during ashing in a plasma asher, 50  $\mu\text{l}$  of whole blood labelled in vivo with  $^{75}\text{Se}$  and 50  $\mu\text{l}$  of the 0.1% silver solution were transferred to the scoop of the asher, and the mixture was dried in the asher and ashed at a temperature assumed to be about 150°C. The same volume of blood, but without added silver solution, was added to another scoop and treated in the same way. After 4 h of ashing, the activity was measured. No loss of selenium was detected in the sample to which silver had been added, whereas without added silver the loss of selenium was 6%.

These experiments showed that nickel and silver have strong stabilizing effects on selenium, and that, in the presence of these metals, whole blood and serum, as well as added inorganic selenium, can be heated to temperatures up to 1050°C (with nickel) or 1250°C (with silver) without loss of selenium. The high ashing temperatures thus possible have the additional advantage of volatilizing substantial amounts of interfering salts such as sodium chloride, before selenium is atomized.

It is interesting to note that the iron present in whole blood is incapable of stabilizing selenium. As to the choice between nickel and silver as the stabilizing agent, the latter metal allows the use of a higher ashing temperature but has the disadvantage of forming a precipitate with the halides present in whole blood and serum. Therefore, in the present work nickel was preferred as the stabilizing metal.

#### *Atomic absorption measurements*

As is apparent from previous papers [1], the electrothermal a.a.s. determination of selenium by measurement at 196.0 nm with the use of deuterium arc background correction is subject to serious spectral interference from iron. The high concentrations of iron in whole blood (about 500 ppm) made it impossible to obtain reliable data for selenium. However, in sera the content of iron is very much less (about 1 ppm) and the interference of iron is negligible. In order to avoid the interference of iron, it has been recommended [1] that measurements be made at the less sensitive 204.0 nm selenium line. In the present study this approach proved to be unsuccessful. When samples of whole blood or serum were ashed at 1050°C for 30 s in the absence of a stabilizing metal (this operation removes all selenium), then atomized and the absorbances measured (with the use of the background corrector) at 204.0 nm, large positive signals were registered although no selenium was present. Thus, at 204.0 nm, a serious unexplained interference occurred, and 196.0 nm was used in all subsequent experiments.

Other preliminary measurements demonstrated that the signals from the metabolized and inorganic forms of selenium coincided and were additive.

The calibration curves obtained by using the recommended procedure were linear upto 100 ppb selenium. Determinations were made with the use of the method of standard addition, and were based on measuring peak heights.

TABLE 1

Determination of selenium in human serum by the proposed method and by neutron activation analysis

Sample	Selenium (ppb)		Sample	Selenium (ppb)	
	Proposed method	N.a.a.		Proposed method	N.a.a.
KS-1	108	108	211	115	114
KS-2	92	104	212	114	111
KS-3	104	97	219	140	121
KS-4	100	126	220	101	88
209	121	121	221	129	122
210	138	142	447	105	—

The technique proposed was applied to the analysis of 12 samples of human serum from individuals unexposed to selenium. Most of these samples were also analyzed by neutron activation (n.a.a.). The results are listed in Table 1. The relative standard deviation of the present method was calculated to be 4%, and the detection limit was 5 ppb. The neutron activation method had a relative standard deviation of 10%. The agreement between the two methods is satisfactory, the differences not being caused by any systematic error.

The a.a.s. data in Table 1 were obtained by a standard addition technique. When the proposed method is to be used in routine analysis, it is recommended that in order to save time, one sample should be selected as the standard, its selenium content be established very carefully, and the other samples be measured against this standard.

The proposed method has the advantages of being direct, simple and rapid; the accuracy and precision are satisfactory, and only small sample volumes are required. The main disadvantage is that the method is applicable to serum but not to whole blood. Unfortunately, the authors did not have at their disposal an instrument based on the Zeeman principle for background correction. Recent studies [2] have demonstrated that the interference of iron on the measurement of selenium at the 196.0 nm line can be avoided by Zeeman a.a.s. It thus seems possible to apply the proposed technique to the determination of selenium in whole blood.

#### REFERENCES

- 1 See, e.g., D. C. Manning, *At. Absorpt. Newsl.*, 17 (1978) 107.
- 2 F. J. Fernandez, S. M. Myers and W. Slavin, Perkin-Elmer Corp., Norwalk, CT, U.S.A., private communication.

## A HEATED-ELECTRODE DISCHARGE LAMP FOR TRACE ANALYSIS BY ATOMIC EMISSION SPECTROSCOPY

KUNYUKI KITAGAWA\* and RYOICHI NARITA

*Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya (Japan)*

TSUGIO TAKEUCHI

*School of Materials Science, Toyohashi University of Technology, Hibarigaoka, Tenpaku-cho, Toyohashi, Aichi (Japan)*

(Received 16th May 1979)

### SUMMARY

Graphite electrodes heated by d.c. power alone, or a combination of d.c. and r.f. power, are investigated for generating atomic emission from cadmium with specially designed discharge lamps. Best results are achieved if the plasma produced by both power sources can be concentrated within a cylindrical electrode.

Techniques which may be applied to the multi-element analysis of samples of small volume include d.c. glow discharge [1], atomic emission spectrometry with electrothermal atomizers [2], atomic fluorescence spectrometry with electrothermal atomizers and continuum light sources [3], and the inductively coupled plasma fitted with an electrothermal atomizer [4]. Although the d.c. glow discharge lamp is a versatile emission source, it has been applied chiefly to measurements at high concentrations, partly because of the low atomization rate by sputtering. In addition, the low excitation temperature (up to 4,000 K) leads to inadequate sensitivity for small sample sizes.

In this study, in order to overcome these problems, a discharge lamp has been constructed which incorporates a heated graphite electrode. The electrode serves as an atomizer, is heated by dissipation of the supplied power and is concurrently located in a discharge plasma. Aspects of the power supply are discussed. The technique is applied to the determination of trace amounts of cadmium.

### EXPERIMENTAL

#### *Instrumentation*

Figure 1 is a schematic diagram of the experimental arrangement. Each of the components is described below.

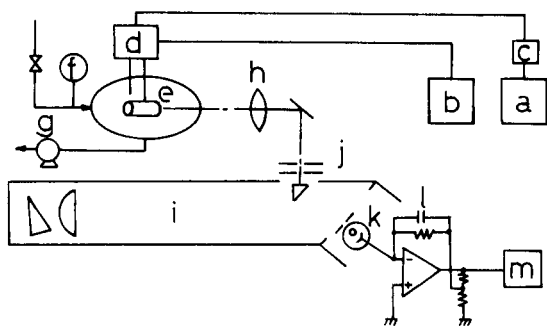


Fig. 1. Schematic diagram of the experimental arrangement: (a) r.f. power supply; (b) d.c. power supply; (c) r.f. power meter; (d) coupling circuit; (e) discharge lamp; (f) Pirani gauge; (g) rotary pump; (h) lens; (i) monochromator; (j) iris diaphragm; (k) photomultiplier tube; (l) pre-amplifier; (m) strip chart recorder.

**Discharge lamps.** Two types of discharge lamp were designed for this work (Fig. 2). Lamp A was used almost exclusively. The anode is located at right angles to the cathode. Lamp B was designed to stabilize the r.f. discharge. The anode and cathode are placed face to face co-axially. Figure 3 shows in detail the two cathode shapes used. The cathode functions simultaneously as an atomizer and as an electrode for the discharge. One of the cathodes is a hollow graphite tube; the other is a semicylindrical graphite tube. Both were made of graphite tube, (2.4 mm o.d., 1.5 mm i.d.) carved from graphite rod of high purity used for spark/arc spectroscopy (Hitachi Kasei). The hollow graphite tube has an opening of 1 mm diameter for sample introduction on the lateral face.

In lamp A, the graphite is fitted to a supporting electrode of graphite rod (5-mm diameter). The electrode is covered with a quartz tube to shield it from the discharge, so that the discharge is concentrated at the atomizing graphite cathode. In lamp B, the atomizing graphite cathode is fitted to a tungsten electrode through a graphite connector which thermally insulates the glass plug from the cathode. The graphite connector is covered with a quartz tube. The anode is made of tungsten rod (2 mm diameter). Both lamps have inlet and outlet capillary tubes of 0.5-mm diameter for stabilizing the inner pressure of the lamp.

**D.c. and r.f. power supplies.** The d.c. power supply used is a current regulator (Hitachi) for the old type of hollow-cathode lamp, which could provide currents up to 100 mA.

Figure 4 shows the circuit diagram of the r.f. power supply and matching circuit. This supplies the discharge lamp with an effective power of 75 W when the anode voltage of the valve is 1,300 V and the frequency is 21 MHz. The output power is transmitted to the discharge lamp through a co-axial cable of 50 ohms impedance. The matching circuit includes a function to



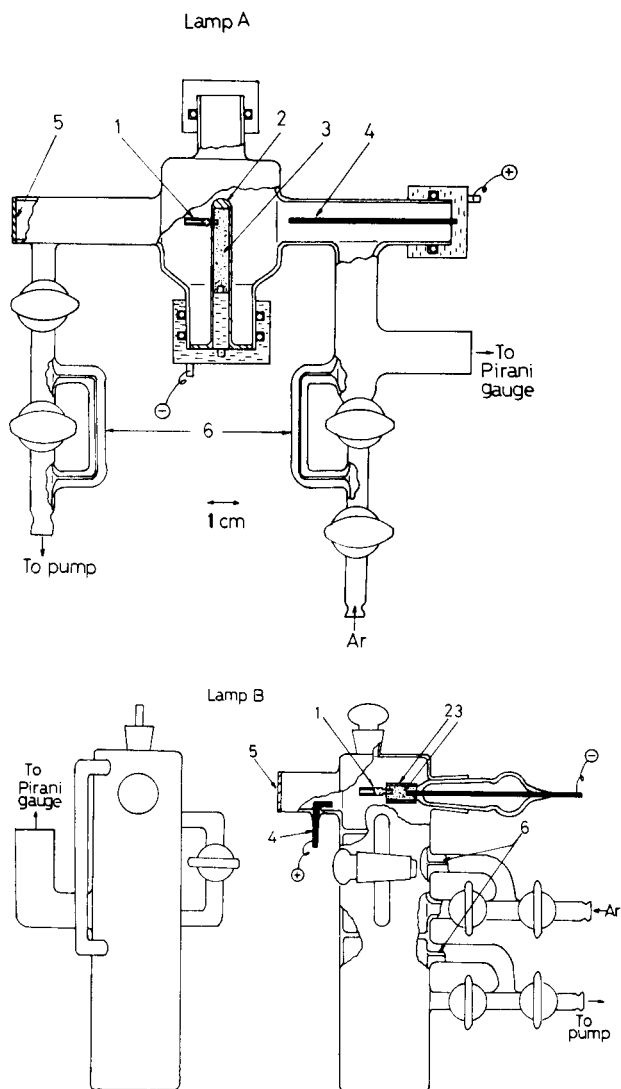


Fig. 2. Two types of discharge lamp: (1) heated graphite cathode; (2) quartz tube; (3) graphite rod; (4) tungsten anode; (5) quartz window; (6) capillary tube.

superimpose d.c. power on r.f. power. An r.f. power meter is connected between the r.f. power supply and the matching circuit for monitoring the reflected power or the standing wave ratio.

*Optics.* A Littrow quartz prism spectrograph (Shimadzu QL-170) of focal length 170 cm was employed. A photomultiplier tube (HTV R306) is located on the focal plane where the photographic plate is usually fitted. The photomultiplier tube is mounted on a scanning block which moves on a screw bar rotated by a synchronous motor, in order to adjust the wavelength.

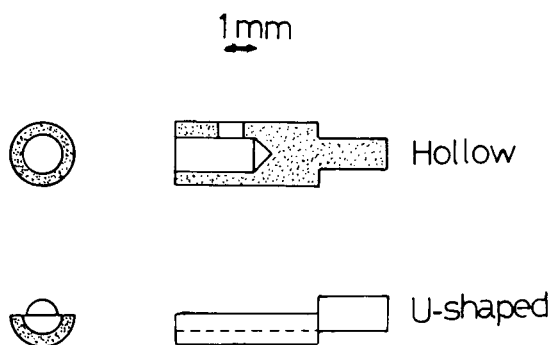


Fig. 3. Two types of graphite cathode.

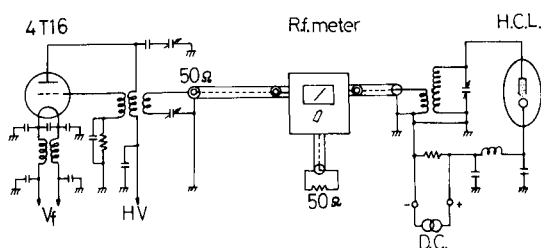


Fig. 4. Circuit diagram of the r.f. power supply and coupling circuit.

An exit slit (0.1 mm) is placed 2 mm in front of the photomultiplier tube, by attaching it to the block. The position of the slit is precisely adjusted to coincide with the focal plane. These elements are assembled in a cabinet. The width of the entrance slit is 0.1 mm. In order to reduce the black body radiation from the heated cathode and the continuum emission from the discharge, an iris of 1-mm aperture is located in front of the entrance slit. The image of the heated cathode is focused on the entrance slit with a magnifying ratio of unity. The analytical line used was Cd I (228.8 nm).

*Photocurrent preamplifier.* A very simple circuit was assembled for preamplifying the resulting photocurrent. An integrating circuit (Intersil LF 356) is incorporated into the circuit, which has a very high input impedance and low enough noise to connect to the photomultiplier tube. The preamplifier is located in the cabinet together with the dry battery power supply.

#### *Discharge gas*

Argon (normal and of high purity, 99.999%) is used for the discharge gas. A rotary pump removes the gas at a pressure of 4.5–16 torr. The pressure in the discharge lamp is measured by a Pirani gauge (Okano). The sensor is fitted to a T-branch of the discharge lamp. The flow rate of argon was 150 ml min<sup>-1</sup> at STP.

### Reagents and procedure

A stock solution of cadmium was prepared by dissolving a suitable amount of cadmium metal in the minimum of nitric acid. Standard solutions were prepared just before use by diluting the stock solution with distilled and deionized water, adjusting the acidity to 0.1 M in nitric acid. Sample solution was transferred to the atomizing graphite cathode by a microsyringe, dried by evacuating for 3 min and atomized by discharge. The temperature of the heated graphite cathode was measured by an optical pyrometer.

## RESULTS AND DISCUSSION

### D.c. glow discharge

Several basic characteristics were estimated for d.c. glow discharge with the hollow graphite cathode in lamp A. Figure 5 shows the dependence of the voltage on the current and pressure. The internal electrical resistance,  $\partial V/\partial I$ , increases as the pressure decreases. This suggests that the discharge lamp operates as an abnormal glow discharge under the given conditions. In the region beyond the broken line, the graphite tube cathode was heated to a visible dark red (ca. 800°C). Figure 6 shows the relation between the outer surface temperature of the hollow graphite cathode, the power and the internal pressure. Except at 16 torr, similar temperatures were attained at any internal pressure, for any given input power. This indicates that the temperature of the heated graphite cathode is defined almost entirely by the

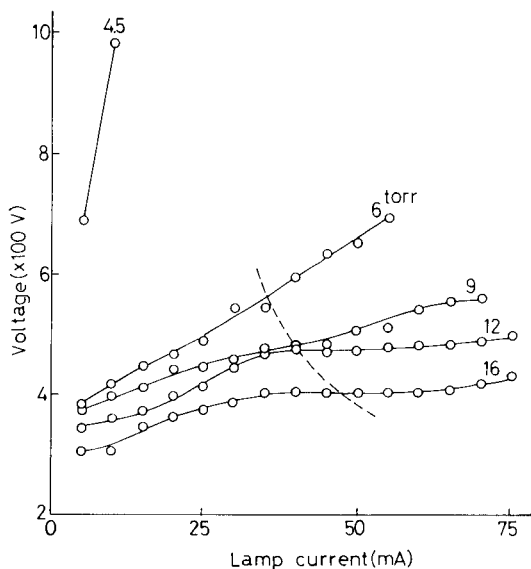


Fig. 5. Relation between the discharge current and voltage for lamp A at the pressures (torr) indicated on the curves.

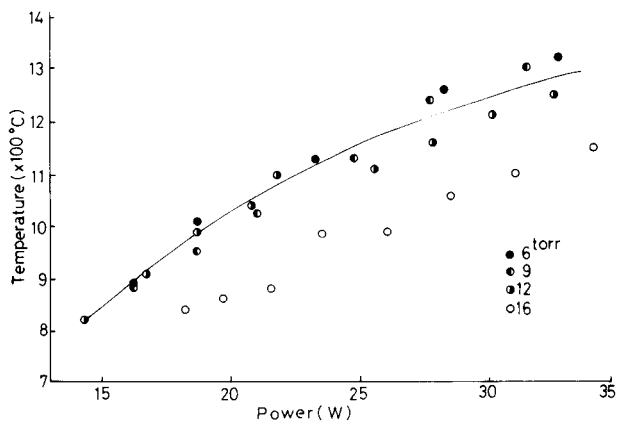


Fig. 6. Relation between the surface temperature of the heated graphite cathode and the power at different pressures.

input power. It is well known that the differential potential in the d.c. glow is largest near the cathode. In this event, the power supplied seems to be converted to Joule heat around the cathode. At 16 torr, the temperature is lower than at the other pressures, partly because the increased loss of heat by thermal conduction through argon gas cannot be ignored.

Figure 7A shows the dependence of the relative emission intensity of the Cd I (228.8 nm) line on the distance between the anode and cathode. The temperature of the cathode surface was controlled at  $1,100^{\circ}\text{C}$ , at 9 torr. The

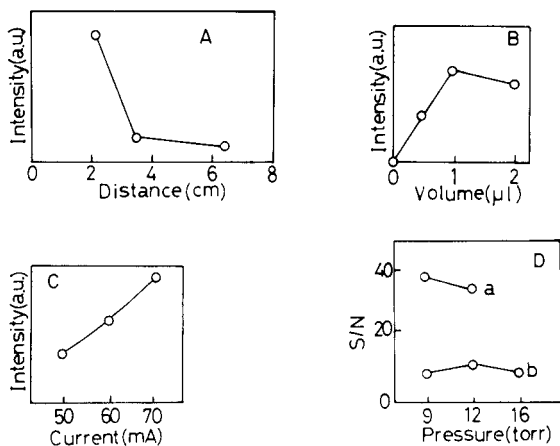


Fig. 7. (A). Dependence of the relative intensity of cadmium emission at 228.8 nm on the distance between the electrodes;  $1\ \mu\text{l}$  of 0.5 ppm Cd solution; 9 torr;  $1,100^{\circ}\text{C}$ . (B) Dependence of the relative intensity on the sample volume taken. (C) Dependence of the relative intensity on the d.c. current. (D) Dependence of the signal/noise ratio on the pressure and flow rate of argon: (a)  $110\ \text{ml}\ \text{min}^{-1}$ ; (b)  $50\ \text{ml}\ \text{min}^{-1}$ .

relative intensity depends inversely on the distance. The empirical equation  $mPd = \text{constant}$  has been proposed for the glow discharge [5]; here  $m$  is the amount of cathode material sputtered by the discharge,  $P$  the pressure and  $d$  the distance between the anode and cathode. If the pressure is constant,  $m \propto d^{-1}$ . Although, strictly, the variation of the excitation temperature and degree of ionization should be taken into account, it has been suggested that the sputtering rate is the predominant factor affecting the intensity of emission from the glow discharge. In this sense, the behaviour of the glow discharge in this experiment agrees with the equation. This was further proved by the fact that the loss of the heated graphite cathode increased as the cathode approached the anode.

Figure 7B shows the dependence of the relative intensity on the sample volume taken. The intensity for a sample volume of  $2 \mu\text{l}$  is reduced; because of the small volume of the hollow cathode, the larger sample solution tends to spread towards the mouth of the tube, so that the residence time of the atoms within the tube becomes shorter and the emission intensity is reduced. In order to overcome this, the volume of the hollow might be increased, but the power introduced for heating the cathode would then also have to be increased, and this would intensify the loss of the graphite cathode. For this reason, a larger graphite cathode cannot be employed if only d.c. power is available for heating. Despite this limitation, the heated graphite cathode seems to be useful in that its single-ended configuration gives a very uniform distribution of temperature. Any temperature gradient at the terminal position could not be distinguished by eye.

Figure 7C shows the relation between the relative emission intensity and the current. As the current increases, the relative intensity increases. This is attributable to the increase in the sputtering rate and the temperature of the graphite cathode.

Figure 7D shows the dependence of the signal-to-noise ratio ( $S/N$ ) on the pressure and the flow rate of argon. This indicates that  $S/N$  is not significantly affected by the pressure but is affected by the flow rate of argon; this happens partly because the background emission increases as the flow rate of argon decreases, and partly because the fluctuation in the background emission intensity increases. It is not clear what is responsible for the background increase when the flow rate is decreased; presumably, the yield of nitrogen oxide, which is responsible for the background emission (see below) changes with the flow rate.

The detection limit ( $S/N = 2$ ) is  $10^{-11}$  g for cadmium.

### *R. f. discharge*

The d.c. glow discharge with the heated hollow graphite cathode gave some desirable improvement in sensitivity. However, a problem is the loss of graphite from the cathode. In order to overcome this, another way of enhancing the excitation temperature was examined. For this purpose, an r.f. discharge was combined with the technique stated above. Owing to the

high-frequency alternating electromagnetic field, the ions in the plasma are confined within a limited region. Since the number of collisions between species is increased, the excitation temperature should be raised.

In preliminary experiments, the mode of coupling between the d.c. and r.f. power was investigated. Figure 8 shows the different coupling configurations. In configuration 1, the r.f. power is inductively coupled, in 2 semi-inductively coupled, and in 3 and 4 capacitively coupled. It was found that in the first two configurations, the r.f. plasma was repelled by the d.c. glow plasma near the heated graphite cathode. There existed a dark region, ca. 3 mm thick between the red r.f. and blue-white d.c. plasmas, and consequently the r.f. power did not contribute to increase in the cadmium emission intensity. In the latter two configurations, the plasmas appeared to unite. Because a common earth can be taken, configuration 4 is recommended.

Figure 9 shows typical traces of the cadmium emission peak obtained with lamp A, incorporating the hollow or semicylindrical graphite cathode. It was noticed that with the hollow graphite cathode, the atomic emission intensity remains constant while the background increases by a factor of 3.5 when the r.f. power is superimposed. As stated above, in configuration 4, the r.f. plasma appeared to be in contact with the d.c. glow. In practice, however, the result suggests that the r.f. plasma cannot progress into the hollow but contacts a sheath of the d.c. glow around the cathode. This contact is reflected in the increase in the background emission intensity because the r.f. plasma excites impurity molecules. Because of the quasi-closed configuration of the hollow graphite cathode, the r.f. power is shielded from the atomic cloud in the hollow.

In contrast, with the semicylindrical graphite cathode, the atomic emission intensity is enhanced concurrently with the background emission intensity when the r.f. power is applied. This suggests that this shape of cathode is not shielded from the r.f. plasma, because of its open configuration, and that the r.f. and d.c. plasmas amalgamate in the region where the atomic cloud is present. Nevertheless, the atomic emission intensity obtainable with the semicylindrical design is lower than that obtainable with the hollow cathode under the same conditions of operation. This happens partly because the semicylindrical cathode does not have the effect of imprisoning the atomic cloud, so that the residence time in the region measured is shortened.

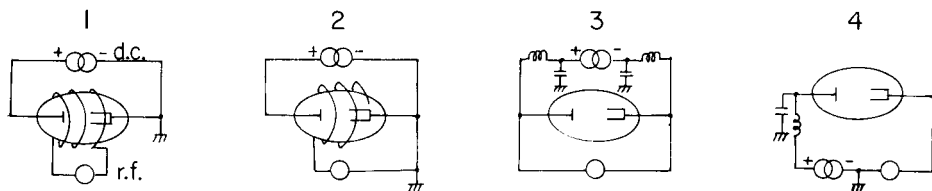


Fig. 8. Various coupling configurations between the r.f. and d.c. powers.

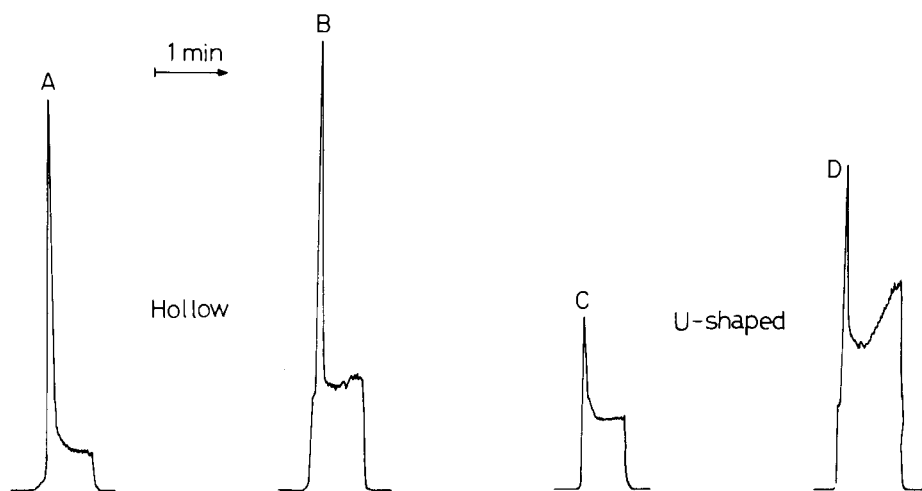


Fig. 9. Typical emission peaks for the two types of heated graphite cathode incorporated into lamp A. Sample, 1  $\mu$ l of 0.8 ppm Cd; pressure, 9 torr. Curves A and C, 80 mA d.c.; curves B and D, 80 mA d.c., 39 W r.f.

#### *Concentration of r.f. plasma in the hollow cathode*

The results described above were obtained with the use of lamp A. The hollow cathode rejected the r.f. plasma and even the use of the semi-cylindrical cathode did not give an overall increase in the atomic emission intensity. In order to overcome the former problem, an attempt was made to concentrate the r.f. power in the hollow cathode. In lamp A, part of the r.f. power is lost between the anode and the supporting electrode. An insulator (a quartz tube) is not useful for isolating the supporting electrode from the r.f. power; it simply results in the r.f. plasma covering the quartz tube. In order to avoid this, lamp B was designed by placing the cathode opposite the anode.

Figure 10 shows typical traces of the emission peak for different modes of power supply with lamp B; the smallest peak from the d.c. glow discharge is the same as that shown in Fig. 9. Thus the effect of the r.f. power is surprisingly pronounced in this type of discharge lamp. The shielding effect seems to be overcome by the converging r.f. power. It is clear from Fig. 10 that changes in the direct current scarcely affect the emission intensity; this was confirmed by applying only the r.f. power to the discharge lamp. The hollow graphite cathode is heated to a temperature somewhat lower than that attained with the d.c. and r.f. power, where part of the r.f. power is converted into heat. However, the atomic emission intensity is similar to those obtained by the other power supplies. Because of the absence of the d.c. glow plasma, the r.f. plasma was observed to enter the hollow. Thus, the effect of the r.f. power on the atomic cloud is increased and the excitation temperature is raised. Probably, this compensates for the lower temperature

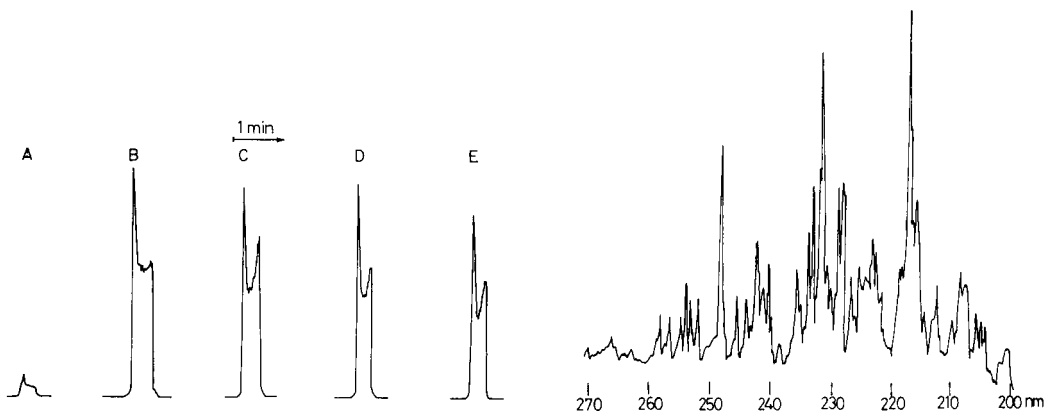


Fig. 10. Typical emission peaks for lamp B. Sample,  $1 \mu\text{l}$  of 0.5 ppm Cd; pressure, 9 torr. Curve A, 60 mA d.c.; curves B–E, 70 W r.f. with 60, 40, 20 and 0 mA d.c., respectively.

Fig. 11. Spectrum of the background emission.

of the cathode. Thus the hollow cathode can be heated by the r.f. power alone.

#### *Background emission*

There remains the problem of the background emission, which limits  $S/N$  and therefore the detection limit. Figure 11 shows the spectrum of the background emission in the u.v. region. When the graphite cathode was replaced by a copper cathode of the same dimensions, the resulting spectrum was the same, except that copper lines were also present. Consequently, the background emission is attributable to the emission from molecules present in the surrounding gas. Analysis of the spectrum indicates that it consists chiefly of the  $\gamma$ -band of NO with a trace of a CO band. These species might be produced by reactions in the plasma from nitrogen, oxygen and  $\text{CO}_2$  impurities. When 99.999% argon was used for the plasma gas, the background emission was five times less intense. The background emission was found in the positive column around the anode, thus a configuration of the discharge lamp should be designed so as to remove the positive column from the measurement region.

#### REFERENCES

- 1 C. G. Bruhn and W. W. Harrison, *Anal. Chem.*, 50 (1978) 16.
- 2 H. Kawaguchi and B. L. Vallee, *Anal. Chem.*, 47 (1975) 1029.
- 3 D. R. Demers, *Appl. Spectrosc.*, 22 (1968) 797.
- 4 A. M. Gunn, D. L. Millard and G. F. Kirkbright, *Analyst*, 103 (1978) 1066.
- 5 G. Grancis, *Handbuch der Physik*, Vol. 22, Springer, Berlin, 1956.



## DIRECT SAMPLING OF ION-EXCHANGER SUSPENSIONS FOR ATOMIC ABSORPTION SPECTROMETRY WITH ELECTROTHERMAL ATOMIZATION\*

ZDENĚK SLOVÁK

*Research Institute of Pure Chemicals, Lachema, CS-621 33 Brno (Czechoslovakia)*

(Received 23rd February 1979)

### SUMMARY

Suspensions of chelating ion-exchange resins with sorbed elements can be injected directly into a Massmann furnace; the reproducibility is similar to that achieved in sampling of solutions. This procedure offers the possibility of preparing standards and samples in the same matrix and so avoiding the usual standardization problems. The technique is discussed in detail for the determination of 1–50 ng of mercury bound on a resin with thiol groups. Methods for the determination of cobalt, nickel and molybdenum (1–16 ng) after sorption on glycolmethacrylate gels with bound 8-hydroxyquinoline are also described.

Most papers devoted to the problems of the sampling of powders for atomic absorption spectrometry (a.a.s) with electrothermal atomization deal with inorganic samples. In addition to numerous procedures with special sampling devices for weighing powder samples (e.g., the solid sampling spoon from Perkin-Elmer), a novel non-weighing sampling system for slurries of rocks has also been described [1]. The volumetric sampling of powders in suspensions stabilized with thixotropic thickening agents makes the analysis faster and simpler than traditional weighing. However, the main disadvantages of the direct a.a.s. analysis of solid inorganic samples in comparison to the dispensing of solutions have not been overcome. These are: problems with reproducibility because of inadequate homogeneity of the sample and because of the possible presence of various chemical compounds of the analyte in unknown matrices; and difficulties with calibration because standards identical with the sample cannot be prepared. These difficulties have not been solved by any previous sampling technique for inorganic powders. However, they are not important, if organic ion-exchangers, especially chelating exchangers, are sampled. The main features of such a technique are that the analyte is bound in the same way to the organic macromolecular matrix, irrespective of its original ambience, and that the preparation of identical calibration standards becomes simple.

---

\*Presented in part at the XXth C.S.I. 7. I.C.A.S., Prague, 1977.

For the present study of the method of direct sampling of chelating resins, hydrophilic glycolmethacrylate gels with chemically bound 8-hydroxyquinoline (Spheron-Oxine) and thiol groups (Spheron-Thiol) were used. Their properties have been described elsewhere [2-4, 6]. Under the reaction conditions used, the sorption of all the elements determined was essentially 100%.

## EXPERIMENTAL

### *Materials and equipment*

The resins used were Spheron-Oxine 1000, 20-40  $\mu\text{m}$ , and Spheron-Thiol 1000, 40-63  $\mu\text{m}$  (Lachema Brno). Both resins are macroporous, semi-rigid, hydrophilic glycolmethacrylate gels with pore diameters up to fractions of a  $\mu\text{m}$  and side chains with chemically bound 8-hydroxyquinoline or thiol groups.

The atomic absorption spectrometer was a Perkin-Elmer 420 with model 56 recorder, and HGA-74 graphite furnace. Standard graphite tubes were used as well as graphite tubes coated with pyrolytic carbon as described by Manning et al. [5].

### *Procedures*

The operating parameters of the spectrometer for all measurements are summarized in Table 1. A 20- $\mu\text{l}$  Eppendorf pipette was used for sampling of water solutions.

*Development of the sampling method (Procedure 1).* Microlitre volumes of standards were placed on the surface of a polytetrafluorethylene (PTFE) foil and known amounts of resin were added, as portions of an aqueous suspension or as weighed powder. After mixing with the pipette tip, the whole drop of suspension was applied from an Eppendorf pipette to the tube, in order to measure the dependence of the signal on the quantity of the resin sampled (Table 2) and on the suspension volume (Table 3). The latter was achieved by repeated transfer and drying of 50- $\mu\text{l}$  aliquots until all the sample had been added to the tube.

TABLE 1

Operating parameters for a.a.s. with appropriate hollow cathode lamps  
(Purge gas argon, mini-flow.)

Element	Co	Hg	Mo	Ni
Wavelength (nm)	240.7	253.6	313.3	232.0
Slit setting (nm)	0.2	0.7	0.7	0.2
Background correction	optional	yes	no	optional
Dry	100°C, 30 s	100°C, 30 s	100°C, 30 s	100°C, 30 s
Temp. ramp (ashing)	125°C min <sup>-1</sup>	no	125°C min <sup>-1</sup>	125°C min <sup>-1</sup>
Char	1000°C, 10 s	no	500°C, 10 s	1000°C, 10 s
Atomize	2600°C, 8 s	1000°C, 8 s	2700°C, 20 s	2600°C, 8 s

TABLE 2

Sampling of slurries from a PTFE surface<sup>a</sup>  
(Procedure 1, 20- $\mu$ l suspension of Spheron-Thiol + 20  $\mu$ l of 1  $\mu$ g Hg ml<sup>-1</sup> solution.)

ng Hg taken	Resin (mg)	n	Abs.	S.d.	C.v. (%)
0	1	3	0.0043	0.0018	
20	1	5	0.2518	0.0065	2.6
0	0.5	3	0.0047	0.0018	
20	0.5	5	0.2568	0.0090	3.5
0	1	6	0.6398 <sup>b</sup>	0.0220	3.4

<sup>a</sup>n = number of determinations; Abs. = maximum absorbance; S.d. = standard deviation; C.v. = coefficient of variation. <sup>b</sup>Without background correction.

TABLE 3

Dependence of absorbance on the suspension volume sampled  
(Procedure 1, 1 mg of Spheron-Thiol in 20  $\mu$ l + sample containing 20 ng Hg, taken as repeated 50- $\mu$ l aliquots.)

Sample vol. ( $\mu$ l)	ppm Hg in sample	n	C.v. (%)	Hg recovery (%)
20	1.0	5	5.3	100
100	0.2	5	3.4	98
200	0.1	4	9.8	90

*Calibration and reproducibility testing (Procedure 2).* Suspensions with 20 mg of resin in 1 ml of 0.04 M acetate buffer (pH 5) or hydrochloric acid containing known amounts of standards were shaken for 2 min: 10, 20 or 50- $\mu$ l portions were immediately sampled by pipette and placed in the graphite furnace. A typical calibration curve for mercury is shown in Fig. 1.

*Analysis after sorption and separation of the resin (Procedure 3).* The optimal amount of the ion-exchanger to be used (in mg) equals the volume of sample solution (in ml), when the sorption capacity of the applied resin is adequate [4]. Such a ratio was used. After shaking for 1 h, or mixing and sedimentation, with pH 5.0, 0.04 M acetate buffer (for Co, Ni and Mo) or water (for Hg) the clear solution was decanted and the suspension centrifuged. After washing with redistilled water, the slurry was diluted with water, so that 50 mg of resin was suspended in 1 ml; 10–50- $\mu$ l portions of this continuously shaken or mixed suspension were sampled and placed in the graphite tube by means of an Eppendorf pipette as described above.

It is also possible to carry out the sorption from a small volume (e.g., 1 ml) with 1–2 mg of resin by shaking for 1 h in a 1-ml reaction vessel. After centrifuging and washing the whole quantity of resin can be transferred to the tube as a suspension in approx. 30  $\mu$ l of water by means of a 50- $\mu$ l pipette.

## RESULTS AND DISCUSSION

The results in Table 2 demonstrate the possibility of sampling mg amounts of chelating resins in suspensions when the whole quantity used is applied at once, so that the homogeneity of the suspension is of no importance. The results are practically independent of the volume of suspension sampled, since there is no diffusion of the analyte into the graphite walls. Therefore it is also possible to make repetitive sampling of diluted suspensions after drying the separate portions in the furnace (Table 3). The sampling of slurries from a PTFE foil serves as a model for the analysis of separated small amounts of exchangers after sorption.

Checks on the reproducibility of the direct sampling of small amounts of metals bound to Spheron-Thiol were made for the determination of mercury by Procedure 2. The results (Table 4) prove the assumed homogeneous distribution of the metal sorbed by the resin and the homogeneity of the suspension. The reproducibility of sampling is similar to that usually obtained by a.a.s. with electrothermal atomization and manual sampling of solutions. The reproducibility of the determinations of other metals (Mo, Co, Ni) is the same or better than the determination of mercury, because the latter is complicated by the low atomization temperature required. The atomization of mercury occurs at the same time as the thermal decomposition of the resin. The Perkin-Elmer 420 spectrometer compensates well for the large non-selective absorbance (Table 2). The high reproducibility again demonstrates the homogeneity of the resin samples used and the repeatability of the programmed thermal conditions in the graphite tube. The lower results for mercury after sorption from 2 M hydrochloric acid

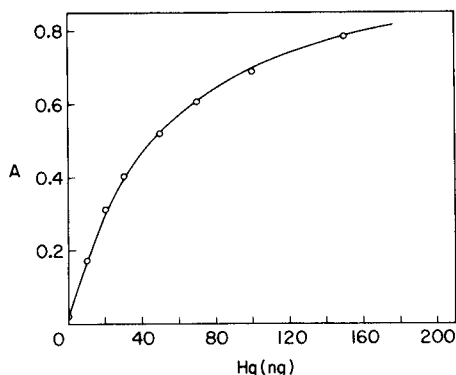


Fig. 1. Calibration curve for mercury. Procedure 2, suspensions in water.

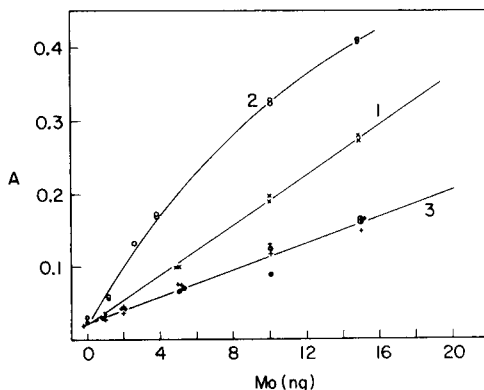


Fig. 2. Calibration graphs for molybdenum. (1) Standard tube, aqueous solution; (2) coated tube, aqueous solution; (3) standard and coated tubes, sampling of 1 mg of Spheron-Oxine in suspensions, Procedures 2 and 3, after sorption from 0.04 M acetate buffer (pH 5).

TABLE 4

Reproducibility of repetitive sampling of Spheron-Thiol  
(Procedure 2, peak-height measurements, 20 ng Hg, 50- $\mu$ l aliquots.)

Sorption medium	n	'Digital'			Recorder		
		Abs.	S.d.	C.v. (%)	Abs.	S.d.	C.v. (%)
Water	7	0.311	0.0055	1.8	0.279	0.007	2.2
2M HCl	7	0.109	0.006	5.2	0.099	0.006	6.4

(Table 4) are due to the formation of volatile  $\text{HgCl}_2$  during the drying step in the furnace. These results demonstrate the need for thorough washing of the slurry before portions are taken for analysis. Other experiments showed that the sorption of mercury on Spheron-Thiol is 100% even from the 2 M acid [6]. The shape and height of the atomization peaks of mercury obtained with Spheron-Thiol were the same for standard and pyrolytically coated tubes.

The atomization of other less volatile metals with atomization temperatures higher than the decomposition of the matrix is more interesting. Molybdenum supposedly reacts with residual carbon during the thermal decomposition of Spheron-Oxine forming its carbide, so that the determination of molybdenum in suspensions with this resin is less sensitive than in aqueous samples (Fig. 2).

A small enhancement of the sensitivity of the determinations of cobalt and nickel in the presence of Spheron-Oxine is achieved in both types of

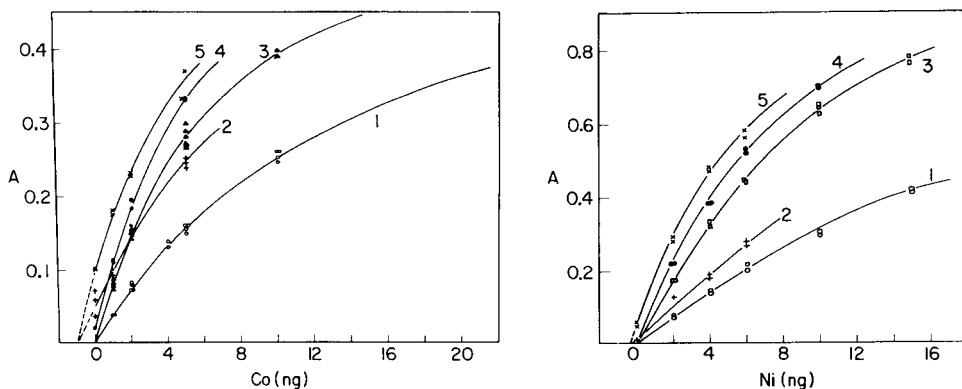


Fig. 3. Calibration graphs for cobalt. (1) Standard tube, aqueous solutions; (2) standard tube, sorption on Spheron-Oxine, Procedure 3; (3) coated tube, aqueous solutions; (4) coated tube, sorption on Spheron-Oxine, Procedure 2; (5) as (4), Procedure 3 (1-ml sample).

Fig. 4. Calibration graphs for nickel. (1) Standard tube, aqueous solutions; (2) standard tube, after sorption on Spheron-Oxine, Procedure 2; (3) coated tube, aqueous solutions; (4) coated tube, after sorption on Spheron-Oxine, Procedure 2; (5) as (4), Procedure 3 (1-ml sample).

tube compared with the aqueous solutions (Figs. 3 and 4). This can be explained by the diffusion of the sample to the graphite wall being prevented in the first stages of the atomization programme, because the analyte remains on the resin at this stage, and only after mineralization reaches the surface of the tube. There is appreciable enhancement of the sensitivity for both elements by the use of pyrolytically-coated graphite tubes, both for aqueous solutions and for the resin (Figs. 3 and 4). This is due to the greater rate of atomization or even to a different mechanism of atomization, and perhaps only a little to the limitations imposed by diffusion.

The measurements with Spheron-Oxine after sorption and separation of the resin (Procedure 3) indicate the completeness of the sorption process, because there is no difference in absorbances compared to that measured without separation after sorption (Procedure 1) (Figs. 3 and 4).

The choice of a suitable chelating resin and optimal reaction conditions can enable highly selective and sensitive analytical procedures to be achieved, thus eliminating matrix effects and giving very simple calibration. After sorption, it is possible to deposit the separated slurry without danger of contamination or loss. In some cases, where elution of metals from ion-exchangers is not possible or very difficult (e.g., cobalt from Spheron-Oxine, mercury from Spheron-Thiol or other thiol polymers), the direct sampling of the suspensions of resins for electrothermal atomization presents the most natural and the simplest possibility for analytical measurement.

The loan of the spectrometer by the Perkin-Elmer Corp. is acknowledged.

#### REFERENCES

- 1 C. W. Fuller and I. Thompson, *Analyst*, 102 (1977) 141.
- 2 Z. Slovák, S. Slováková and M. Smrž, *Anal. Chim. Acta*, 75 (1975) 127.
- 3 Z. Slovák and J. Toman, *Fresenius Z. Anal. Chem.*, 278 (1976) 115.
- 4 Z. Slovák and S. Slováková, *Fresenius Z. Anal. Chem.*, 292 (1978) 213.
- 5 D. C. Manning, F. J. Fernandez and G. E. Peterson, A.A. Application Study No. 631, Perkin-Elmer, 1976.
- 6 Z. Slovák, M. Smrž, B. Dočekal and S. Slováková, *Anal. Chim. Acta*, in press.

## DEVELOPMENT OF A PROCEDURE FOR STUDIES OF THE CHROMIUM(III) AND CHROMIUM(VI) CONTENTS OF WELDING FUMES

D. NARANJIT, Y. THOMASSEN<sup>\*a</sup> and J. C. VAN LOON

*Departments of Geology, Chemistry and the Institute for Environmental Studies, University of Toronto, Toronto M5S 1A1 (Canada)*

(Received 30th April 1979)

### SUMMARY

A method for speciation studies of chromium in welding fumes is described. Separation of chromium(III) and chromium(VI) in aqueous extracts of welding fumes is obtained by using anion- and cation-exchange resins. Atomic absorption spectrometry is used for quantification. At pH 3–5, there is no loss of chromium(III) as the hydroxide nor reduction of chromium(VI) by iron(II). Two types of welding fumes were studied: for ESAB OK 67–52 and AROSTA 316 L fumes, 57 and 91%, respectively, of the total chromium content was water-soluble; the total chromium contents were 5.9 and 4.4%, respectively. Chromium(III) was not detected in the aqueous extracts of either type of fumes ( $< 0.010 \mu\text{g ml}^{-1}$  of extract).

As a part of continuous programs for monitoring worker exposure to chromium, the atmospheric chromium concentration and the chromium level in biological samples, e.g. urine, are examined. The threshold limit values listed in 1978 by the American Conference of Governmental Industrial Hygienists for chromium(III) and chromium(VI) compounds are  $0.5$  and  $0.05 \text{ mg m}^{-3}$ , respectively. Since hexavalent chromium compounds have been reported to induce cancer in man [1], the threshold limit value is expected to be lowered to  $1 \mu\text{g m}^{-3}$  [2]. This intended change makes it necessary to establish selective and sensitive methods for the determination of chromium(VI). Where both oxidation states are present in the working atmosphere, it is necessary to determine the ratio between them. When stainless steel is welded by manual arc welding, some of the chromium in the welding fumes will be present as chromium(VI) [3]. Tola et al. [4] determined chromium(VI) in aqueous extracts of welding fumes by spectrophotometry, in order to study the relationship between exposure and biological indicators.

There does not seem to be a practical valid procedure available for the separation and determination of chromium(III) and chromium(VI) in welding

<sup>a</sup>On leave from Institute of Occupational Health, Box 8149 Dep., Oslo-1, Norway.

fumes. The results of a study leading to the development of such a procedure are described here.

## EXPERIMENTAL

### *Reagents and equipment*

A Perkin-Elmer Model 603 atomic absorption spectrometer equipped with a deuterium arc background corrector and a Perkin-Elmer Model 56 recorder was used with an air-acetylene flame. Perkin-Elmer Intensitron hollow-cathode lamps were used at the recommended current settings.

The pH measurements were done with a Fisher Accumet Model 144 pH-meter. The undissolved welding fumes were characterized with a Jeol Model JSM-35 scanning electron microscope equipped with a PGT-100 energy-dispersive micro-analyzer.

All reagents used were of analytical grade. Anga 316 anion-exchange resin and Dowex 50W-8X cation-exchange resin were employed for the separations. Buffer solutions with pH values ranging from 1–12 were prepared [5]. Single-element or multi-element secondary standard solutions were prepared from 1000-ppm stock solutions and acidified to a pH of about 2.

### *Procedures*

*Sampling.* A special fume box similar to a Swedish Model [6] with a capacity of 0.3 m<sup>3</sup> was used for collecting welding fumes from manual metal arc welding on stainless steel (18.5% Cr, 9% Ni) with two types of electrodes AROSTA 316 L (16–18% Cr, 10–14% Ni) and ESAB OK 67.52 (18% Cr, 9% Ni). The fumes were collected on membrane filters (Acropore AN 1200) by pumping at a rate of 20 l min<sup>-1</sup>.

*Determination of total metals.* For the determination of total metals, each sample of the welding fumes was acid-digested as follows. A 4.5-ml portion of a mixture of aqua regia and hydrofluoric acid (8 + 1) was added to 100 mg of the sample, and the solution was heated at 100°C in a Teflon decomposition vessel for 30 min. Saturated boric acid solution (3 ml) was then added and the solution reheated for a further 15 min. The solution was then cooled and diluted to 100 ml with water.

*Water extractions.* Aqueous extracts of the welding fumes on the filters were obtained by using various buffer solutions in the range pH 1–12. Samples (100 mg) of each of the welding fumes were extracted with the appropriate buffer solution. The extract was then filtered through a 0.45- $\mu$ m membrane filter.

*Separation of chromium(III) and chromium(VI).* Chromium in the two valency states was separated by using cation- and anion-exchange resins. The water-soaked resins (2 ml) were placed in separate 10-ml burets. Portions (5 ml) of the aqueous extracts were passed through the columns at a flow rate of about 1 ml min<sup>-1</sup>. The columns were washed with water and



the first 25 ml of liquid was collected for analysis by atomic absorption spectrometry.

*Recommended procedure for the determination of chromium(III) and chromium(VI) in aqueous extracts of welding fumes*

Extract the welding fumes (powder or sample filter) with an aqueous buffer solution of pH 3–5. Filter the extracts through membrane filters (0.45- $\mu$ m pore size). Pass portions of the extracts through both an anion- and a cation-exchange resin and rinse with distilled water. Dilute the effluents to a known volume. Analyze for chromium by atomic absorption spectrometry by using either flame or electrothermal atomization with appropriate standardization.

## RESULTS AND DISCUSSION

*Determination of total metal concentrations in welding fumes and aqueous extracts*

The fume samples from stainless steel welding were analyzed as described above. Chromium, iron, manganese and nickel results are given in Table 1.

In the welding arc, part of the chromium remains as metallic chromium, while the rest is oxidized mainly to chromium(III) and chromium(VI). The extent of oxidation and the ratio of the oxidation states depend on the method of welding and on the reduction intensity coefficients of silicon and manganese [7]. It is likely that the great difference in the water-soluble chromium content of the welding fumes was due to the composition of the welding rods. The pH values of the extracts from the ESAB and AROSTA fumes in distilled water were 10.0 and 7.0, respectively. The solubility of chromium(III) at these pH values is very small (Fig. 1).

The insoluble particles left after the water-extraction experiments were deposited onto a Nuclepore filter (0.45  $\mu$ m) and analyzed by scanning electron microscopy. The particles containing chromium showed high con-

TABLE 1

Total concentration (%) of Cr, Fe, Mn and Ni in welding fumes and the percentage of the total which is soluble at pH 1

Element	ESAB OK 67-52		AROSTA 316 L	
	% in fumes	% soluble at pH 1	% in fumes	% soluble at pH 1
Cr	5.9	57	4.4	91
Fe	20.0	17	3.7	65
Mn	17.0	21	3.3	61
Ni	1.9	11	0.5	60

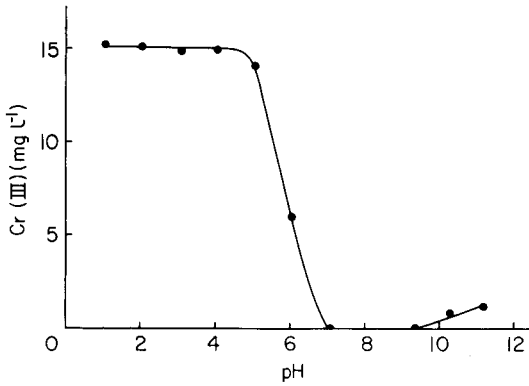


Fig. 1. Solubility of chromium(III) in the pH range 1–12.

centrations of Ca, Fe, Mn, K, Ti and Si, indicating the presence of insoluble silicates. The oxidation state of chromium in the residue was apparently the trivalent.

The amounts of water-extractable metal at various pH values ranging from 1.0 to 12.0 are presented in Fig. 2. These results demonstrate that the total extractable chromium in the two listed types of fumes do not vary over this pH range. Iron and manganese were precipitated completely at a pH of about 3.5. However, no loss of chromium to the precipitating elements was found.

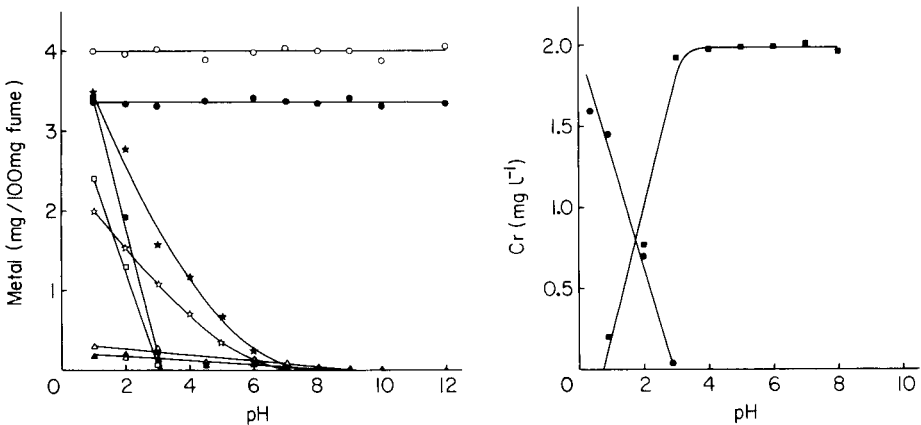


Fig. 2. Principal metals extracted from welding fumes from ESAB OK 67–52 and AROSTA 316 L at pH values from 1 to 12. (○, ●) Cr; (□, ■) Fe; (△, ▲) Ni; (☆, ★) Mn. Open symbols refer to AROSTA 316 L and filled symbols to ESAB OK 67–52.

Fig. 3. Reduction of chromium(VI) to chromium(III) in the presence of iron(II) at pH values in the range 1–8: (●) Cr(III); (■) Cr(VI).

Tola et al. [4] extracted the collected welding fumes with water at 80°C. It was found in the present study that the amount of water-extractable chromium was constant over the temperature range 15–90°C.

*Determination of chromium(III) and chromium(VI) in the aqueous extracts*

To test the validity of an ion-exchange procedure, aqueous solutions containing 1 mg of chromium(III) or chromium(VI) were passed separately through the ion-exchange columns. The procedure was tested for solutions ranging in pH from 1 to 8. The effluents and eluents from the columns were analyzed with the results given in Table 2. The results did not depend on the pH of the sample, hence only one set of values for each column is given in the Table. These results demonstrate that a combination of anion-exchange and cation-exchange systems is necessary to obtain quantitative results (i.e., the eluents from the cation- and anion-exchange columns give low results for chromium(III) and chromium(VI), respectively). No eluents could be found which would give quantitative recovery in both cases.

One of the fumes (AROSTA) was extracted at pH levels of 1.0 and 5.0 and these solutions were passed through the resins to separate chromium(III) and chromium(VI). Analysis of the effluents by atomic absorption spectrometry showed that about 13% of the total chromium in the extract at pH 1 was present as chromium(III). There was no significant increase in the total chromium content of the latter extract. This indicated that at low pH some chromium(VI) was reduced to chromium(III), probably as a result of some reducing species such as iron(II) in the aqueous extract.

Because of the presence of iron(II) in most welding fumes, the reduction of chromium(VI) to chromium(III) by iron(II) was studied as a function of pH (Fig. 3). The results show that at pH values higher than 3 there was no reduction of chromium(VI).

Thus, the present study demonstrates that it is possible to extract the welding fumes at pH 3–5 without any loss of chromium(III) as the hydroxide and without reduction of chromium(VI). It is only under these pH conditions that valid chromium(III)/chromium(VI) data can be obtained for aqueous extracts of welding fumes.

TABLE 2

Recoveries (in mg) of chromium(III) and chromium(VI) (1 mg each) from an aqueous solution

Oxidation state	Cation column		Anion column	
	Effluent water pH 5	Eluent 1 M HCl	Effluent water pH 5	Eluent 2 M NaOH
Cr(III)	< 0.001	~0.35	> 0.99	—
Cr(VI)	> 0.99	—	< 0.001	~0.40

*Determination of chromium by atomic absorption spectrometry*

The determination of chromium in an air-acetylene flame is subject to numerous anionic and cationic interferences. Many potential interferences are present in solutions of welding fumes. Fortunately, the problems can be overcome by using a very fuel-lean flame. This resulted in a 5-fold loss in sensitivity. The method of standard addition is normally recommended when using an air-acetylene flame; this was used to compensate for the lack of sensitivity and for residual interferences.

This work was supported by grants from the Ontario Ministry of the Environment under the Research Grants Programme of the Air Resources Branch, the Royal Norwegian Council for Scientific and Industrial Research and the University of Toronto. Perkin-Elmer Corp., Norwalk, Conn., kindly lent the atomic absorption equipment. The authors thank Dr. O. Bjørseth, SINTEF, Trondheim, Norway, for donating the welding fumes, and Dr. D. Nicholson, Institute of Occupational Health, Oslo, for the scanning electron microscopy.

## REFERENCES

- 1 S. Langård and T. Norseth, Chromium in Toxicology of Metals, Vol. II, EPA-600/1-77-022, Environmental Health Effects Research Series, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, 1975, p. 164.
- 2 Occupational Exposure to Chromium(VI), National Institute of Occupational Safety and Health HEW Publication No. 76-129 (1975).
- 3 S. Fregert and P. Øvrum, Acta Derm. Venereol., 43 (1963) 119.
- 4 S. Tola, Y. Kilpiö, M. Virtamo and K. Haapa, Scand. J. Work Environ. Health, 3 (1977) 192.
- 5 Handbook of Chemistry and Physics, 49th edn., CRC, Cleveland, 1968, p. D79.
- 6 E. J. Magnusson, The Problems of Fumes in Welding, ESAB Information Paper, DSL April 1973, Svejsning, 1 (1975) 11.
- 7 Y. Zeke and J. Janosiova, Zvaranie, 24 (7) (1975) 193.

## INCREASED MERCURY CONTAMINATION OF DISTILLED AND NATURAL WATER SAMPLES CAUSED BY OXIDIZING PRESERVATIVES

JAMES H. CRAGIN

*U.S. Army Cold Regions Research and Engineering Laboratory Hanover, NH  
03755 (U.S.A.)*

(Received 25th April, 1979)

### SUMMARY

The passage of mercury vapor from ambient air through the walls of conventional polyethylene (CPE), linear polyethylene (LPE), and Teflon (FEP) containers can seriously contaminate solutions of distilled and natural water stored in these containers. The rate of mercury contamination is dramatically increased when the sample solution contains oxidizing agents such as nitric acid or potassium permanganate, which are commonly used as preservatives to prevent loss of mercury(II) ion. The rate of contamination also depends on container material and decreases in the order CPE > LPE > FEP > glass. Freezing the samples in plastic containers is an effective way to prevent mercury contamination. When freezing is not practical, storage in glass containers minimizes sample contamination from ambient mercury vapor.

The instability of dilute ( $\mu\text{g l}^{-1}$  and below) mercury solutions is of widespread interest. Previous studies have dealt primarily with preventing losses of mercury from solution by the addition of preservatives such as hydrochloric acid [1, 2], nitric acid [1, 3—6], sulfuric acid [7], acid potassium permanganate [8—10], acid potassium dichromate [11—14], cystine [15, 16], gold(III) [12, 17], and sodium chloride [7]. Although there is still considerable debate as to which preservative is best, it is generally agreed that acidification to a pH of 1 or less prevents loss of mercury by adsorption onto container walls, and that oxidizing agents (permanganate, dichromate, gold(III)) keep mercury in the divalent state and thus prevent loss by reduction and subsequent volatilization.

In most past work concerned with mercury losses, relatively little attention has been given to the possibility of mercury contamination, aside from obvious sources such as high reagent blanks and improperly cleaned labware. Bothner and Robertson [1] reported contamination of sea-water samples stored in polyethylene bottles and attributed this either to leaching of mercury from container surfaces or to transport of mercury vapor from ambient air through the container wall and into the solution. The present study supports a mercury vapor contamination mechanism not only

for sea water but for distilled and fresh-water samples as well. It is further shown that the common practice of adding nitric acid or nitric acid/potassium permanganate as preservatives markedly increases the rate of mercury contamination.

## EXPERIMENTAL

### *Instrumentation and reagents*

Mercury concentrations were determined by cold-vapor atomic absorption spectrometry with a Perkin-Elmer Model 403 spectrometer equipped with a mercury electrodeless discharge lamp and a Hewlett-Packard 7100 B recorder. The detection limit of this method was  $10 \text{ ng Hg l}^{-1}$ .

Standards were prepared from a  $1000 \text{ mg l}^{-1}$  stock solution of mercury(II) chloride. Doubly-distilled deionized water (DD-water) was used for all dilutions and rinsings; this was prepared by deionizing, distilling in a tin-lined still, and then distilling in a pyrex still. Other solutions used were 5% (w/v) potassium permanganate (reagent grade), redistilled nitric acid (G. Frederick Smith Chemical Co.), and 10% (w/v) tin(II) chloride (reagent-grade) in 6 M hydrochloric acid. Baker reagent-grade sulfuric acid was used for all digestions, because it was found to have a blank as low ( $<10 \mu\text{g Hg l}^{-1}$ ) as the more expensive "mercury-free sulfuric acid." Hydroxylammonium chloride, commonly used to reduce excess of permanganate, was not used because of its high mercury blank and the ease with which it became contaminated. Tin(II) chloride reduced both excess of permanganate and mercury(II).

Doubly-deionized distilled water (Q-water) was used in some experiments; this was prepared from tap water by deionizing, distilling in a tin-lined still, and finally deionizing again in a commercial mixed-bed system.

### *Containers*

All containers used in this study (500-ml borosilicate glass bottles, Nalgene 1-l linear polyethylene (LPE) bottles, Nalgene 1-l conventional polyethylene (CPE) bottles, and Nalgene 1-l Teflon (FEP) bottles) were cleaned by rinsing with DD-water, leaching in concentrated redistilled nitric acid for 24 h, and finally rinsing thoroughly with DD-water.

### *Procedure*

A series of distilled water and  $100 \text{ ng Hg l}^{-1}$  standards were prepared and, along with Greenland glacial ice melt-water, analyzed periodically during time spans of about one month. For each type of sample, 1-l aliquots were stored, without preservatives, with 1% (v/v) redistilled nitric acid, or with oxidizing reagents (2 drops of 5% potassium permanganate, 4 ml of concentrated nitric acid and 12 ml of concentrated sulfuric acid per 100 ml of sample). All samples were prepared, stored, and analyzed in a Class 100 laminar-flow clean-air station.

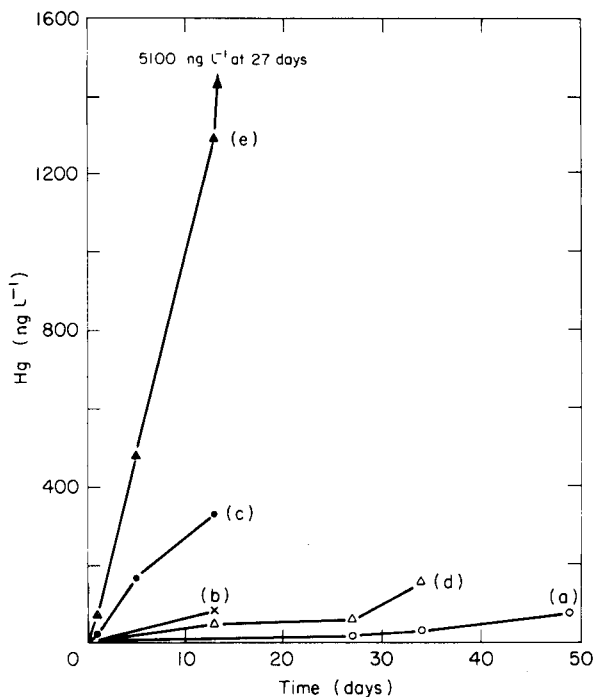


Fig. 1. Mercury contamination vs. time for glacial ice melt-water (MC1067) and Q-water samples stored in tightly-capped LPE bottles. "R" (reagents) consisted of 2 drops of 5% (w/v)  $\text{KMnO}_4$ , 4 ml of concentrated  $\text{HNO}_3$ , and 12 ml of concentrated  $\text{H}_2\text{SO}_4$  per 100 ml of sample. (a) Q-water, (b) Q-water + 1%  $\text{HNO}_3$ , (c) Q-water + R, (d) glacial ice melt-water, (e) glacial ice melt-water + R.

## RESULTS AND DISCUSSION

Initial results are shown in Fig. 1, where a sample of glacial ice melt-water was allowed to "digest" with oxidizing reagents (R) in a tightly-capped LPE bottle. Mercury concentrations increased dramatically, reaching  $5100 \text{ ng l}^{-1}$  at 27 days when the sample was exhausted. This increase could not all have been due to oxidation and release of bound mercury in the sample because a Q-water blank ( $<10 \text{ ng Hg l}^{-1}$  initially) also showed a steady increase in mercury concentration during this period. Duplicate glacial and Q-water samples, without oxidizing reagents, stored concurrently with the above samples showed similar but smaller mercury concentration increases. A Q-water sample containing 1% nitric acid showed a contamination rate intermediate between that of pure Q-water and that of Q-water with oxidizing reagents, indicating that the rate of mercury contamination was directly proportional to the oxidizing ability of the sample solution. Bothner and Robertson [1] have reported this contamination of sea-water samples stored in polyethylene containers but at much slower rates. The higher contamination

rates observed in the present study are probably related to the greater oxidizing strength of the samples.

To determine the effect of the water blank on the mercury contamination rate, samples of DD-water ( $<5 \text{ ng Hg l}^{-1}$ ) and Q-water ( $<5 \text{ ng Hg l}^{-1}$ ), both with and without oxidizing reagents, were stored for 25 days and mercury was measured periodically (Fig. 2A). During this storage period, the mercury concentration of all samples increased almost linearly with time. Contamination rates were much greater for samples with oxidizing reagents than for samples without reagents. The dependence of contamination rate on the oxidizing strength of the solution is also evident in Fig. 1 where the order is Q-water  $<$  Q-water with 1% nitric acid  $<$  Q-water with reagents. A mechanism consistent with these observations is that, after passing through the walls of the LPE container, mercury is stabilized in solution by the nitric acid and potassium permanganate which oxidize it to mercury(II); to maintain equilibrium, more mercury goes into solution and is oxidized to mercury(II). The oxidizing reagents thus make the sample solution a sink for ambient mercury vapor.

From Fig. 2A it is also evident that the contamination rate of Q-water samples is greater than that of the corresponding DD-water samples. Since the last step in the preparation of Q-water was ion exchange, a small amount of the resin may have been present in the water which would provide a

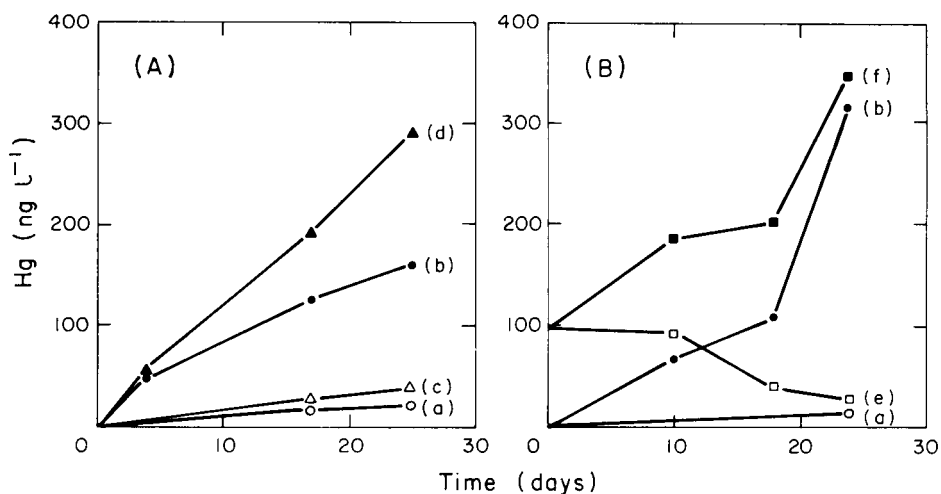


Fig. 2. Mercury contamination with time. Comparison of (A) Q-water with DD-water, and (B)  $100 \text{ ng Hg l}^{-1}$  standard with DD-water. LPE bottles and reagents were the same as for Fig. 1. (a) DD-water, (b) DD-water + R, (c) Q-water, (d) Q-water + R, (e)  $100 \text{ ng Hg l}^{-1}$ , (f)  $100 \text{ ng Hg l}^{-1}$  + R.



stabilizing effect for any mercury(II) present. To eliminate this possibility, DD-water was used in all subsequent experiments.

In the concentration versus time studies, the mercury concentrations reported are the net total mercury in solution and thus represent the difference between mercury gained by contamination and that lost by adsorption and/or volatilization. To check the rate of mercury loss from solution, 100 ng Hg l<sup>-1</sup> standards were allowed to sit for several weeks in LPE bottles. Figure 2B compares the concentration change of the 100 ng Hg l<sup>-1</sup> standard with that of DD-water. As expected, the mercury concentration of the DD-water both with and without reagents increased over the 24-day span from <5 ng Hg l<sup>-1</sup> to 15 ng Hg l<sup>-1</sup> and 320 ng Hg l<sup>-1</sup>, respectively. These curves compare reasonably well with the curves for DD-water and DD-water with reagents in Fig. 2A. (The sharp increase in mercury concentration of the standard with reagents and DD-water with reagents observed after the 18th day in Fig. 2B may have been caused by elevated room air mercury levels during that time.)

The increase in concentration of the 100 ng Hg l<sup>-1</sup> standard with reagents quite closely parallels the increase of the DD-water with reagents, the oxidizing ability of the reagents being the controlling factor in the rate of mercury absorption by the solutions. In contrast, the 100 ng Hg l<sup>-1</sup> standard containing no acid or reagents actually lost 70 ng Hg l<sup>-1</sup> (probably by adsorption) during the 24-day storage period. This net loss is actually the difference between the total loss and the amount gained by vapor transport. If it is assumed that the vapor-transport gain in mercury concentration is the same as that observed for DD-water, i.e. 15 ng l<sup>-1</sup>, then the loss from adsorption is actually 85 ng Hg l<sup>-1</sup>.

To verify that the observed mercury contamination was caused by the mercury vapor being transported from ambient air through container walls into the sample solution rather than simply being leached (desorbed) from the container walls, several containers with samples of DD-water were capped tightly and allowed to stand in a sealed polyethylene bag containing an open bottle of mercury metal. The bag air outside the sample containers was thus saturated with mercury vapor (ca. 20 ng Hg cm<sup>-3</sup> at 25°C). Rates of contamination for samples in LPE bottles were one to two orders of magnitude greater (Fig. 3) than for samples surrounded by ambient air.

In this and previous storage studies, all containers were tightly capped to prevent direct air leaks. Therefore, the only way that ambient mercury vapor could contaminate a sample solution was by actually passing through the walls of the container. This route was further supported by the results for a sample of DD-water in the LPE (sealed) bottle. Although this tightly-capped bottle containing 1-l of DD-water was heat-sealed in a dust-free (Class 100) polyethylene bag, it still gained 1400 ng Hg l<sup>-1</sup> in 15 days. Even the rate of contamination by mercury vapor (slope of curve (e) in Fig. 3) does not appear to have been reduced appreciably (compared with slopes for other samples) by sealing the sample in a polyethylene bag. This is

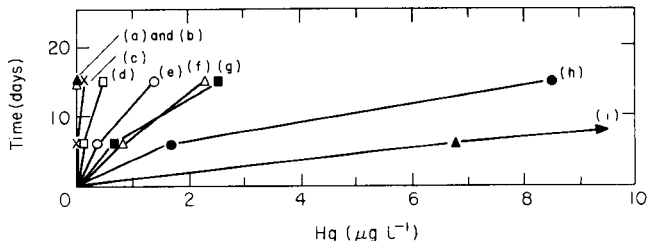


Fig. 3. Mercury contamination of DD-water stored in conventional polyethylene (CPE), linear polyethylene (LPE), Teflon (FEP), and glass containers. (a) DD-water in LPE, frozen; (b) DD-water + R in LPE, frozen; (c) DD-water + R in glass; (d) DD-water in FEP; (e) DD-water in LPE, sealed; (f) DD-water in CPE; (g) DD-water + R in FEP, (h) DD-water + R in LPE; (i) DD-water + R in CPE. After 15 days, sample (i) contained  $32.50 \mu\text{g Hg l}^{-1}$ .

probably because the rate of mercury vapor transport is primarily limited by the wall of the plastic container, which was much thicker (0.185 mm) than that of the plastic bag (0.024 mm).

It is interesting to note that storage of samples in a Class 100 clean-air station did not prevent mercury contamination of samples. The high-efficiency particulate air (HEPA) filters in these clean-air stations are 99.97% efficient for all particles  $0.5 \mu\text{m}$  or larger in diameter. Apparently ambient mercury exists as atomic or molecular species that are not removed by the HEPA filters.

Also shown in Fig. 3 is a comparison of mercury contamination of DD-water stored in containers of various materials (CPE, LPE, FEP, and glass). The rate of contamination decreased in the order CPE > LPE > FEP for both the DD-water and the DD-water + reagents samples. Glass was much more effective in preventing mercury vapor contamination, as shown by curve (c) of Fig. 3; the small amount of contamination observed was probably due to vapor diffusion through the conical polyethylene insert in the Bakelite cap used on the bottle. Glass has previously been recommended [18] as the preferred container for minimizing losses of mercury(II) from solution and present results show that glass is also the preferred container for minimizing sample contamination from ambient mercury vapor.

The least amount of contamination ( $<20 \text{ ng Hg l}^{-1}$ ) occurred in DD-water and DD water + reagents samples that were kept in the frozen state (at  $-10^\circ\text{C}$  during storage. (They were melted for a few hours for analysis on the 8th and 15th days.) Part of the reason for the lower contamination rates was the lower air concentration of mercury at  $-10^\circ\text{C}$  (saturation corresponds to  $0.66 \text{ ng Hg cm}^{-3}$  at  $-10^\circ\text{C}$  and  $20 \text{ ng Hg cm}^{-3}$  at  $25^\circ\text{C}$ ). But this 30-fold reduction in mercury air concentrations is still considerably less than the more than 400-fold reduction in sample contamination rate. Thus, freezing seems to be a very effective way to prevent mercury vapor contami-

nation, because mercury vapor cannot enter into solution to be oxidized to mercury(II).

#### REFERENCES

- 1 M. H. Bothner and D. E. Robertson, *Anal. Chem.*, 47 (1975) 592.
- 2 M. Stoeppler and W. Matthes, *Anal. Chim. Acta*, 98 (1978) 389.
- 3 R. V. Coyne and J. A. Collins, *Anal. Chim.*, 44 (1972) 1093.
- 4 R. M. Rosain and C. M. Wai, *Anal. Chim. Acta*, 65 (1973) 279.
- 5 H. V. Weiss and K. Chew, *Anal. Chim. Acta*, 67 (1973) 444.
- 6 R. A. Carr and P. E. Wilkness, *Environ. Sci. Technol.*, 7 (1973) 63.
- 7 M. Ambe and K. Surwabe, *Anal. Chim. Acta*, 92 (1977) 55.
- 8 Mercury Analysis Working Party of the Bureau International Technique Du Chlore, *Anal. Chim. Acta*, 72 (1974) 37.
- 9 J. E. Hawley and J. D. Ingle, Jr., *Anal. Chem.*, 47 (1975) 719.
- 10 P. Avotins and E. A. Jenne, *J. Environ. Qual.*, 4 (1975) 515.
- 11 C. Feldman, *Anal. Chem.*, 46 (1974) 99.
- 12 J. Lo and C. M. Wai, *Anal. Chem.*, 47 (1975) 1869.
- 13 A. A. El-Awady, R. B. Miller and M. J. Carter, *Anal. Chem.*, 48 (1976) 110.
- 14 D. R. Christmann and J. D. Ingle, Jr., *Anal. Chim. Acta*, 86 (1976) 53.
- 15 V. Dokiay, S. Yamazaki and K. Fuwa, *Environ. Lett.*, 7 (1974) 67.
- 16 H. V. Weiss, W. H. Shipman and M. A. Guttman, *Anal. Chim. Acta*, 81 (1976) 211.
- 17 J. R. Moody, P. J. Paulsen, T. C. Rains and H. L. Rook, NBS Special Publication 422 (Proceedings of the 7th IMR Symposium, October 1974) (1976) 267.
- 18 J. Carron and H. Agemian, *Anal. Chim. Acta*, 92 (1977) 61.

## Short Communication

---

### PERCHLORATE-SELECTIVE ELECTRODES WITH URUSHI AS THE MEMBRANE MATRIX

KAZUO HIRO\*, AKINORI KAWAHARA and TAKASHI TANAKA

*Government Industrial Research Institute, Ikeda-shi, Osaka (Japan)*

(Received 22nd February 1979)

*Summary.* Perchlorate-selective electrodes prepared from a new matrix, Urushi, and tri-n-octylmethylammonium perchlorate or the Corning perchlorate liquid ion-exchanger are described. The electrodes have linear response ranges and selectivity similar to those of commercial perchlorate-selective electrodes. The membranes are hard, lustrous and smooth; their useful lifetimes exceed 1000 h.

Various materials such as silicone rubber [1], polyvinyl chloride [2], paraffin wax [3], etc. have been recommended as matrices for heterogeneous membrane electrodes. In a search for more durable and rigid materials than these, Urushi was found to be valuable for immobilizing both solid and liquid electro-active substances. Urushi is a natural oriental lacquer used extensively for Japanese lacquer-ware [4]. The components of Urushi [5] are Urushiol [6] (60-80%), water (10-30%), rubbery substances (7-8%), nitrogen compounds (2-3%) and laccase, an oxidizing enzyme; the proportions of these components depend on the place and season of the Urushi production. As Urushi lacquer has excellent durability and mechanical strength [4], it was examined for use as a matrix for ion-selective electrodes.

An iodide-selective electrode based on Urushi and powdered silver iodide has already been described [7]. Not only powdered materials but also liquid ion exchangers can be used as the electro-active material, however, and solidification of ion-selective liquid membranes is possible. In this communication, an investigation of an Urushi membrane perchlorate-selective-electrode is described. The liquid ion-exchanger is tri-n-octylmethylammonium perchlorate [8] or a commercial perchlorate-selective exchanger.

#### *Experimental*

*Preparation of perchlorate ion-exchanger.* Tri-n-octylmethylammonium chloride (Capriquat; Dojin Research Laboratories Co.) was converted to the perchlorate form by shaking its solution in chloroform (10 g in 40 g) with three 40-ml aliquots of 0.1 M sodium perchlorate (analytical-reagent grade; Wako Pure Chemical Co.). The chloroform was removed by evaporation after

the extract has been passed through a dry filter paper. Commercial perchlorate ion-exchanger (Corning Scientific Instruments, No. 477359) was used as received.

**Construction of the Urushi membrane electrodes.** The perchlorate ion exchanger was mixed in different proportions (see below) with Urushi latex (Ise Urushi; Nishizawa Urushi Co.) on a small watch glass. [Caution: Urushi lacquer should not be allowed to contact the skin.] The mixtures were initially brown, but gradually became black and viscous as Urushi was oxidized by atmospheric oxygen through the presence of laccase. The mixture was coated on the copper internal contact of the electrode body (Fig. 1) which was made from glass or plastic tubing (12 mm diameter, 120 mm long). The copper base (10 mm diameter) was fitted tightly into the external tubing. The rest of the construction is clear from Fig. 1.

After coating the mixture of ion exchanger and Urushi was hardened in air at defined temperatures. Mixtures containing the Corning ion exchanger required 5–15 days at 20–35°C (80% relative humidity) for complete hardening depending on the composition of the mixture. When the tri-n-octylmethylammonium perchlorate exchanger was used, hardening was possible at 35°C or at 130°C, because the ion exchanger was not decomposed at the higher temperature; the higher temperature was preferred as complete hardening was attained within 3–5 h. The surface of the Urushi membranes was lustrous and smooth, and the thickness of the membrane prepared with a single coating was about 0.3 mm.

### Results and discussion

**Potential–activity curves.** When Corning ion exchanger (45 parts) and Urushi (55 parts) were mixed for preparation of the membrane, the

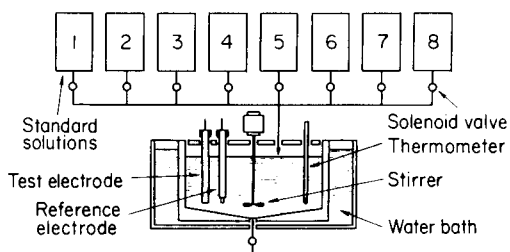
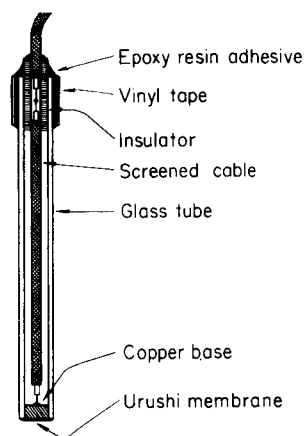


Fig. 1. Structure of Urushi membrane electrode.

Fig. 2. Automatic electrode testing apparatus.

electrode showed a linear potential—activity graph within the range  $10^{-1}$ — $10^{-5}$  M sodium perchlorate; the slope was about 57 mV per decade change in perchlorate activity. When the electrode membrane contained only 40 parts of the Corning exchanger, the linear response range was reduced to  $10^{-1}$ — $10^{-4}$  M and the slope was about 38 mV per decade; with 35 parts, the slope was only about 27 mV per decade and with 30 parts, linear calibration graphs could not be obtained. However, when membranes were prepared from 50 parts of the Corning exchanger, they did not harden properly, although the linear range and slope were satisfactory. The best amount of the liquid ion exchanger was therefore 45 parts.

When tri-*n*-octylmethylammonium perchlorate (40 parts) was used with Urushi (60 parts) under either hardening condition, identical linear calibration graphs were obtained within the activity range  $10^{-1}$ — $10^{-4}$  M perchlorate; the slope of the curve was about 55 mV per decade. Even when the membrane contained only 30 parts of the exchanger the calibration graphs were linear though the slope was reduced to 51 mV per decade. When the content of the exchanger was 50, 55, 60 or 70 parts, the electrodes showed linear calibration plots with slopes of about 55 mV per decade change in the activity range  $10^{-1}$ — $10^{-4}$  M. Membranes prepared from 25 parts of dioctylphthalate, nitrobenzene or *n*-decanol, 25 parts of tri-*n*-octylmethylammonium perchlorate and 50 parts of Urushi did not show improved characteristics. Electrodes prepared from another Urushi latex (Tikkei Urushi; Saito Co.) gave the same calibration graphs as electrodes prepared from Ise Urushi.

*Methods of preparation.* Various amounts of a mixture containing 45 parts of Corning ion exchanger and 55 parts of Ise Urushi, were coated onto the base of electrode bodies. Application of amounts between 29 mg and 17 mg of the mixture did not affect electrode characteristics significantly, nor did application of 24 mg of the mixture in one, two or three portions with hardening between applications in the latter cases. All these membranes had thicknesses of 0.3 mm when 24 mg of the mixture was used, and showed identical potential—activity curves. Electrodes made from 40 parts of tri-*n*-octylmethylammonium perchlorate and 60 parts of Ise Urushi stored in the laboratory for 8 months and stored for the same time in a dark helium-filled box showed properties identical with those of freshly prepared electrodes.

*Response time.* The static response time, i.e., the time needed to reach constant potential after immersion of the electrode in a stirred solution, was several seconds, independently of the perchlorate activity within the linear range. The dynamic response time measured by adding 20 ml of water to 20 ml of  $1.95 \times 10^{-3}$  M sodium perchlorate solution, was about 10 s; when  $1.80 \times 10^{-2}$  M sodium perchlorate solution was added to  $1.95 \times 10^{-3}$  M solution a steady potential was attained after 10–30 s.

*Selectivity of the electrodes.* Constant potential readings were obtained between pH 5 and 7 for  $0.97 \times 10^{-3}$  M sodium perchlorate solution with the Corning exchanger Urushi electrode (45:55). The potential decreased slightly at lower and higher pH values; selectivity in the presence of hydroxide ions was poor.

TABLE 1

Selectivity coefficients by the mixed solution method

Interfering ion	Activity (M)	$K_{ij}$	Interfering ion	Activity (M)	$K_{ij}$
F <sup>-</sup>	$0.75 \times 10^{-1}$	$2.3 \times 10^{-4}$	ClO <sub>3</sub> <sup>-</sup>	$0.75 \times 10^{-1}$	$5.1 \times 10^{-3}$
Cl <sup>-</sup>	$0.75 \times 10^{-1}$	$2.4 \times 10^{-4}$	BrO <sub>3</sub> <sup>-</sup>	$0.90 \times 10^{-2}$	$2.2 \times 10^{-2}$
Br <sup>-</sup>	$0.90 \times 10^{-2}$	$2.1 \times 10^{-3}$	IO <sub>3</sub> <sup>-</sup>	$0.97 \times 10^{-3}$	$1.9 \times 10^{-2}$
I <sup>-</sup>	$0.97 \times 10^{-3}$	$3.3 \times 10^{-2}$	NO <sub>3</sub> <sup>-</sup>	$0.90 \times 10^{-2}$	$8.0 \times 10^{-3}$

The selectivity coefficients for this electrode in the presence of other ions are listed in Table 1; the order of decreasing selectivity for the halide and halate ions coincides with the order of increasing ionic radii. These values are similar to those measured with commercial perchlorate-selective liquid-membrane electrodes [9].

*Durability tests.* The lifetime of the perchlorate-selective electrodes prepared from the Corning exchanger Ise Urushi (45:55) was measured using a specially designed sample-circulating apparatus which comprised potentiometers, a pulse generator, timers and a high-speed recorder. Figure 2 shows a general view of the apparatus. Perchlorate solutions of various activities were passed by gravity one after another through tubes (6 mm i.d.) controlled by solenoid valves into the measuring cell (200-ml capacity) which held three sets of test electrodes and reference electrodes. The potentials of the electrodes were plotted along with the number of perchlorate solution tested and the temperature. The electrodes could be used continuously for more than 1000 h; data were not obtained for the exact lifetime of the electrodes.

## REFERENCES

- 1 E. Pungor, J. Havas and K. Tóth, *Acta Chim. Acad. Sci. Hung.*, 41 (1964) 239.
- 2 A. Shatkey, *Anal. Chem.*, 39 (1967) 1056.
- 3 H. J. C. Tendeloo and A. Krips, *Rec. Trav. Chim.*, 76 (1957) 703.
- 4 Kirk-Othmer, *Encyclopedia of Chemical Technology*, 2nd edn., Wiley, New York, Vol. 17, 1968, p. 387.
- 5 *Encyclopaedia Chimica*, Kyoritsu Pub. Co., Tokyo, Vol. 1, 1960, p. 807.
- 6 *The Merck Index*, 9th edn., Merck and Co., 1976, p. 1270.
- 7 K. Hiio, T. Tanaka and A. Kawahara, *Jpn. Anal.*, 25 (1976) 653.
- 8 C. J. Coetzee and H. Freiser, *Anal. Chem.*, 41 (1969) 1128.
- 9 G. J. Moody and J. D. R. Thomas, *Selective Ion-Sensitive Electrodes*, Mellow, Watford, 1971, p. 23.

## Short Communication

---

# A NON-INTRUSIVE VERY HIGH-FREQUENCY CONDUCTIVITY DETECTOR FOR CONTINUOUS FLOW MONITORING

J. F. ALDER\* and P. K. P. DREW

*Chemistry Department, Imperial College, London SW7 2AY (Gt. Britain)*

(Received 19th April 1979)

**Summary.** A non-intrusive inductively-coupled conductance detector operating at 115 MHz is described. The flowing sample passes through a straight glass tube confined within the inductance coil of a parallel tuned high- $Q$  circuit. Changes in  $Q$  caused by the resistive component of the sample are measured. Potassium chloride in water can be monitored down to 2 ppm with a linear response over three orders of magnitude of concentration.

There are many applications where the monitoring of the conductivity of electrolyte solutions is required on a continuous basis. Ion-exchange methods [1] and chromatography [2–4] with aqueous electrolyte eluents prove the importance of suitable methods for the detection of low concentrations of ions in small volumes of solution. The detectors used generally require application of kHz voltages to pairs of platinum or stainless steel electrodes in contact with the effluent. With such devices, there is always the risk of contamination or chemical attack on the electrodes and very often the machining tolerances for the cells are most exacting.

Much less attention has been paid to high-frequency conductance measurements where the coupling between the cell and the detector can be either capacitive or inductive [5]. Capacitive cells have been shown to perform well [6, 7]. In the work described here, inductive coupling between the cell and the detector has been exploited. Electric current is induced in the effluent by the alternating magnetic field of a coil forming part of a resonant circuit. The power dissipated in the resistive component of the liquid lowers the quality factor ( $Q$ ) of the coil and hence of the resonant circuit. Such an approach has been used previously to measure the conductivity of metals and plasmas [8], but not in high-performance liquid chromatography.

### *Theory*

The quality factor ( $Q$ ) of a resonant circuit can be defined as  $Q = 2\pi$  (energy stored per half-cycle)/(energy dissipated per half-cycle). For a coil of negligible resistance this energy is dissipated through inductive coupling into the sample stream within the coil in accordance with the equations derived by Brown et al. [9]. Under conditions of complete magnetic penetration, the equation for  $Q$  can be developed:  $Q \approx A_c K / 4A_s^2 \omega \mu f$ . Here  $A_c$  is the



cross-sectional area of the coil ( $m^2$ ),  $A_s$  the cross-sectional area of the stream ( $m^2$ ),  $\sigma$  the conductivity of the sample stream ( $\Omega^{-1}m^{-1}$ ),  $\mu$  the permeability of the medium within the coil ( $H m^{-1}$ ),  $f$  the frequency of the magnetic field (Hz), and  $K$  a shape factor for the coil.

Thus  $Q$  is inversely proportional to the conductivity and hence to the total ionic concentration.  $Q$  can also be defined as the voltage magnification of the circuit, in this case the ratio of the rectified voltage measured ( $V_m$ ) across the tuned load compared to the voltage across the source ( $V_s$ ). For a small change ( $\Delta\sigma$ ) in conductivity,  $\Delta V_m = V_s \Delta Q \propto \Delta\sigma \sigma^{-2} \propto \Delta c$ , i.e. a linear change in voltage will be obtained.

### Experimental

The detector (Fig. 1) was built in-house. The output from the detector was fed to a Servoscribe strip chart recorder. Solutions were pumped through the cell by a Masterflex (Cole-Palmer Inc.) peristaltic pump. The cell and detector were not thermostatted. All reagents used were of the highest purity available; the water was distilled only.

The cell was a plain silica or glass tube supported by two brass bulkhead couplings (Drallim Ltd.) mounted in the oscillator shielding box. A self-supporting coil made from silver-coated copper wire (20 swg; Scientific Wire Co. Ltd.) to give minimum high-frequency resistance and maximum  $Q$  was wound round a section of the tube (Fig. 1). This construction allowed for rapid replacement of either coil or tube for optimization purposes. The LC parallel circuit resonant at 116 MHz ( $L_D C_D$ , Fig. 1) was coupled to a 9.6490 MHz crystal oscillator, the output of which had been multiplied up to 115.79 MHz. To set the zero point of the measurement, the solvent alone was pumped through the detector cell, coaxial with the inductor  $L_D$  and the capacitor  $C_D$  was altered until the load was resonant with the oscillator at 115.79 MHz. The resultant voltage was applied to the input of the external amplifier VA 1 (gain = 10) and the output backed off to zero. Any small

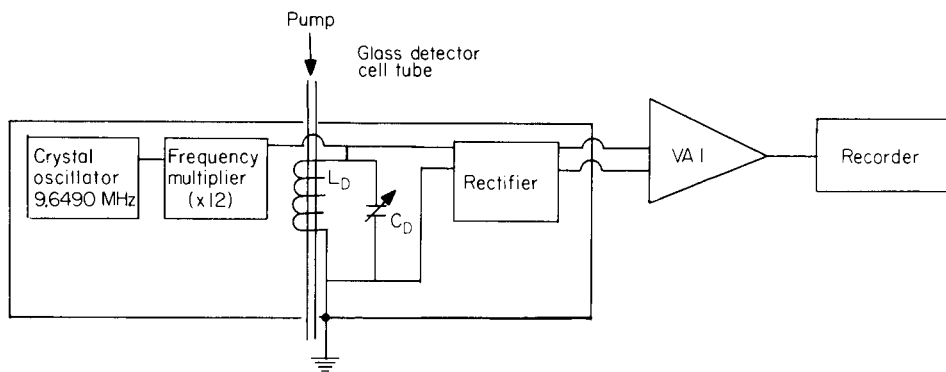


Fig. 1. Block diagram of detector system.

changes in  $Q$  of the inductor  $L_D$  resulting from a change in the conductivity of the medium in the coil were exhibited as a change in the output of VA 1 from zero.

### Results and discussion

Several different coil and tube sizes were tested. The response curves for solutions of potassium chloride in water are given in Fig. 2 for tubes of different internal diameter fitted coaxially in a coil of 4 mm i.d. The log-log plots are linear with change in concentration over three orders of magnitude with a gradient of 1.0. With the glass tube of 1 mm i.d., the limit of detection (signal:background noise = 2:1) was 2 ppm potassium chloride in water vs. water. The volume of the detector tube within the coil was about  $9 \mu\text{l}$ . The relative standard deviation for twelve replicate determinations of 100 ppm KCl was 0.3%. Day-to-day reproducibility was about 2%.

The responses to equimolar solutions of chlorides at the 200-ppm level showed an almost linear dependence on the metal ion mobilities (Table 1), illustrating that the effect measured is almost entirely conductive.

A change in the dielectric constant of the medium results in a signal output from the detector, as would be expected. For example, changing the medium stepwise from 100% water to 100% methanol causes an almost linear change in response; the voltage change is 4.1 mV which is equal in magnitude but opposite in sign to the signal from 400 ppm KCl in water (Fig. 3). The dielectric constants for methanol and water are 33.6 and 80.4, respectively, at  $25^\circ\text{C}$  [11].

The effect of flow rate was examined; over the range  $1\text{--}3 \text{ ml min}^{-1}$  through the 2 mm i.d. tube, there was no noticeable change in instrumental response.

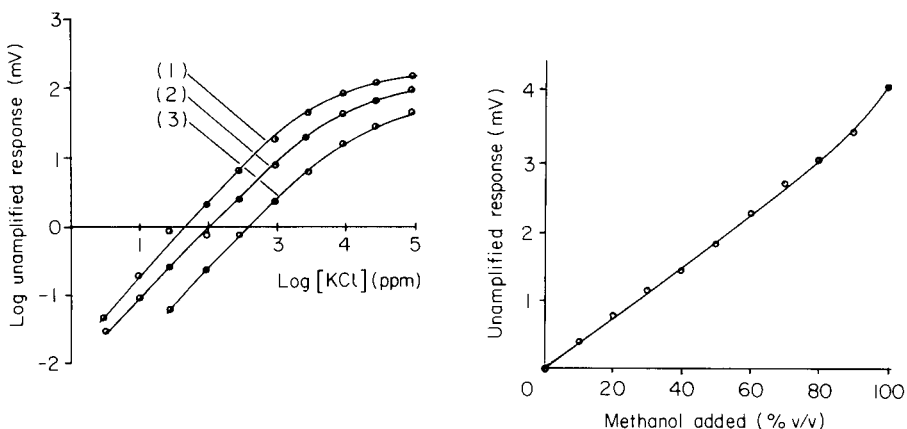


Fig. 2. Log-log response for an 11 turn coil for aqueous solutions of potassium chloride in tubes of different internal diameters: (1) 2.2 mm; (2) 1.0 mm; (3) 0.8 mm.

Fig. 3. Response curve for methanol-water mixtures.

TABLE 1

Unamplified instrumental response against molar conductance for solutions containing 200 ppm chloride

Chloride salt	Response (mV)	Molar conductance <sup>a</sup> ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	Chloride salt	Response (mV)	Molar conductance <sup>a</sup> ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )
K <sup>+</sup>	4.92	143.2	Mn <sup>2+</sup>	4.04	114.3
Ba <sup>2+</sup>	4.45	127.5	Ni <sup>2+</sup>	4.10	111.8
Ca <sup>2+</sup>	4.09	123.8	Li <sup>+</sup>	3.76	109.0
Na <sup>+</sup>	4.25	120.3			

<sup>a</sup>Corrected to 200 ppm chloride [10]. The values given by Parsons [10] are for infinite dilution and have been corrected to 200 ppm chloride. Some of the values are also available from ref. [11].

In conclusion, this work demonstrates the potential of this simple, cheap conductivity detector for continuous flow monitoring. Its robust design makes it well suited to long-term applications and the isolated electrodes make it possible to work with corrosive solutions. The sensitivity is reasonable and design optimization will provide improvements by reducing drift and circuit noise. The low cell volume should be suitable for high-performance liquid chromatographic application.

The authors are grateful to the SRC for support of P.K.P.D., to the Central Research Fund, University of London for an equipment grant and to B. Skilton for designing the detector.

#### REFERENCES

1. H. Small, T. S. Stevens and W. C. Bauman, *Anal. Chem.*, 47 (1975) 1801.
2. V. Svoboda and J. Marsal, *J. Chromatogr.*, 148 (1978) 111.
3. K. Tesarik and P. Kalab, *J. Chromatogr.*, 78 (1973) 357.
4. R. L. Pecsok and D. L. Saunders, *Anal. Chem.*, 40 (1968) 1757.
5. E. Pungor, *Oscillometry and Conductometry*, Pergamon Press, Oxford 1965.
6. G. Johansson, K. J. Karrman and A. Norman, *Anal. Chem.*, 30 (1958) 1397.
7. F. M. Everarts, J. L. Beckers and T. P. E. M. Verheggen, in *Isotachopheresis*, Elsevier, Amsterdam, 1976, Chapter 6.
8. M. Sugawara and T. Ieiri, *J. Phys. D*, 7 (1974) L142.
9. G. H. Brown, C. N. Hoyler and R. A. Bierworth, *Theory and Application of Radio-frequency Heating*, Van Nostrand, New York, 1947, p. 30.
10. R. Parsons (Ed.), *Handbook of Electrochemical Constants*, Butterworths, London, 1959, p. 81.
11. *Handbook of Chemistry and Physics*, 58th edn., Chemical Rubber Co., Cleveland, 1977.

## Short Communication

---

### EXTRACTION—SPECTROPHOTOMETRIC DETERMINATION OF NICKEL WITH 4-CHLORO-2-NITROSO-1-NAPHTHOL AND CRYSTAL VIOLET

KYOJI TÔEI\*, SHOJI MOTOMIZU and HIROCHIKA YOKOSU\*\*

*Department of Chemistry, Faculty of Science, Okayama University, Tsushima-naka, Okayama-shi, 700 (Japan)*

(Received 21st February 1979)

*Summary.* Six nitrosonaphthol derivatives are evaluated for the determination of nickel(II) after ion-pair formation with zephiramine or crystal violet, 4-chloro-2-nitroso-1-naphthol is the best; its nickel complex forms an extractable pair with crystal violet. The apparent molar absorptivity is  $8.2 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  at 611 nm; calibration graphs are linear in the range  $0\text{--}10^{-5}$  M nickel(II).

Nitrosophenol and nitrosonaphthol derivatives are selective and sensitive colorimetric reagents for several metals, especially cobalt [1], iron [2] and palladium [3]. Such derivatives also react with nickel to form colored complexes, but the molar absorptivities of the nickel complexes are much smaller than those of the cobalt complexes. Barbalat et al. [4] stated that 2-nitroso-1-naphthol and 1-nitroso-2-naphthol react with nickel to form 1:2 complexes which can be extracted into chloroform, and that compounds of the type  $\text{MeA}_2 \cdot x\text{HA}$  ( $\text{Me} = \text{Cu}^{2+}$  or  $\text{Ni}^{2+}$ ) are not formed. In contrast, Callahan et al. [5], reporting the formation constants, stated that nitrosonaphthols react with nickel to form 1:3 complexes in aqueous 50% dioxane. 2-Nitroso-1-naphthol-4-sulfonic acid reacts with nickel to form a 1:3 complex, which can be extracted into chloroform with zephiramine [6]. Accordingly, nitrosonaphthols and their derivatives are expected to react with nickel to form an anionic 1:3 complex, which can be extracted into immiscible solvents as ion-pairs with large cations.

In this work, the extraction mechanism of nickel was studied by using six nitrosonaphthol derivatives and tetradecyldimethylbenzylammonium chloride (zephiramine) or crystal violet. A sensitive determination method for nickel with 4-chloro-2-nitroso-1-naphthol and crystal violet is reported.

#### *Experimental*

*Apparatus.* Instrumentation included a Hitachi-Horiba Model F-5ss pH

---

\*\*Present address: Tokyo Kasei Kogyo Co., Ltd., 6-15-9, Toshima, Kita-ku, Tokyo, Japan.

TABLE 1

Nitrosonaphthol derivatives and their acid dissociation constants in an aqueous solution ( $\mu = 0.1$ , 25°C)

Reagent		Wavelength (nm)	$pK_a$
I	1-Nitroso-2-naphthol	420	7.83 $\pm$ 0.04
II	6-Chloro-1-nitroso-2-naphthol	425	7.48 $\pm$ 0.03
III	6-Bromo-1-nitroso-2-naphthol	420	7.52 $\pm$ 0.04
IV	2-Nitroso-1-naphthol	434	7.41 $\pm$ 0.04
V	4-Chloro-2-nitroso-1-naphthol	450	6.98 $\pm$ 0.04
VI	4-Bromo-2-nitroso-1-naphthol	450	6.88 $\pm$ 0.04

meter, a Hitachi Perkin-Elmer Model 139 spectrophotometer and a Hitachi Model EPS-3T recording spectrophotometer (10-mm and 20-mm glass cells) and an Iwaki Model KM shaker.

*Reagents.* Nitrosonaphthol derivatives (see Table 1) were obtained by nitrosation of the parent compounds as described previously [7, 8]; the products were recrystallized twice from ethanol and once from water. The 6-chloro-derivative was synthesized from 2-naphthol-6-sulfonic acid [9], and the 4-bromo parent compound from 1-aminonaphthol [10] as follows. First, recrystallized 4-bromo-1-acetonaphthalide (5 g), synthesized from 1-aminonaphthol, was refluxed for 10 h in 100 ml of saturated ethanolic potassium hydroxide solution; distilled water was then added to precipitate 4-bromo-1-naphthylamine, which was recrystallized from ethanol. This product was diazotized with sodium nitrite in dilute sulfuric acid, and the solution was added dropwise to boiling water. After filtering hot and cooling the filtrate, 4-bromo-1-naphthol precipitated. Other parent compounds were purchased from the Tokyo Kasei Kogyo Co., Japan.

For use, the recrystallized nitrosonaphthols were dissolved in ca. 0.01 M sodium hydroxide solution.

The acid dissociation constants of the synthesized nitrosonaphthols were determined spectrophotometrically (20-cm cells) in aqueous solution at 25°C and ionic strength 0.1 (potassium chloride). The results are shown in Table 1.

*Nickel(II) solution.* Sponge nickel metal (99.999%, Mitsuwa Chemical Company) was dissolved in hydrochloric acid; the solution was diluted to a final acidity of 0.1 M and standardized by EDTA titration.

*Tetradecyldimethylbenzylammonium chloride solution.* Zephiramine chloride (Dotite, Dojindo Co. Ltd., was dried at reduced pressure (about 5 mm Hg) and 50–60°C to constant weight, and dissolved in distilled water. Solutions were not standardized [11].

*Crystal violet solution* ( $10^{-3}$  M). Crystal violet (0.408 g, Merck) was dissolved in 1 l of 0.001 M hydrochloric acid solution.

*Buffer solutions.* Acetic acid–sodium acetate, potassium dihydrogenphosphate–disodium hydrogenphosphate, ammonia–ammonium chloride, and sodium hydroxide solutions were used.

**Recommended procedure.** Pipette 5 ml of sample solution into a stoppered test tube, and add 0.5 ml of aqueous 4-chloro-2-nitroso-1-naphthol solution ( $10^{-3}$  M) and 1 ml of buffer solution (pH 7). Mix well and add 0.5 ml of crystal violet solution ( $10^{-3}$  M). Shake with 5 ml of toluene for 30 min. After phase separation, measure the absorbance of the organic phase at 611 nm. The calibration graph was rectilinear in the range  $0-1 \times 10^{-5}$  M nickel(II).

### Results and discussion

**Effect of experimental variables.** Shaking the aqueous phase with organic phase in the presence of zephiramine or crystal violet for 30 min sufficed for complete extraction of all the complexes.

The effect of pH on the extraction of the nickel complex was examined by a general procedure similar to that recommended above; the concentrations of nickel(II), nitrosonaphthols and zephiramine (Zeph) were  $2 \times 10^{-5}$ ,  $2 \times 10^{-4}$  and  $2 \times 10^{-4}$  M, respectively, and the concentrations of nickel(II),

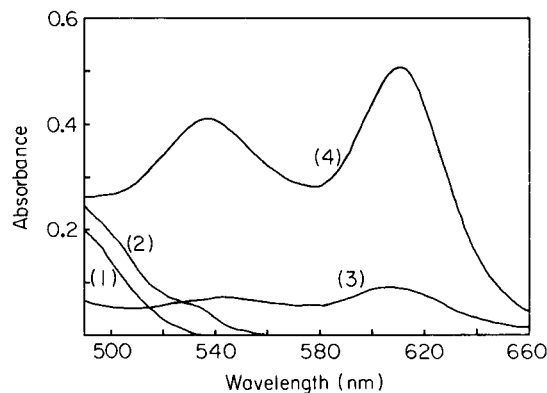


Fig. 1. Absorption spectra for 4-chloro-2-nitroso-1-naphthol (R) in toluene. (1)  $[R] = 5 \times 10^{-5}$  M,  $[Zeph] = 5 \times 10^{-5}$  M; (2)  $[Ni] = 5 \times 10^{-6}$  M,  $[R] = 5 \times 10^{-5}$  M,  $[Zeph] = 5 \times 10^{-5}$  M; (3)  $[R] = 1 \times 10^{-4}$  M,  $[CV] = 2 \times 10^{-4}$  M; (4)  $[Ni] = 5 \times 10^{-6}$  M  $[R] = 1 \times 10^{-4}$  M,  $[CV] = 2 \times 10^{-4}$  M; reference, toluene; pH 7.

TABLE 2

Optimal pH region for the extraction of nickel complexes of reagents I-VI (see Table 1) into toluene

Reagent	Cation	Optimal pH	Recommended pH	Reagent	Cation	Optimal pH	Recommended pH
I	Zeph	6.5-8.0	7.5	IV	Zeph	5.5-7.5	6.5
	CV	6.5-8.0	7.5		CV	6.0-7.5	7.5
II	Zeph	6.5-7.5	7.0	V	Zeph	5.5-9.0	7.0
	CV	6.5-7.5	7.0		CV	6.0-9.5	7.5
III	Zeph	5.5-8.0	6.5	VI	Zeph	6.0-7.0	6.5
	CV	6.5-8.0	7.5		CV	6.0-7.5	7.0

TABLE 3

Molar absorptivities ( $l \text{ mol}^{-1} \text{ cm}^{-1}$ )

Reagent	Zephiramine				Crystal violet		
	in chloroform		in toluene		in toluene		
	$\lambda(\text{nm})$	$\epsilon(\times 10^4)$	$\lambda(\text{nm})$	$\epsilon(\times 10^4)$	$\lambda(\text{nm})$	$\epsilon(\times 10^4)$	Abs. <sup>a</sup>
I	470	1.2		— <sup>b</sup>			— <sup>c</sup>
II	460	1.7	460	1.7	614	7.0	0.35
III	460	1.7	470	1.2	606	6.1	0.30
IV	516	1.2		— <sup>b</sup>	613	— <sup>d</sup>	0.14
V	530	1.2	530	1.2	611	8.2	0.41
VI	530	1.3	530	1.2	606	6.5	0.32

<sup>a</sup>Absorbances obtained in the standard procedure when  $[\text{Ni}^{2+}] = 5 \times 10^{-6} \text{ M}$ ,  $[\text{R}] = 1 \times 10^{-4} \text{ M}$  and  $[\text{CV}] = 2 \times 10^{-4} \text{ M}$ . <sup>b</sup>Precipitation of the complex in the organic or aqueous phase. <sup>c</sup>Ion-pair not extracted at all. <sup>d</sup>Calibration graph was curved.

nitrosonaphthols and crystal violet (CV) were  $5 \times 10^{-6}$ ,  $1 \times 10^{-4}$  and  $2 \times 10^{-4} \text{ M}$ , respectively. The optimal pH regions, where the absorbances of the organic phase were the largest and constant, are shown in Table 2 along with the pH recommended for use.

*Absorption spectra.* Absorption spectra were obtained by a similar general procedure. A representative example (4-chloro-2-nitroso-1-naphthol and its complexes) is shown in Fig. 1. Table 3 shows the maximum absorption wavelengths and molar absorptivities of the nickel complexes. In the case of crystal violet, the absorbances of the organic phase are also shown.

When zephiramine and crystal violet were not added to the extraction system and the concentrations of nickel ion and nitrosonaphthol were  $4 \times 10^{-5}$  and  $4 \times 10^{-4} \text{ M}$ , respectively, the percentage extraction of the nickel complexes of reagents I–VI (see Table 1) into chloroform were about 70, 70, 70, 2, 60 and 6% respectively. In the presence of zephiramine, the nickel complexes of all six nitrosonaphthols were extracted quantitatively into chloroform, but the nickel complexes of the nitrosonaphthols without a halogen-substituent could not be extracted quantitatively into toluene and precipitated in the organic or aqueous phase. In the presence of crystal violet, the 2-nitroso-1-naphthol derivatives were extracted more readily than those of 1-nitroso-2-naphthol, and the chloro-substituent enhanced the extraction of the nickel complex more than the bromo-substituent. As a result of these tests, 4-chloro-2-nitroso-1-naphthol is recommended as the most sensitive of these reagents for nickel.

*Composition of the extracted species.* The compositions of the nickel complexes (Ni:reagent) were examined by the molar ratio method, in which the concentration of the nickel ion was varied. The results obtained (Table 4) show that the composition (Ni:R) of the extracted complexes into organic phases is 1:3, and the composition (Ni:cation) is 1:1. Thus the extraction equilibria are

TABLE 4

Composition of the extracted species, (Ni:R) and (Ni:Zeph or CV)

Reagent	(Ni:R) with Zeph		(Ni:Zeph)		(Ni:R) with CV	(Ni:CV)
	CHCl <sub>3</sub>	C <sub>7</sub> H <sub>8</sub>	CHCl <sub>3</sub>	C <sub>7</sub> H <sub>8</sub>	C <sub>7</sub> H <sub>8</sub>	C <sub>7</sub> H <sub>8</sub>
I	1:3.0	—	1:1.1	—	—	—
II	—	—	1:1.0	1:1.0	—	—
III	1:3.2	—	—	—	—	—
IV	1:3.2	—	1:1.2	—	—	—
V	1:3.5	1:3.2	1:1.1	1:1.0	1:3.3	1:1.1
VI	1:3.0	1:3.1	1:1.0	1:1.1	1:3.3	1:1.2



where HR and C<sup>+</sup> are nitrosonaphthols and zephiramine or crystal violet, respectively, and subscript "o" refers to the organic phase.

*Other cationic dyes and extracting solvents.* Rhodamine B, malachite green and brilliant green were also examined, but crystal violet showed superior properties. In the extraction with crystal violet, benzene was as efficient a solvent as toluene, but toluene is preferable because of its lower vapor pressure.

### Conclusions

In contrast to the results obtained by Barbalat et al. [4], nickel reacts with nitrosonaphthols to give 1:3 complexes which are monovalent anions and can be extracted into an organic phase as ion-pairs with large cations. The extraction of nickel complexes with crystal violet into toluene is advantageous for spectrophotometry, giving high sensitivity and rapid phase separation. In such extractions, the 2-nitroso-1-naphthol complexes are more readily extracted than the 1-nitroso-2-naphthol complexes, presumably because the 2-nitroso-1-naphthols form more stable nickel 1:3 complexes; the stability constants of the 1:3 nickel complexes of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol in aqueous 50% dioxane are 23.05 and 24.62, respectively [5]. Furthermore, a nitrosonaphthol possessing a strong electron-attracting group is preferable. The large monovalent anions with charges well distributed as a result of the electron-attracting force of the halogen atom, form ion-pairs more easily with large cations. These ion-pairs are readily extracted into organic phases. Thus, 4-chloro-2-nitroso-1-naphthol is the best of the six reagents examined. The ion-pair between the nickel complex of 4-chloro-2-nitroso-1-naphthol and crystal violet is extracted quantitatively into toluene, and by measuring the absorption of crystal violet in toluene at 611 nm, nickel can be determined spectrophotometrically with excellent sensitivity.



## REFERENCES

- 1 K. Tōei and S. Motomizu, *Analyst*, 101 (1976) 497.
- 2 K. Tōei, S. Motomizu and T. Korenaga, *Analyst*, 100 (1975) 629.
- 3 K. Tōei, S. Motomizu and S. Hamada, *Anal. Chim. Acta*, 101 (1978) 169.
- 4 Yu. A. Barbalat, G. N. Zubacheva and V. M. Peshkova, *Zh. Anal. Khim.*, 26 (1971) 2326.
- 5 C. M. Callahan, W. C. Fernelius and B. P. Block, *Anal. Chim. Acta*, 16 (1957) 101.
- 6 S. Motomizu and K. Tōei, *Anal. Chim. Acta*, 97 (1978) 335.
- 7 K. Tōei and S. Motomizu, *Nippon Kagaku Zasshi*, 92 (1971) 92.
- 8 T. Korenaga, S. Motomizu and K. Tōei, *Nippon Kagaku Kaishi*, (1972) 2445.
- 9 A. Claus and O. Zimmermann, *Ber.*, 14 (1881) 1477.
- 10 P. Rother, *Ber.*, 4 (1871) 850.
- 11 K. Tōei and K. Kawada, *Jpn. Anal.*, 21 (1972) 1510.

## Short Communication

---

# THE FLUORESCENT REACTION PRODUCT IN THE DETERMINATION OF AROMATIC ALDEHYDES WITH 2,2'-DITHIOBIS(1-AMINO-NAPHTHALENE)

KENJI OHTSUBO, YUJI OKADA, KIYOSHI ZAITSU and YOSUKE OHKURA\*

*Faculty of Pharmaceutical Sciences, Kyushu University 62, Maidashi, Higashi-ku, Fukuoka 812 (Japan)*

(Received 6th April 1979)

*Summary.* The fluorescent product formed from benzaldehyde or *p*-hydroxybenzaldehyde with the reagent in the presence of tri-*n*-butylphosphine, phosphite and sulphite has been characterized by elemental and structural analysis as the corresponding 2-arylnaphtho[1,2-*d*]thiazole.

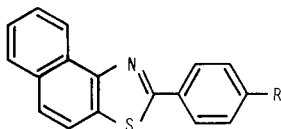
A sensitive and selective fluorimetric method for the determination of aromatic aldehydes has been reported [1] based on their reactions in dilute sulfuric acid with 2,2'-dithiobis(1-aminonaphthalene) (DTAN) in the presence of tri-*n*-butylphosphine, phosphite and sulfite ions at ambient temperature. This communication describes the isolation and characterization of the fluorescent compounds produced under the conditions of the method from benzaldehyde and *p*-hydroxybenzaldehyde.

### *Experimental*

*Reagents and apparatus.* All chemicals were of reagent grade unless otherwise specified. Double-distilled water was used throughout. A solution containing DTAN (0.4 g l<sup>-1</sup>) and tri-*n*-butylphosphine (0.8 g l<sup>-1</sup>) in 7.5% (w/v) sulphuric acid was prepared as previously described [1].

Fluorescence spectra were measured with a Hitachi MPF-4 spectrofluorimeter in quartz cells of 10 × 10-mm optical pathlength; the slit-widths, in terms of wavelengths, were set at 10 nm in both the exciter and analyzer. The spectra are uncorrected. U.v. spectra were measured with a Shimadzu UV 200S spectrophotometer in ethanolic solutions in 10-mm quartz cells. I.r. spectra were measured with a Nihonbunko DS 701G spectrometer in potassium bromide pellets. <sup>1</sup>H- and <sup>13</sup>C-n.m.r. spectra were obtained with JEOL JNM-PS-110 and JEOL FX-100 spectrometers at 100 and 25 MHz, respectively, for ca. 15% dimethylsulfoxide-*d*<sub>6</sub> solutions of samples containing tetramethylsilane as an internal standard. In <sup>13</sup>C-n.m.r. spectra, signals from quaternary carbons were assigned by both the complete decoupling and off-resonance decoupling techniques. Mass spectra were measured with a JEOL JMS-01-SG spectrometer. Melting points are uncorrected.

*Isolation of the product from benzaldehyde and its spectral properties.* Freshly distilled benzaldehyde (120 mg) dissolved in 400 ml of water was mixed with 800 ml of DTAN solution and 200 ml each of aqueous 15% (w/v) sodium phosphite pentahydrate solution and aqueous 0.05% (w/v) sodium sulfite solution. The mixture was warmed at 37°C for ca. 20 h with stirring; the yellowish precipitate was isolated, washed with small portions of water, dissolved in ethanol, decolorized with a small amount of charcoal, and recrystallized from ethanol to colorless prisms (I; m.p. 103°C; yield, 56 mg). No depression of m.p. was observed on admixture of I with an authentic sample of 2-phenylnaphtho[1,2-d]thiazole [2]. Its u.v., i.r., <sup>1</sup>H- and <sup>13</sup>C-n.m.r., and mass spectra were identical with those of an authentic sample.



(I), R = H ; (II), R = OH

*Isolation of the product from p-hydroxybenzaldehyde and its spectral properties.* *p*-Hydroxybenzaldehyde (120 mg) dissolved in 1 ml of methanol was mixed with 250 ml of water, 500 ml of DTAN solution and 125 ml each of aqueous 15% (w/v) sodium phosphite pentahydrate solution and aqueous 0.05% (w/v) sodium sulfite solution. The mixture was warmed at 37°C for ca. 20 h with stirring; the pale yellow precipitate was filtered, washed with water and dried in vacuo, dissolved in a small amount of ethyl acetate, and poured onto a glass column (1.2 cm diam., 50 cm long) packed with ca. 5 g of silica gel G (Merck) and eluted with ethyl acetate. The largest fraction, which showed a blue fluorescence, was concentrated to dryness in vacuo. The residue, dissolved in a small amount of benzene, was again subjected to silica gel column chromatography with benzene as eluant. The main fraction was concentrated almost to dryness in vacuo and recrystallized from *n*-hexane to colorless prisms (II; m.p. 142°C; yield, 66 mg). Calcd. for C<sub>17</sub>H<sub>11</sub>NOS: 73.7% C, 4.0% H, 5.0% N; found 73.7% C, 4.0% H, 5.05% N. U.v. spectrum (in ethanol) λ nm (logε): 217(4.49), 231(4.56), 265(4.21), 322(4.29), 344(4.39). I.r. spectrum ν<sub>max</sub> cm<sup>-1</sup>: 3470(OH), 1607 and 1590 (aromatic C=C and/or C=N), 1525 and 1385 (thiazole ring [3]). <sup>1</sup>H-n.m.r. spectrum δ (ppm): 7.02 (2H, doublet, *J* = 8.7 Hz, aromatic protons), 6.92 (2H, doublet, *J* = 8.7 Hz, aromatic protons), 7.55–8.80 (6H, complex multiplet, aromatic protons), 10.2 (1H, broad singlet hydroxyl proton, disappeared on adding a small amount of heavy water). <sup>13</sup>C-n.m.r. spectrum

$\delta$  (ppm): 166.611 (singlet, a quaternary carbon at which hydroxyl group is substituted), 151.682, 149.153, 130.283, 127.322 and 124.015 (singlet each, 6 quaternary carbons, the signal at 149.153 probably arising from carbon at the 9 and 10 positions of the naphthalene moiety). Mass spectrum *m/e*: 277 ( $M^+$ , base peak), 249 ( $M^+ - CO$ ), 248 ( $M^+ - CHO$ ).

### Results and discussion

The conditions described for the isolation of the fluorescent products were almost identical to those in the method of determination, except for prolonging the reaction time and omitting the addition of  $\beta$ -mercaptoethanol to stop the fluorescence development.

The excitation and emission spectra of compound I, dissolved in the reagent blank for the method of determination, were identical with those of the reaction mixture of benzaldehyde. From the data described, I was identified as 2-phenylnaphtho[1,2-d]thiazole.

The excitation and emission spectra of compound II, dissolved in the reagent blank for the method of determination, were identical with those of the reaction mixture of *p*-hydroxybenzaldehyde. The elemental analysis data and the molecular ion in the mass spectrum of II indicate that the compound has a molecular formula,  $C_{17}H_{11}NOS$ , consistent with that of 2-(*p*-hydroxyphenyl)naphtho[1,2-d]thiazole, the expected reaction product from *p*-hydroxybenzaldehyde. The presence of a *p*-hydroxyphenyl group is suggested by the two doublets in the  $^1H$ -n.m.r. spectrum. The i.r.,  $^1H$ - and  $^{13}C$ -n.m.r., and mass spectral patterns of II are in agreement with the thiazole structure.

From these observations, the fluorescent product of a given aromatic aldehyde in this reaction is the corresponding 2-arylnaphtho[1,2-d]thiazole; the carbon atom of the aldehyde group is incorporated in the five-membered heterocyclic moiety of the fluorescent compound under the analytical reaction conditions; this is analogous to the fluorescence reactions of aromatic aldehydes with 2-aminothiophenol [4] and with 1,2-diaminonaphthalene [5] to yield 2-arylbenzothiazole [4, 6] and 2-arylnaphtho[1,2-d]imidazole [7], respectively.

A Grant from Takeda Science Foundation (Osaka, Japan) is gratefully acknowledged.

### REFERENCES

- 1 Y. Ohkura, K. Ohtsubo, K. Zaitso and K. Kohashi, *Anal. Chim. Acta*, 99 (1978) 317.
- 2 P. Jacobson, *Ber.*, 20 (1887) 1895.
- 3 J. B. Lambert, H. F. Shurvell, L. Verbit, R. G. Cooks and G. H. Stout, *Organic Structural Analysis*, Macmillan, New York, 1976, p. 284.
- 4 T. Uno and K. Taniguchi, *Bunseki Kagaku*, 21 (1972) 76.
- 5 Y. Ohkura and K. Zaitso, *Talanta*, 21 (1974) 547.
- 6 S. Nakamura, K. Taniguchi and T. Furubashi, *Yakugaku Zasshi*, 92 (1972) 411.
- 7 K. Zaitso and Y. Ohkura, *Chem. Pharm. Bull. (Tokyo)*, 23 (1975) 1057.

## Short Communication

---

### SIMULTANEOUS DETERMINATION OF NITROGEN, CARBON, AND HYDROGEN BY THERMAL NEUTRON PROMPT $\gamma$ -RAY SPECTROMETRY

ERNEST S. GLADNEY, DAVID B. CURTIS and EDWARD T. JURNEY

*University of California, Los Alamos Scientific Laboratory, P.O. Box 1663, Los Alamos,  
NM 87545 (U.S.A.)*

(Received 25th April 1979)

*Summary.* Thermal neutron prompt  $\gamma$ -ray spectrometry is applied to the determination of nitrogen, carbon, and hydrogen in environmental materials. Useful, simultaneous, non-destructive analyses with 1-g samples can be achieved at concentrations greater than 500 ppm, 10% and 5 ppm, respectively.

In-situ spectrometry of prompt  $\gamma$ -rays produced by irradiating materials in a thermal neutron flux provides a means of elemental analysis that can have advantages over alternative methods. Two primary factors govern the detection limit for elemental analysis based on  $(n, \gamma)$  reactions: the partial capture cross-section for producing a useful transition and the elemental composition of the matrix material being examined. Limitations of the first type are fundamental and can be assessed from the known nuclear properties of the elements. Figure 1 illustrates these considerations [1–3]; plotted are the partial thermal  $(n, \gamma)$  cross-sections per unit mass of the most intense transition (regardless of energy) emitted by most of the elements. In most cases the intensity of the characteristic  $\gamma$ -rays varies over about 2.5 orders of magnitude. It is in those cases where elements have a substantial part of the capture cross-section concentrated into one  $\gamma$ -energy that prompt  $(n, \gamma)$  spectrometry can be considered as a vital tool for trace analysis. Otherwise, the main analytical usefulness of prompt  $\gamma$ -ray spectrometry lies in its ability to give fairly rapid, non-destructive determinations of many elements at moderately high concentrations, generally without chemical separations or other complicated sample preparation. An earlier paper from this Laboratory demonstrated the utility of the technique for measuring submicrogram quantities of boron and cadmium in complex materials [4]. Subsequent work has been concerned with applications where more conventional analytical techniques are difficult or manpower-intensive. Detailed studies have been made of the determination of sulfur in complex matrices [5] and of the analysis of standard lithic materials for most of their major and minor constituents [6]. The work reported here is an assessment of the feasibility

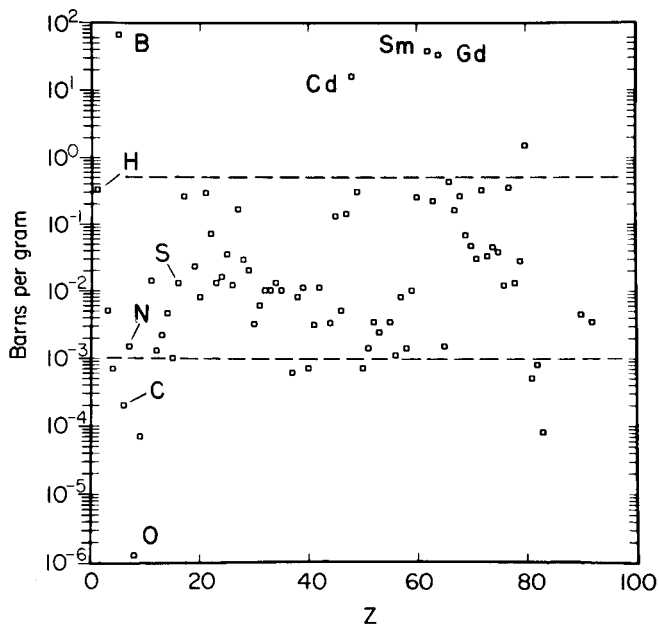


Fig. 1. Plot of the single most intense prompt  $\gamma$ -ray emitted by the elements after thermal neutron capture. Points for the noble gases and for radioactive elements, except thorium and uranium, are not included.

of determining carbon, nitrogen and hydrogen by prompt  $\gamma$ -ray spectrometry. These are elements which have traditionally been measured by destructive combustion methods [7] or, in the case of nitrogen, by the classical Kjeldahl determination [8]. None of the three is accessible by conventional neutron activation analysis, because, in all three cases, no useful radioactive products result from neutron capture.

The information plotted in Fig. 1 does not consider variations in detector efficiency relative to the energy of the  $\gamma$ -ray. Therefore, as a practical matter, relative detection limits among elements will vary from those shown in Fig. 1, depending on the  $\gamma$ -ray energies. Ignoring this consideration, Fig. 1 shows that the limits of detection for nitrogen will be roughly an order of magnitude greater than for sulfur and similarly the limit for carbon will be 10 greater than that for nitrogen. Extrapolation from the detection limits determined earlier for sulfur [5] indicates that determinations for these elements will be restricted to materials containing more than 0.5% N or 5% C. The analytical sensitivity for hydrogen is relatively high and detection should be possible in materials containing a few micrograms of hydrogen.

The work discussed here was restricted to the analysis of stoichiometric salts, organic compounds and nitrogenous and carbonaceous natural materials. Clearly, the bulk ( $n, \gamma$ ) cross-section and the complexities of the

constituent spectra contribute to a background which sets a limit on the ability to observe weak  $\gamma$ -lines in many matrices. A more insidious problem is that of an element in the matrix which produces an intense  $\gamma$ -peak with an energy close to that from the element of interest. Various materials were analyzed for carbon, nitrogen and hydrogen, however, by using  $\gamma$ -rays which appeared to be free of interferences and readily observable above the background. These analytical results were compared with known quantities of the elements in the materials to determine the accuracy and precision that can be obtained by the proposed technique.

### *Experimental*

Analyses were done by placing the sample in an irradiation channel in the thermal column of the Los Alamos Omega West Reactor (OWR). The physical configuration is such that only  $\gamma$ -rays emitted from the sample are seen by a Ge(Li) detector located externally to the thermal column. Details of the prompt  $\gamma$ -ray facility have been reported [4-6, 9].

A beryllium sample holder that could accommodate about 1 g of material was specially built, because  $\gamma$ -radiation from the normal containers (graphite and polyethylene) would be indistinguishable from those from the samples being analyzed. Beryllium was chosen because it has a small neutron capture cross-section and can be obtained in high purity. The irradiation channel was evacuated prior to data collection to avoid biases resulting from neutron capture by nitrogen, CO<sub>2</sub>, water and other constituents of the atmosphere.

Amplifier gains were set to accumulate  $\gamma$ -rays within an energy range of 1.5-11.0 MeV in the memory of a 4096-channel pulse-height analyzer. Counting times varied between 5 and 40 min depending upon elemental concentrations. A neutron monitor measured the neutron fluence during each period of data collection. All results were normalized to this fluence to compensate for neutron flux variations during the irradiations. Concentrations were calculated by direct comparison of the fluence-normalized intensities of a particular  $\gamma$ -ray in a standard and in the sample being analyzed.

### *Results and discussion*

Five different capture  $\gamma$ -ray lines were investigated for nitrogen determinations. The 5269- and 5298-keV  $\gamma$ -rays gave equivalent accuracy and precisions, while the 1888-, 5532-, and 10824-keV lines yielded less accurate and rather imprecise results. Only the first two lines were used for the data in Table 1. Since these two lines lie very close together, with no discernible interferences, they were summed to yield lower detection limits. Two  $\gamma$ -rays, 3684 and 4945 keV, were examined for the carbon measurements. The former has an overlapping nitrogen line, so only the latter was used for the data reported in Table 2. Hydrogen has only a single transition, 2223 keV. When these  $\gamma$ -rays were used the following detection limits were achieved with 1-g samples irradiated for 1 h: N, 500 ppm; C, 10%; and H, 5 ppm.

TABLE 1

Nitrogen concentrations in environmental standards (%)

Standard	LASL (This work)	Previous work <sup>a</sup>	Ratio LASL/Previous
<i>NBS</i>			
193	13.5 ± 0.1	13.85	0.97
194	13.5 ± 1.1	12.15	1.11
1570	6.0 ± 0.4	(5.9)	1.02
1571	2.7 ± 0.4	2.76	0.98
1573	4.9 ± 0.2	(5.0)	0.98
1575	1.3 ± 0.2	(1.2)	1.08
1577	10.4 ± 0.8	10.6	0.98
1632	1.2 ± 0.2	None	—
<i>ISGS Coal</i>			
15263	1.53 ± 0.11	1.37	1.12
16139	1.30 ± 0.08	1.23	1.06
16408	1.17 ± 0.11	1.35	0.87
14630	1.72 ± 0.13	1.60	1.08
15231	1.36 ± 0.10	1.43	0.95
17215	1.76 ± 0.08	1.60	1.10
		$\bar{x} \pm \sigma$	1.02 ± 0.08

<sup>a</sup>Values in parentheses are NBS "informational values."

The results of analyses of a variety of National Bureau of Standards (NBS) Standard Reference Materials (SRM), Eastman-Kodak organometallic atomic absorption standards, and Illinois State Geological Survey (ISGS) Standard Reference Coals are presented in Tables 1 and 2. Each measurement represents the mean ± one standard deviation amongst three replicate aliquots of each standard material. NBS certified and informational values are taken from the relevant certificates. Carbon content, not reported by NBS, was determined by another Los Alamos analytical group using classical gravimetric combustion techniques: samples were burned in a stream of oxygen at 1100°C, and the resulting gases were scrubbed to remove oxides of nitrogen and sulfur, water and halogens before carbon dioxide was absorbed in Ascarite and weighed. Some analyses were cross-checked with a Leco Wide-Range Carbon Analyzer.

Elemental concentrations in the Eastman Kodak standards were calculated from the lot analyses provided by the manufacturer. The ISGS used American Society for Testing and Materials standard methods of ultimate and proximate analyses of coal to determine the values reported for nitrogen, carbon and hydrogen [10]. For each element, the ratio of the present value to other values was calculated; a ratio greater than one indicates a positive bias while a ratio of less than one reflects a negative bias in the present results. The summarized ratios of 1.02 ± 0.08,



TABLE 2

Carbon and hydrogen concentrations in environmental standards (%)

Standard	Carbon			Hydrogen		
	LASL (This work)	Previous work <sup>a</sup>	Ratio LASL/Previous	LASL (This work)	Previous work	Ratio LASL/Previous
<i>Kodak</i>						
(C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> FO	70 ± 15	66	1.06	4.8 ± 0.02	4.6	1.04
(C <sub>20</sub> H <sub>34</sub> O <sub>2</sub> )Ni	63 ± 3	60	1.05	8.0 ± 0.4	8.6	0.93
(C <sub>20</sub> H <sub>34</sub> O <sub>4</sub> )Pb	41 ± 4	44	0.93	6.5 ± 0.3	6.2	1.05
(C <sub>27</sub> H <sub>27</sub> O <sub>6</sub> )Fe	60 ± 3	60	1.00	5.0 ± 0.3	5.0	1.00
<i>ISGS-Coal</i>						
15263	69 ± 4	73.2	0.94	4.5 ± 0.2	5.3	0.85
16139	69 ± 4	66.2	1.04	4.4 ± 0.2	4.6	0.96
16408	72 ± 4	71.2	1.01	4.5 ± 0.3	4.9	0.92
14630	76 ± 5	73.7	1.03	4.5 ± 0.2	4.8	0.94
15231	68 ± 4	68.1	1.00	5.4 ± 0.3	5.0	1.08
17215	67 ± 4	65.3	1.03	4.7 ± 0.2	5.0	0.94
<i>NBS</i>						
1570	—	—	—	5.6 ± 0.1	None	
1571	47 ± 5	45.8 ± 1.3	1.03	6.1 ± 0.1	None	
1573	—	—	—	5.0 ± 0.1	None	
1575	54 ± 2	50.4 ± 1.5	1.07	6.5 ± 0.1	None	
1577	51 ± 2	49.6 ± 1.5	1.03	7.0 ± 0.1	None	
1632	73 ± 3	69.6 ± 2.1	1.05	4.3 ± 0.1	None	
			$\bar{x} \pm \sigma$ 1.02 ± 0.04			$\bar{x} + \sigma$ 0.97 ± 0.07

<sup>a</sup>Previous work on NBS materials done by LASL Group CMB-1 by combustion.

1.02 ± 0.04, and 0.97 ± 0.07 for nitrogen, carbon and hydrogen, respectively (see Tables) quantitatively demonstrate that capture  $\gamma$ -ray techniques are both accurate and precise for the measurements of these elements in environmental and synthetic matrices.

The method provides an alternative to combustion or Kjeldahl methods for these determinations. It is also applicable to matrices which will not burn.

We thank Herman Ashley of LASL Group CMB-1 for his carbon analyses and the staff of the OWR for assistance with the irradiations. Work performed under the auspices of the U.S. Department of Energy.

## REFERENCES

- 1 N. C. Rasmussen, Y. Hukai, T. Inoue and V. Orphan, Report AFCRL-69-0871, U.S. Air Force, Cambridge Research Lab., Bedford, MA, 1969.
- 2 D. Duffey, A. El-Kady and F. E. Senftle, Nucl. Instrum. Methods, 80 (1970) 149.
- 3 F. E. Senftle, H. D. Moore, D. B. Leep, A. El-Kady and D. Duffey, Nucl. Instrum. Methods 93 (1971) 425.
- 4 E. S. Gladney, E. T. Journey and D. B. Curtis, Anal. Chem., 48 (1976) 2139.
- 5 E. T. Journey, D. B. Curtis and E. S. Gladney, Anal. Chem., 49 (1977) 1741.
- 6 E. S. Gladney, D. B. Curtis and E. T. Journey, J. Radioanal. Chem., 46 (1978) 299.
- 7 R. D. Condon, Microchem. J., 10 (1966) 408.
- 8 R. B. Bradstreet, The Kjeldahl Method for Organic Nitrogen, Academic Press, New York, 1965.
- 9 E. T. Journey, H. T. Motz and S. H. Vegors, Jr., Nucl. Phys. A, 94 (1967) 351.
- 10 R. R. Ruch, H. J. Gluskoter and N. F. Shrimp, Environ. Geol. Notes, Ill. State Geol. Surv., 72 (1974) 13.

## Short Communication

---

### RAPID ACCURATE ANALYSIS OF METAL (OXIDE)-ON-SILICA CATALYSTS BY ATOMIC ABSORPTION SPECTROMETRY

B. A. H. G. JÜTTE, A. HEIKAMP and J. AGTERDENBOS\*

*Analytisch Chemisch Laboratorium der Rijksuniversiteit, Croesestraat 77 A, 3522 AD Utrecht (The Netherlands)*

(Received 12th February 1979)

**Summary.** The catalysts, which contain 10–60% copper, chromium, nickel and silicon, are decomposed in sealed Teflon-lined vessels and analyzed by atomic absorption spectrometry. Matrix matching and bracketing standards are applied. The RSD of a single determination is about 1% for all components.

Studies of catalysts consisting of one or more metal oxides or hydroxides on silicon dioxide have recently been of interest; the metals applied are chromium, copper and nickel and the content of each metal generally lies within the range 10–40% [1]. These catalysts were originally analyzed by classical techniques involving NaOH fusion, gravimetry as SiO<sub>2</sub> and EDTA titration of the metals [1]. This procedure is laborious, requiring technical expertise, and EDTA titrations are not applicable for all the combinations of metals of interest. Faster methods were therefore sought. The procedure described below is rapid, simple enough to be applied by non-specialized workers, and applicable without much modification to catalysts made from silicon dioxide and a wide range of metals or combinations of metals. The compositions of some typical catalysts analyzed in this work are given in Table 1.

#### *Experimental*

**Apparatus and reagents.** Uniseal Teflon-lined decomposition vessels (capacity 23 ml) and an Instrumentation Laboratories Model 351 atomic absorption spectrometer equipped with the necessary hollow-cathode lamps were used. Volumetric apparatus was all made of polythene.

The acids used were of the highest purity available (Suprapur or analytical-reagent grade) and the water was twice-distilled from quartz apparatus. Silica (Akzo Chemie, Fluid silica F-2), nickel and chromium powder (Fluka reinst) and electrolytic copper wire were used in preparation of standards.

**Matrix solution.** A solution containing 6 g of boric acid and 8 ml of 40% hydrofluoric acid in 500 ml of water is needed to dilute standard solutions of the elements to be determined and as a blank in the atomic absorption spectrometric measurements. This solution is stored in polythene flasks.

TABLE 1

Percentage composition of some catalysts analyzed

Catalyst	Cu	Ni	Cr	Si
I	—	40.1	—	37.2
II	30.3	—	—	57.2
III	22.1	—	10.7	46.7
IV	—	38.2	—	39.0

*Stock metal solutions.* Dissolve 0.50 g of the metal in 25 ml of nitric acid (1 + 1) for Cu and Ni or of hydrochloric acid (1 + 1) for Cr, with gentle heating if necessary. After cooling to room temperature, add a solution of 6 g of boric acid in 75 ml of water. Transfer the solution to a 500-ml volumetric flask, add 8 ml of 40% hydrofluoric acid and dilute the solution to the mark with water.

*Stock silicon solutions.* Ignite silicon dioxide in a muffle furnace at 900°C and cool to room temperature over P<sub>2</sub>O<sub>5</sub>. Weigh ca. 0.50 g into the Uniseal Teflon beaker and wet it with 1 ml of acid mixture (1 part HNO<sub>3</sub> to 3 parts HCl). After addition of 4 ml of 40% hydrofluoric acid, close the vessel and heat for 60 min in an oven at 120°C. After cooling for 15 min in air and 60 min in an ice bath, open the vessel. Transfer the contents to a 250-ml volumetric flask with a solution of 3 g of boric acid in 75 ml of water, and dilute the solution to the mark with water.

*Procedure for catalysts.* Weigh about 0.15 g of catalyst (dried previously at 120°C and cooled for 1 h over P<sub>2</sub>O<sub>5</sub>) into the Uniseal Teflon beaker. Then follow the procedure described above for the stock silicon solution; this gives a sample stock solution. From this solution, prepare the final solutions for measurement by suitable dilution (if necessary) with the matrix solution. These final sample solutions should give absorbance values within the range 0.6–0.9 for the element to be determined (this may require preliminary measurements), corresponding to concentrations of about 50 mg Cr l<sup>-1</sup>, 100 mg Ni l<sup>-1</sup> and 150 mg l<sup>-1</sup> for Si and Cu. These values may differ slightly depending on the apparatus and experimental conditions used (see below).

For standardization, prepare solutions of appropriate concentrations of the elements to be determined from the stock solutions by suitable mixing. These standards and the sample solutions must contain the same concentrations of boric acid and hydrofluoric acid. Matching is also required to within ± 20% in the sample and standard solutions for the other components in the sample solution that originate from the sample but are not measured; adequate matching of these concomitants is possible from a knowledge of the method of preparation of the catalyst.

*Measurements.* The instrumental settings are as follows: the spectral band-pass is 0.3 nm in all cases; the wavelengths used are 251.6 nm for Si, 425.4

nm for Cr, 222.6 nm for Cu and 351.5 nm for Ni; a nitrous oxide—acetylene flame is used for Si and Cr, and an air—acetylene flame for Cu and Ni, in accordance with the manufacturer's recommendations.

Each sample is bracketted between two standards (S1 and S2), the concentrations of which are selected empirically to give absorbances in the range 0.6—0.9 (see above). Readings are made in the order S1 (5×), sample (5×) and S2 (5×), each measurement requiring 15 readings. An integration time of 4 s is recommended.

### *Results and discussion*

The concentration of the required element in the sample,  $c_s$ , is calculated by linear interpolation from the mean absorbance values  $A_1$ ,  $A_s$  and  $A_2$  found for standard S1, sample and standard S2, respectively. The relative standard deviation (RSD) in  $c_s$  depends on the RSD of a single reading,  $RSD_r$ . Because five readings are made for each of the values  $A_1$ ,  $A_s$  and  $A_2$ , the RSD in each of these values is  $RSD_r/5^{1/2}$ . The RSD in  $c_s$  is about  $2^{1/2}$  times this value, i.e. about 0.6  $RSD_r$  or 0.7  $RSD_r$ .

Weighing errors and volumetric errors can be neglected. Experiments showed that errors arising from the chemical sample preparation are small enough to be neglected if the work is done carefully (see below, however). If the sample and standard solutions are matched as described above, any systematic error from differences in the matrices can also be neglected.

Calibration curves were found to be not exactly linear, and this feature introduces a (positive) systematic error in the value calculated for  $c_s$ . This error is at a maximum if  $c_s$  is midway between the concentrations of the two standards S1 and S2. With other factors kept constant, the error increases approximately by a factor  $p^2$  if  $(1 - R)$  increases by a factor  $p$  ( $R$  is the ratio of the concentrations of S1 and S2). Tests showed that the systematic errors introduced by the non-linearity of the calibration curve were well below 0.3% if  $R > 0.6$  for Cu,  $R > 0.7$  for Cr and Si, and  $R > 0.9$  for Ni. Curvature may depend somewhat on the apparatus and experimental conditions, however, so that checking is advised.

Under the experimental conditions described above, the value of  $RSD_r$  within the absorbance region 0.6—0.9 was about 0.7%, so that the RSD in a  $c_s$  value should be about 0.5%. However, when a catalyst containing about 20% of copper was analyzed 36 times, the RSD was found to be about 1.2% (i.e., the absolute value of the standard deviation was about 0.25%). The discrepancy between the values 1.2% and 0.5% suggests that the fluctuations between measurements are much larger than the fluctuations during the period required for making one measurement (it must be recalled that each "measurement" consists of 15 readings as described under Experimental). It is suggested, therefore, that if high demands are placed on the accuracy of the final results, a sample solution should be measured several times. This is both more effective and less time-consuming than preparing several sample solutions. It is, however, advisable that the latter procedure be applied from

time to time as a check that the sample preparation step has been done with good precision.

The precision values given above were found for copper, but very similar results were obtained for other components, so that the same procedure can be recommended.

The authors thank Drs. J. M. Ravensberg for preliminary investigations and A. J. M. Glissenaar for technical assistance.

#### REFERENCE

- 1 A. J. van Dillen, J. W. Geus, L.A.M. Hermans and J. v.d. Meijden in G. C. Bond, P. B. Wells and F. C. Tompkins (Eds.), *Proc. Int. Congr. Catal.*, 6th 1976, Vol. 2, Chemical Society, London, 1977, pp. 677-685.

## Book Reviews

---

M. L. Hitchman, *Measurement of Dissolved Oxygen*, (Volume 49 in Chemical Analysis series), Wiley-Interscience, New York, 1978, xvi + 255 pp., price £16.50.

This book is recommended reading for every practitioner of dissolved oxygen measurements. Many techniques are critically assessed with respect to applicability and limits, with emphasis on the membrane-covered polarographic detector (MPOD). A largely physical chemistry approach is taken, at least for discussions of electrochemistry, to assess the design, operation and limitations of devices. Discussions are limited to the principles of measurement, although the author's bias towards oceanography measurements is evident. References and review articles for specific applications are given throughout.

The book begins logically by describing the thermodynamic aspects of dissolved oxygen, including effects of pressure (depth), temperature and salinity on solubility and activity. The chapter on principles of voltammetry will probably do little to alleviate the author's claim that electrochemistry is not regularly used because it is inadequately learned. The chapters on the MPOD consider electrode, membrane and electrolyte selection, time response, geometry, flow rate, temperature and salt effects, and pulsed measurements. The fact that these electrodes measure activity is stressed. One chapter describes other electrochemical methods, especially the Hersch cell, and the last one discusses the Winkler method and, briefly, colorimetric and gaseous phase measurements.

There are thirteen appendices, which give more detailed derivations of some of the equations and a table of oxygen solubilities at different temperatures, pressures, and salinities.

G. D. Christian

R. M. Barnes, (Ed.), *Applications of Inductively Coupled Plasmas to Emission Spectroscopy*, Franklin Institute Press, Philadelphia, 1978, 188 pp., price \$18.95.

The stated intention of this publication, which is based on part of the 1977 Eastern Analytical Symposium, is that it should be an introduction to the subject, and it largely succeeds in this purpose. After a well reasoned review of the numerous advantages of using inductively coupled plasmas for emission spectroscopy, written by the editor, several application papers follow. The section dealing with precision and accuracy is well worth reading, not only by the tyro but by those claiming expertise, and is in accord with the reviewer's experience.

The application papers give an idea of the possible scope of the method, and will be useful to newcomers to the subject provided they ignore some of the more dogmatic statements about what can and cannot be done with ICPs; in particular, some stated limitations are excessively restrictive. This is a relatively new technique, and many of the findings may well be unique to the expert's own equipment; the degree of sophistication of equipment varies greatly in different laboratories.

S. Greenfield

E. Grunwald, D. F. Dever and P. M. Keehn, *Megawatt Infrared Laser Chemistry*, Wiley-Interscience, New York, 1978, xii + 107 pp., price \$21.50.

In five chapters, this book addresses itself to several important components in laser chemistry. Chapter 2 is devoted to some observed reactions, including reactions with  $\text{CCl}_2\text{F}_2$  and other halides of carbon. Both thermal and photo-induced reactions are discussed. Chapter 3 discusses photophysics, including coherent and incoherent absorption, detectors, pulse duration and theoretical models of vibrating molecules. Chapter 4 is devoted to molecular energy-flow patterns and discusses the transfer of energy between vibrational, rotational and translational modes. The fifth chapter is concerned with practical chemistry including the economics of the system where it is estimated that the price would be between \$20,000 and \$60,000 per metric ton for synthesis. It also discusses  $^{235}\text{U}$  separation, controllability of reaction and the effects of power, pressure and sensitizers. The scope of the process is also discussed and some reactions are studied including aromatic substitution and isotope separation. There follows an Appendix which includes terminology and the principal laser lines emitted from various kinds of laser systems.

This is perhaps the first comprehensive book on this new topic and therefore can be forgiven for being brief. It approaches the topic logically and progressively and provides a good review of laser chemistry and a comparison with thermal chemical reactions. The book is also broad enough to discuss the economics of the system and to introduce therein some of the features which would be of interest to industrial companies interested in using laser chemistry as a means of synthesis.

It would make a good book for anyone entering the field for research purposes or for investigating the economic possibilities of new avenues of industrial production. The text is brief and probably could be expanded to be several times its size with some effort. However, the important features of the phenomenon are discussed and there is a good bibliography.

J. W. Robinson

A. Pryde and M. T. Gilbert, *Applications of High Performance Liquid Chromatography*, Chapman and Hall, London, 1979, xii + 255 pp., price £10.50.

This book was written primarily as a review of progress in the applications of h.p.l.c. and the authors have restricted the discussion of chromatographic theory to those aspects which, in their view, have a direct bearing on practical results. Equipment and modes of chromatography are given slightly more attention. It is to be regretted that the discussion of solvent choice omits Snyder's work on classification by specific solute-solvent functionality interactions which allows a less empirical approach, at least to adsorption chromatography.

The main value of the book lies in the very readable application reviews (876 references up to Spring 1977) which are divided as follows: pharmaceutical (52 pp.), biochemical (58 pp.), environmental (18 pp.), and miscellaneous, including plant products, foods, organometallic and inorganic complexes, optical resolutions (10 pp.). Chromatographic conditions are given in reasonable detail and convey the potential of the methods. Appendices deal with calculation of diffusion coefficients, materials, sieves, and the use of reverse-phase h.p.l.c. to predict biological activity, etc.

Those with h.p.l.c. problems should find the book useful in retrieving data for similar separations to use as a start in method development; to that end, both compound and subject indexes are provided.

D. Thorburn Burns

J. C. Touchstone and M. F. Dobbins, *Practice of Thin Layer Chromatography*, J. Wiley, New York, 1978, 00 + 000 pp., price \$27.30.

Thin-layer chromatography is a technique of astonishing vitality. Over twenty years after its widespread adoption, it continues to develop and to find new adherents, and the recent introduction of, for example, reversed-phase and high-performance t.l.c. plates has ensured that it will remain a favourite method in many fields. In spite of the vast literature on t.l.c. there has remained a need for a clear introductory text on its principles and practice, and this volume fills the need admirably. A carefully- and clearly-written introduction is followed by chapters on stationary phases, sample preparation and application, choice of mobile phase and development techniques, and visualisation and quantification procedures. Extensive tables list suppliers and types of stationary phase, mobile phases suitable for various classes of solute, and visualisation reagents. Inevitably some of these are already somewhat out-of-date: in addition, the hazardous properties of some reagents are not emphasised, and one or two common ones (e.g. dansyl chloride) are omitted. Nonetheless the tables remain immensely valuable sources of information. Further chapters deal with the



reproducibility of t.l.c., special techniques (including less-common development procedures, radiochromatography, enzyme-inhibition methods, and combinations of t.l.c. with other methods) and preparative applications. There is a useful glossary of t.l.c. terms and a good index. The book is well produced and contains only a few trivial errors: no novice contemplating the serious application of t.l.c. to analytical problems should fail to read it.

J. N. Miller

P. A. Russell and A. E. Hutchings, *Electron Microscopy and X-ray Applications to Environmental and Occupational Health Analysis*, ISBN 0-250-40222-X, Ann Arbor Science Publishers, Ann Arbor, 1978, ix + 278 pp., price £17.65.

This volume, based on the papers presented at the Second Symposium on Environmental and Occupational Health Analysis held at Denver, Colorado in April 1977, contains 3 sections: X-ray Fluorescence (7 papers), X-ray Diffraction (5 papers), and Electron Microscopy (12 papers). With the exception of one British contribution, all are by American authors. The standard of the contributions is generally high; the presentation of this volume is satisfactory, with the exception of some free-hand illustrations. The contents range over well-known environmental topics, e.g. determinations of lead in atmospheric particulates, analyses of respirable dusts, mercury, sulfur in coals and air samples, impurities in powdered talc, the identification of asbestos, and studies of smoke plume aerosols; two of the papers give more general "state-of-the-art" reviews. This book is worthy of scrutiny by environmental and occupational health specialists but they should borrow a library copy before making a personal purchase.

P. N. Cheremisinoff and A. C. Morresi, *Air Pollution Sampling and Analysis Desk book*, ISBN 0-250-40234-3, Ann Arbor Science Publishers, Ann Arbor, 1978, vi + 489 pp., price £18.60.

In contrast to the volume reviewed immediately above, there could be a considerable demand for personal copies of this "desk book", which was written to assist engineers, managers and technicians concerned with air pollution to choose the best method for a specific problem from the many described in the literature. Although it was not written specifically for analytical chemists, this book contains a lot of information for them. The first 6 chapters are devoted to flow measurements and to the techniques and equipment available for sampling stacks, particulates, and gases (ambient and general); the next 5 chapters deal with inorganic, organic, elemental, anion, and fuel analysis; the final two chapters discuss atmospheric air quality and compare source emission limits respectively. An appendix (85 pp.) gives the standards of performance for new stationary sources, and there is a comprehensive subject index.

This is a useful, timely and pertinent book which tries to do what is claimed in the blurb on the jacket — “tells you the method to use, why it’s good, what it’s good for, and what its limitations are”. But beware of the misprints — “spectropyotometer”, “tetrachloride amercurate”, “colimeter”, etc. seemed to cause a lot of problems for the printer. There is a great deal of information in this book, but its applicability outside the U.S.A. may be restricted.

D. M. W. Anderson

## Announcement

---

### 8th International Microchemical Symposium

The Austrian Society of Microchemistry and Analytical Chemistry will organize the 8th International Microchemical Symposium in Graz on August 25–30th, 1980. The aim of this symposium, to which about 600 participants from all over the world are expected, will be to deal with the most modern areas of microchemistry in theory, synthesis and analysis and intends to emphasize interdisciplinary relations between the different fields of chemistry, biochemistry, clinical chemistry, medical chemistry, pharmacy, physics and material sciences.

Further information from: Prof. Dr. A. Holasek, Institut für Medizinische Biochemie, Universität Graz, Harrachgasse 21, A-8010 Graz, Austria.

## Errata

---

R. S. Collard and W. A. Pryor, A Specific Spectrophotometric Determination of Ozone in Air in the Presence of Sulfur Dioxide and Nitrogen Oxides. *Anal. Chim. Acta*, 108 (1979) 255–260.

- p. 255. The final sentence of the first paragraph should read:  
Additionally, the immediate separation of the formaldehyde produced in the ozonolysis step ensures that formaldehyde does not undergo further reaction prior to determination.
- p. 257, line 9 of the text should read:  
DPE impinger in the sampling train, and determine the formaldehyde concentration.
- p. 258. The first sentence of the second paragraph should read:  
The molozonide, I, produced by reaction of ozone with an olefin decomposes to give a zwitterion and a carbonyl fragment as follows.
- p. 259. Table 1. The heading of the second column should be: % Concentration (in solvent).  
The second paragraph should read:  
The yield of formaldehyde from DPE was investigated for ozone concentrations in the range 0–9  $\mu\text{g g}^{-1}$  of air. It was found to be constant, with an average value of  $90 \pm 2\%$ , for the range 0.05–5.00  $\mu\text{g g}^{-1}$ , above which negative deviations occurred.

## AUTHOR INDEX

- Agterdenbos, J., see Jütte, B. A. H. G. 345  
 Alder, J. F.  
 — and Drew, P. K. P.  
 A non-intrusive very high-frequency conductivity detector for continuous flow monitoring 325  
 Allain, P., see Mauras, Y. 271  
 Amian, W.  
 —, Hecker, R. and Stöver, D.  
 Determination of silver fission product in high-temperature nuclear reactor fuels by ion-exchange separation and  $\gamma$ -counting 81  
 Anderson, L.  
 Simultaneous spectrophotometric determination of nitrite and nitrate by flow injection analysis 123  
 Andren, A. W., see Doskey, P. V. 129  
 Årmansson, H.  
 Dithizone extraction and flame atomic absorption spectrometry for the determination of cadmium, zinc, copper, nickel, cobalt and silver in sea water and biological tissues 21  
 Baeyens, W.  
 — and de Moerloose, P.  
 Fluorescence properties of domperidone and its determination in pharmaceutical preparations 261  
 Boughriet, A., see Wartel, M. 211  
 Brull, E. E.  
 — and Golden, G. S.  
 Microcoulometric determination of total inorganic and organic sulfur in trace amounts in waters 167  
 Buck, R. P., see Rhodes, R. K. 185  
 Budevsky, O.  
 Correction: Acid-base equilibria in the mixed solvent 80% dimethylsulfoxide—20% water 183  
 Burgess, C., see Fogg, A. G. 107  
 Burrows, K. C.  
 — and Hughes, M. C.  
 Rapid analysis for polynuclear aromatic hydrocarbons by linear-sweep differential pulse voltammetry 255  
 Butler, L. R. P., see Ip, J. 1  
 Bye, R., see Lund, W. 279  
 Calcagno, C., see Scarano, E. 95  
 Cameron, A. J., see Pik, A. J. 61  
 Campbell, A. D., see Grime, J. K. 139  
 Chuaqui, C. A., see Lynn, K. R. 175  
 Cignoli, L., see Scarano, E. 95  
 Clement, G.  
 — and Paris, M. R.  
 Dosage électrochimique du cobalt. I. Etude des courbes intensité-potentiel du système cobalt(III)/cobalt(II) en milieu picolique 219  
 Clement, G.  
 — and Paris, M. R.  
 Dosage électrochimique du cobalt. II. Application aux aciers à faible ou à moyenne teneurs 227  
 Cragin, J. H.  
 Increased mercury contamination of distilled and natural water samples caused by oxidizing preservatives 313  
 Curtis, D. B., see Gladney, E. S. 339  
 Danzer, K.  
 — and Marx, G.  
 Application of two-dimensional variance analysis for the investigation of homogeneity of solids 145  
 de Moerloose, P., see Baeyens, W. 261  
 Doskey, P. V.  
 — and Andren, A. W.  
 High-volume sampling of airborne polychlorobiphenyls with Amberlite XAD-2 resin 129  
 Drew, P. K. P., see Alder, J. F. 325  
 Eberling, C., see Slemr, F. 35  
 Eckert, J. M., see Pik, A. J. 61  
 Ellis, J., see Hamilton, T. W. 87  
 Elson, C. M.  
 — and Macdonald, A. S.  
 Determination of selenium in pyrite by an ion exchange—electrothermal atomic absorption spectrometric method 153

- Fayad N. M., see Fogg, A. G. 107  
 Fischer, J.-C., see Wartel, M. 211  
 Florence, T. M., see Hamilton, T. W. 87  
 Fogg, A. G.  
 — Fayad, N. M. and Burgess, C.  
 Differential pulse polarographic study of the degradation of cephalixin. Determination of hydrogen sulphide and other degradation products 107  
 Fujinaga, K.  
 — and Kudo, K.  
 Multi-element analysis of Japanese tea leaves by neutron activation analysis and the single comparator method 75  
 Gladney, E. S.  
 —, Curtis, D. B. and Jurney, E. T.  
 Simultaneous determination of nitrogen, carbon, and hydrogen by thermal neutron prompt  $\gamma$ -ray spectrometry 339  
 Golden, G. S., see Brull, E. E. 167  
 Grime, J. K.  
 —, Campbell, A. D. and Yahaya, A. H.  
 The determination of selenium(IV) by thermometric enthalpy titration with thiosulphate 139  
 Hamilton, T. W.  
 —, Ellis, J. and Florence, T. M.  
 Determination of selenium and tellurium in electrolytic copper by anodic stripping voltammetry at a gold film electrode 87  
 Hanif, M.  
 —, Jamshaid, F. and Parveen, S.  
 Determination of isonicotinic acid hydrazide (isoniazid) by the Weisz ring-oven technique 171  
 Hecker, R., see Amian, W. 81  
 Heikamp, A., see Jütte, B. A. H. G. 345  
 Hiro, K.  
 —, Kawahara, A. and Tanaka, T.  
 Perchlorate-selective electrodes with Urushi as the membrane matrix 321  
 Holub, I., see Trojanek, A. 161  
 Hughes, M. C., see Burrows, K. C. 255  
 Hulanicki, A.  
 —, Lewandowski, R. and Lewenstam, A.  
 The mechanism of the potential response of bromide-selective electrodes based on mercury salts 197  
 Hurtubise, R. J.  
 — and Phillip, J. D.  
 Characterization of polycyclic aromatic hydrocarbons in shale oil by chromatography and fluorescence densitometry 245  
 Ip, J.  
 —, Thomassen, Y., Butler, L. R. P., Radziuk, B. and van Loon, J. C.  
 Combined furnace-flame non-dispersive atomic fluorescence spectrometry for direct simultaneous multi-element analysis of air filters 1  
 Iwasaki, K.  
 Determination of microgram amounts of palladium in titanium alloys by x-ray fluorescence spectrometry after solvent extraction and collection on a filter paper 67  
 Iwase, A.  
 —, Kudo, S. and Tanaka, N.  
 A new catalytic electrode for the amperometric determination of hydrogen peroxide 157  
 Jamshaid, F., see Hanif, M. 171  
 Jurney, E. T., see Gladney, E. S. 339  
 Jütte, B. A. H. G.  
 —, Heikamp, A. and Agterdenbos, J.  
 Rapid accurate analysis of metal (oxide)-on-silica catalysis by atomic absorption spectrometry 345  
 Kamiura, T.  
 — and Tanaka, M.  
 Determination of nitrate in suspended particulate matter by high-performance liquid chromatography with u.v. detection 117  
 Kawahara, A., see Hiro, K. 321  
 Kitagawa, K.  
 —, Narita, R. and Takeuchi, T.  
 A heated-electrode discharge lamp for trace analysis by atomic emission spectroscopy 291  
 Kudo, K., see Fujinaga, K. 75  
 Kudo, S., see Iwase, A. 157  
 Langmyhr, F. J., see Saeed, K. 285  
 Lewandowski, R., see Hulanicki, A. 197  
 Lewenstam, A., see Hulanicki, A. 197  
 Loon, J. C. van, see Ip, J. 1  
 Loon, J. C. van, see Naranjit, D. 307

- Lund, W.  
— and Bye, R.  
Flame atomic absorption analysis for selenium after electrochemical preconcentration 279
- Lynn, K. R.  
— and Chuaqui, C. A.  
A spectrophotometric kinetic assay for acid phosphatases with aromatic phosphates 175
- Macdonald, A. S., see Elson, C. M. 153
- Marx, G., see Danzer, K. 145
- Mauras, Y.  
— et Allain, P.  
Dosage du baryum dans l'eau et les liquides biologiques par spectrométrie d'émission avec source plasma haute fréquence 271
- Motomizu, S., see Tôei, K. 329
- Moerloose, P. de, see Baeyens, W. 261
- Musha, S., see Yao, T. 203
- Naranjit, D.  
—, Thomassen, Y. and van Loon, J. C.  
Development of a procedure for studies of the chromium(III) and chromium(VI) contents of welding fumes 307
- Narita, R., see Kitagawa, 291
- Ohkura, Y., see Ohtsubo, K. 335
- Ohta, K.  
— and Suzuki, M.  
Atomic absorption spectrometry of tellurium with electrothermal atomization in a molybdenum microtube 49
- Ohtsubo, K.  
—, Okada, Y., Zaitso, K. and Ohkura, Y.  
The fluorescent reaction product in the determination of aromatic aldehydes with 2,2'-dithiobis(1-aminonaphthalene) 335
- Okada, Y., see Ohtsubo, K. 335
- Paris, M. R., see Clement, G. 219
- Paris, M. R., see Clement, G. 227
- Parveen, S., see Hanif, M. 171
- Phillip, J. D., see Hurtubise, R. J. 245
- Pik, A. J.  
—, Cameron, A. J., Eckert, J. M., Sholkovitz, E. F. and Williams, K. L.  
The determination of metals at ppb levels by thin-film x-ray fluorescence spectrometry after coprecipitation with a molybdenum carrier complex 61
- Potter, N. M.  
— and Waldo, R. A.  
Determination of platinum in alumina-supported automotive catalyst material by electrothermal atomic absorption spectrometry 29
- Radziuk, B., see Ip, J. 1
- Rhodes, R. K.  
— and Buck, R. P.  
Interfacial properties of precipitate-based ion-selective electrodes. Rotating disk impedance measurements of the  $\text{Ag}_2\text{S}/\text{Ag}^+$  (aqueous) interface 185
- Roggendorf, P., see Slemr, F. 35
- Ryan, D. E., see Ward, N. I. 9
- Saeed, K.  
—, Thomassen, Y. and Langmyhr, F. J.  
Direct electrothermal atomic absorption spectrometric determination of selenium in serum 285
- Scarano, E.  
—, Calcagno, C. and Cignoli, L.  
A reliable source of very small amounts of hydrogen chloride for analytical purposes 95
- Seiler, W. see Slemr, F. 35
- Sholkovitz, E. F., see Pik, A. J. 61
- Slemr, F.  
—, Seiler, W., Eberling, C. and Roggendorf, P.  
The determination of total gaseous mercury in air at background levels 35
- Slovák, Z.  
Direct sampling of ion-exchanger suspensions for atomic absorption spectrometry with electrothermal atomization 301
- Stephens, R., see Ward, N. I. 9
- Stöver, D., see Amian, W. 81
- Suzuki, M., see Ohta, K. 49
- Takeuchi, T., see Kitagawa, K. 291
- Tanaka, M., see Kamiura, T. 117
- Tanaka, N., see Iwase, A. 157
- Tanaka, T., see Hiro, K. 321
- Thomassen, Y., see Ip, J. 1
- Thomassen, Y., see Saeed, K. 285
- Thomassen, Y., see Naranjit, D. 307

- Tōei, K.  
 —, Motomizu, S. and Yokosu, H.  
 Extraction—spectrophotometric determination of nickel with 4-chloro-2-nitroso-1-naphthol and crystal violet 329
- Tominaga, M.  
 — and Umezaki, Y.  
 Determination of submicrogram amounts of tin by atomic absorption spectrometry with electrothermal atomization 55
- Trojanek, A.  
 — and Holub, I.  
 Current sampling in polarography without synchronization with the drop time 161
- Umezaki, Y., see Tominaga, M. 55
- Upadhyaya, K. N.  
 Stepwise precipitation of barium sulphate, chromate and vanadate by cation release 179
- van Loon, J.C., see Ip, J. 1
- van Loon, J. C., see Naranjit, D. 307
- Waldo, R. A., see Potter, N. M. 29
- Ward, N. I.  
 —, Stephens, R. and Ryan, D. E.  
 Comparison of three analytical methods for the determination of trace elements in whole blood 9
- Wartel, M.  
 —, Boughriet, A. et Fischer, J.-C.  
 Détermination des constantes de dissociation ionique du chlorure de nitrosyle et de  $N_2O_4$  dans le sulfolane 211
- Williams, K. L., see Pik, A. J. 61
- Yahaya, A. H. see Grime, J. K. 139
- Yamaya, K.  
 Determination of the water content in muscovites containing large amounts of fluorine by Karl Fischer titration after fusion with silicon dioxide 233
- Yao, T.  
 — and Musha, S.  
 Electrochemical enzymatic determinations of ethanol and L-lactic acid with a carbon paste electrode modified chemically with nicotinamide adenine dinucleotide 203
- Yokosu, H., see Tōei, K. 329
- Zaitsu, K. see Ohtsubo, K. 335

## AUTHOR INDEX

### VOLUMES 101–110

*The volume number is placed in parentheses before the page number*

- Abaychi, J.K. (107) 1  
 Adams, F. (105) 219, (108) 21, (109) 85, (109) 307  
 Adsul, J.S. (101) 157  
 Agemian, H. (101) 193, (104) 285  
 Agterdenbos, J. (108) 315, (110) 345  
 Aguiar Neto, P.L.A. (101) 229  
 Ahmed, Y.Z. (101) 211  
 Aikawa, K. (106) 369  
 Al-Tamrah, S.A. (105) 433  
 Albano, C. (103) 429  
 Alder, J.F. (107) 231, (110) 325  
 Ali, M.M. (102) 181, (107) 415  
 Allain, P. (110) 271  
 Allen, G.C. (103) 73  
 Allen, P.D. (101) 401  
 Aly, M.M. (106) 379  
 Amian, W. (110) 81  
 Anderson, D.H. (105) 177  
 Anderson, D.M.W. (105) 147  
 Anderson, L. (109) 425, (110) 123  
 Andersson, L. (103) 489  
 Andre, J.C. (105) 297  
 Andren, A.W. (110) 129  
 Anfält, T. (103) 379, (109) 425  
 Antonijević, V.V. (106) 347  
 Appala Raju, N. (102) 237  
 Ardrey, R.E. (107) 327  
 Árén, K. (106) 15, (107) 29  
 Ariel, M. (101) 1, (102) 99, (108) 395  
 Ármannsson, H. (110) 21  
 Armentrout, D.N. (102) 229  
 Arnaud, N. (104) 181  
 Arrhenius, G. (109) 181  
 Aruscavage, P.J. (109) 171  
 Asabe, Y. (106) 59  
 Asper, R. (101) 253  
 Åström, O. (105) 67  
 Attiyat, A.S. (106) 225
- Bacon, J.R. (105) 163  
 Baeyens, W. (107) 291, (110) 261  
 Bajo, S. (105) 281, (106) 103  
 Baker, A.A. (107) 339  
 Bakowski, W. (104) 363  
 Balcerzak, M. (109) 123  
 Balsenc, L.R. (104) 319  
 Barends, D.M. (105) 139  
 Barkley, D.J. (105) 83  
 Barnes, R.M. (101) 99  
 Beck, M.T. (102) 185
- Beezer, A.E. (105) 77  
 Beisel, N.F. (108) 45  
 Belcher, R. (105) 433  
 Benaben, P. (101) 145  
 Beneyto, J.E. (108) 411  
 Bergamin, H.F.<sup>c</sup>. (101) 9, (101) 17, (104) 279,  
 (107) 309, (109) 45  
 Bergveld, P. (109) 145  
 Berkoff, C.E. (103) 469  
 Bernal-Melchor, A. (108) 39  
 Bhatt, P.M. (104) 113  
 Bhattacharyya, S.N. (102) 221  
 Bhatti, K.M. (105) 43  
 Bjørseth, A. (105) 119  
 Blockx, P. (103) 409  
 Blondiaux, G. (104) 129, (109) 411  
 Bloom, H. (109) 157  
 Boase, D.R. (104) 233  
 Bogdanski, S.L. (105) 433  
 Boll, K. (103) 237  
 Bond, A.M. (101) 309  
 Bone, K.M. (107) 219  
 Bonelli, J.E. (101) 437  
 Bonnekessel, J. (103) 29  
 Booker, J.L. (103) 201  
 Borgen, O.S. (103) 389  
 Bos, M. (103) 151, (103) 367, (108) 309, (109) 145  
 Bouchy, M. (105) 297  
 Boughriet, A. (110) 211  
 Bound, E.A. (104) 385  
 Boutron, C. (106) 127  
 Bower, E.L.Y. (101) 319, (102) 1  
 Bower, J.N. (108) 351, (109) 229  
 Bower, N.W. (105) 199  
 Bradshaw, J.D. (108) 351, (109) 229  
 Braithwaite, J.I. (106) 395  
 Breant, M. (104) 181  
 Breban, P. (104) 129  
 Bremser, W. (103) 355  
 Brittain, H.G. (106) 401  
 Broeckeaert, I. (103) 409  
 Broekaert, J.A.C. (109) 73  
 Brown, M.W. (105) 451  
 Brown, S.D. (107) 13  
 Bruland, K.W. (105) 233  
 Brull, E.E. (110) 167  
 Brumleve, T.R. (109) 259  
 Bruninx, E. (109) 419  
 Bruno, P. (104) 379  
 Büchi, R. (103) 21



- Buck, R.P. (101) 231, (103) 167, (109) 259,  
 (110) 185  
 Buckley, J. (103) 469  
 Budesinsky, B.W. (104) 1  
 Budevsky, O. (101) 139, (110) 183  
 Buffle, J. (101) 339  
 Buldini, P.L. (104) 139, (106) 137  
 Bureau Intern. Techn. du Chlore Mercury  
 Analysis Working Party (108)1, (109)209  
 Burger, K. (107) 113  
 Burgess, C. (108) 205, (110) 107  
 Burrows, K.C. (110) 255  
 Bursey, M.M. (105) 129  
 Bütikofer, H.P. (108) 179  
 Butler, L.R.P. (104) 11, (108) 31, (110) 1  
 Bye, R. (107) 169, (110) 279  
  
 Calcagno, C. (110) 95  
 Calokerinos, A.C. (105) 433  
 Cameron, A.J. (110) 61  
 Campbell, A.D. (110) 139  
 Campbell, B.H. (101) 215  
 Campbell, E.Y. (109) 171  
 Carrondo, M.J.T. (106) 309  
 Casassas, E. (106) 151, (107) 401  
 Caselli, M. (104) 379  
 Chakrabarti, C.L. (104) 99  
 Chakrabarti, D. (109) 307  
 Chalk, P.M. (104) 245  
 Chan, C.Y. (101) 33  
 Chan, H.K. (105) 423, (109) 341  
 Chanysheva, T.A. (108) 45  
 Chao, T.T. (105) 247, (108) 357  
 Chapman, J.F. (101) 203  
 Chateau-Gosselin, M. (102) 215, (107) 83  
 Chau, Y.K. (105) 255, (108) 31  
 Cheam, V. (101) 193  
 Cheng, F.S. (104) 47  
 Cheng, H.S. (106) 341  
 Chouaib, F. (108) 333  
 Chow, A. (106) 161  
 Christian, G.D. (104) 47, (106) 225, (107) 83,  
 (108) 149  
 Chuaqui, C.A. (110) 175  
 Cignoli, L. (110) 95  
 Čížek, Z. (109) 381  
 Claude, M. (104) 299  
 Clement, G. (110) 219, (110) 227  
 Clementi, S. (103) 477  
 Clerc, J.T. (103) 21  
 Coates, J.P. (103) 303, (103) 323  
 Collard, R.S. (108) 255  
 Compton, B.J. (105) 409  
 Comtat, M. (106) 131  
 Comte, P.A. (101) 239, (101) 247  
 Coomans, D. (103) 409  
 Corriveau, L.P.V. (102) 61  
 Cosgrove, R.F. (105) 77  
 Cospito, M. (106) 385  
 Costa Dantas, C. (108) 93  
 Covington, A.K. (108) 179  
 Cox, R.A. (106) 51  
 Cragin, J.H. (110) 313  
 Craven, T.L. (107) 273  
 Crenshaw, G.L. (105) 247  
  
 Cresser, M.S. (109) 431  
 Crisp, P.T. (104) 93  
 Cromer-Morin, M. (104) 299  
 Curran, D.J. (108) 379  
 Curtis, D.B. (110) 339  
 Czárán, E. (101) 409  
  
 Da Silveira Dantas, H. (108) 93  
 Dahl, J.H. (105) 327  
 Dal Pont, G. (108) 13  
 Dale, L.S. (101) 203  
 D'Amboise, M. (104) 355  
 Damen, H. (103) 289  
 Dams, R. (107) 159  
 Danielsson, L.-G. (106) 15  
 Danzer, K. (105) 1, (110) 145  
 Das, N.R. (102) 221  
 DaSilva, J.A. (104) 285  
 Davies, I.M. (102) 189  
 Day, M.J. (108) 425  
 De Boer, H.S. (102) 141, (108) 389  
 De Boer, J.L.M. (109) 177  
 De Goeij, J.J.M. (109) 139  
 De Haseth, J.A. (103) 109  
 De Jonghe, W. (108) 21  
 De Moerloose, P. (107) 291, (110) 261  
 De Oliveira, E. (101) 177  
 Debrun, J.L. (104) 129, (109) 411  
 Deladoey, P. (101) 339  
 Deming, S.N. (108) 227  
 Den Hartigh, J. (102) 141  
 Denis, M. (107) 383  
 Desai, H.B. (107) 415  
 Deschamps, N. (101) 145  
 Desmettre, S. (104) 181  
 Dessy, R.E. (103) 459  
 Devaux, M. (104) 129  
 Devynck, J. (107) 47  
 Di Fano, A. (104) 379  
 Dijkstra, A. (103) 313  
 Distèche, A. (106) 23  
 Doerffel, K. (105) 1  
 Dogan, S. (101) 433  
 Doležal, J. (101) 413, (109) 381  
 D'Orazio, P. (109) 25  
 Doronin, A.N. (102) 91  
 Doskey, P.V. (110) 129  
 Drew, P.K.P. (110) 325  
 Dryhurst, G. (108) 193  
 Duewer, D.L. (103) 201  
 Dumarey, R. (107) 159  
 Duncan, H.J. (102) 241, (106) 319  
 Dunmire, D.L. (105) 445  
 Dunn, W. III (103) 429  
 Dupuis, P.F. (103) 313  
 Durliat, H. (106) 131  
 Duyckaerts, G. (106) 23  
  
 Ebel, M.F. (109) 279  
 Eberling, C. (110) 35  
 Eckert, J.M. (104) 93, (108) 293, (110) 61  
 Edlund, U. (103) 429  
 Edmonds, T.E. (108) 155  
 Efron, C. (108) 395  
 Efstathiou, C.E. (107) 91, (109) 319

- Eggli, R. (101) 253  
 Ehrhardt, H. (105) 1  
 Ehrlich, G. (105) 1  
 Eklund, G. (105) 119  
 Eklund, R.H. (108) 53, (109) 97  
 El-Alaoui, M. (109) 187  
 El-Defrawy, M.M.M. (102) 185  
 Elamin, B. (107) 405  
 Elliott, W.G. (101) 99  
 Ellis, J. (110) 87  
 Elson, C.M. (110) 153  
 Elton-Bott, R.R. (108) 285  
 Emara, M.M. (102) 181  
 Eriksen, R. (107) 37  
 Erni, P.E. (103) 189  
 Espersen, D. (105) 327, (108) 241  
 Evans, J.C. (103) 175  
 Eyde, B. (107) 211  
  
 Fabregas, J.L. (106) 151, (107) 401, (108) 411  
 Farino, J. (105) 335  
 Fayad, N. (102) 205  
 Fayad, N.M. (106) 365, (108) 205, (110) 107  
 Fehér, Z. (101) 261, (109) 1  
 Feldman, C. (108) 221  
 Ferreira Marques, F. (106) 103  
 Ferri, D. (106) 137  
 Fink, D.W. (106) 389  
 Fischer, J.-C. (110) 211  
 Fisher, G.L. (106) 299  
 Fisk, M.B. (108) 63  
 Florence, T.M. (110) 87  
 Fodor, P. (102) 15  
 Fogarty, M.P. (109) 361  
 Fogg, A.G. (101) 211, (102) 205, (105) 423,  
 (106) 365, (108) 205, (109) 341, (110) 107  
 Fox, A. (106) 389  
 Franks, R.P. (105) 233  
 Frech, W. (104) 67, (104) 75, (108) 75  
 Fringuelli, F. (103) 477  
 Fritz, G. (107) 301  
 Fujii, T. (104) 167, (107) 335  
 Fujinaga, K. (110) 75  
 Fujino, T. (107) 365  
 Fujiwara, K. (109) 229  
 Fuwa, K. (107) 335  
  
 Gadow, P. (105) 1  
 Gammage, R.B. (107) 261  
 Gardner, D. (108) 13  
 Garg, B.S. (104) 191  
 Gaylor, V.F. (101) 393  
 Geary, S. (103) 303  
 Geissler, M. (105) 1  
 Geladi, P. (105) 219  
 Gemmill, F.Q. Jr. (107) 59  
 Georgieva, M. (101) 139, (110) 183  
 Gether, J. (108) 137  
 Geyer, R. (108) 293  
 Gharib, A.E.-A. (102) 181  
 Gibson, N.A. (104) 93, (108) 293  
 Giesin, R. (101) 187  
 Gijbels, R. (101) 45  
 Gillain, G. (106) 23  
 Gillespie, A.M. (104) 11  
  
 Giovagnoli, A. (104) 129, (109) 411  
 Gladney, E.S. (104) 121, (110) 339  
 Glass, G.E. (101) 79  
 Glodowski, S. (104) 55  
 Goethals, P. (101) 63, (108) 367  
 Golan (Goldhirsh), A. (107) 399  
 Gold, H.S. (103) 167  
 Golden, G.S. (110) 167  
 Gómez-Beltrán, F. (103) 263  
 Goncharov, Y.A. (102) 91  
 Gopala Rao, G. (108) 417  
 Gorton, L. (105) 43  
 Goto, J. (101) 111  
 Goto, M. (101) 131  
 Gough, D.S. (108) 347  
 Grabaric, B.S. (101) 309  
 Granéli, A. (103) 489, (109) 425  
 Grasserbauer, M. (109) 279  
 Grassi, J. (107) 47  
 Gratzl, M. (102) 85, (109) 1  
 Greenhalgh, D.A. (106) 361  
 Greenhow, E.J. (109) 129  
 Gregorowicz, Z. (104) 363  
 Griffiths, T.R. (107) 279  
 Grime, J.K. (105) 361, (105) 369, (106) 39,  
 (106) 251, (107) 319, (108) 363, (109) 393,  
 (110) 139  
 Groh, C. (106) 81  
 Grover, Y.P. (101) 225  
 Growcock, G. (104) 177  
 Gupta, N. (104) 113  
  
 Hadjiioannou, T.P. (107) 91, (108) 375, (109) 319  
 Haerdi, W. (101) 339, (101) 433  
 Hamada, S. (101) 169  
 Hamid, S.T. (105) 403  
 Hamilton, T.W. (110) 87  
 Hampson, N.A. (101) 401  
 Hanck, K.W. (107) 75  
 Hancock, R.G.V. (102) 157  
 Hanif, M. (110) 171  
 Hansen, E.H. (106) 207  
 Hara, K. (106) 243  
 Hargreaves, M. (104) 85  
 Harvan, D.J. (105) 129  
 Hasegawa, M. (101) 111  
 Hass, J.R. (105) 129  
 Haukka, M.T. (105) 177  
 Hawkings, R.C. (102) 61  
 Hawkrige, F.M. (105) 91  
 Hayakawa, Y. (106) 261  
 Hayashi, K. (104) 389  
 Hays, T.R. (103) 121  
 Headridge, J.B. (102) 33, (107) 339  
 Hecker, R. (110) 81  
 Heikamp, A. (110) 345  
 Heindryckx, R. (107) 159  
 Heite, F.H. (103) 313  
 Heithmar, E.M. (101) 89  
 Heller, S.R. (103) 141  
 Henderson, D.E. (101) 117  
 Henneberg, D. (103) 289  
 Hepler, B.R. (102) 41  
 Herber, R.F.M. (109) 177  
 Hernández-Córdoba, M. (104) 397

- Hernández-Méndez, J. (108) 39  
 Hertogen, J. (101) 45  
 Heunisch, G.W. (101) 221  
 Hibbert, W.D. (107) 219  
 Hiiron, K. (110) 321  
 Hikuma, M. (109) 33  
 Hill, C.J. (108) 405  
 Hill, J. (103) 469  
 Hiraki, K. (106) 67  
 Hishiyama, Y. (108) 103  
 Hitchcock, A. (105) 375  
 Hlaváč, R. (105) 263  
 Hoffman, E.L. (102) 157  
 Hoke, E. (109) 279  
 Holcombe, J.A. (108) 53, (109) 97  
 Holub, I. (110) 161  
 Holuk, J.M. (104) 195  
 Honda, S. (105) 153, (108) 421  
 Hoogewijs, G. (106) 271  
 Horák, J. (101) 367  
 Horton, A.D. (108) 221  
 Horvai, G. (102) 85, (107) 101, (109) 1  
 Hoste, J. (101) 45, (101) 63, (107) 159, (108) 127,  
 (108) 367  
 Howard, A.G. (106) 361  
 Hu, H.-C. (107) 387  
 Hughes, M.C. (110) 255  
 Hulanicki, A. (107) 121, (110) 197  
 Hulshoff, A. (105) 139  
 Hurtubise, R.J. (101) 333, (110) 245  
 Hwang, T.L. (106) 341  
  
 Ichise, M. (101) 273  
 Iida, C. (108) 87  
 Ikeda, S. (105) 417  
 Ikegawa, S. (101) 111  
 Ikenoya, K. (101) 131  
 Imai, S. (108) 103  
 Ingle, J.D. Jr. (104) 267, (105) 199  
 Ip, J. (110) 1  
 Isenhour, T.L. (103) 109, (103) 213  
 Ishii, D. (101) 131  
 Ishii, H. (101) 423  
 Itoh, J. (105) 383  
 Iu, K.L. (106) 319  
 Iwasaki, K. (110) 67  
 Iwase, A. (110) 157  
  
 Jackwerth, E. (107) 177  
 Jagner, D. (105) 33, (106) 15, (107) 29  
 Jain, P. (104) 191  
 Jakob, K. (106) 103  
 Jambor, J. (101) 367  
 Jamshaid, F. (110) 171  
 Janata, J. (101) 239, (101) 247, (108) 161  
 Janjic, T.J. (107) 359  
 Jasink, G. (103) 151  
 Jean, R. (102) 233  
 Jenkins, R.A. (108) 221  
 Jensen, A. (105) 327, (108) 241  
 Jensen, M.A. (101) 125  
 Johansson, B.-L. (102) 121  
 Johansson, E. (103) 429  
 Johansson, P.-A. (104) 21  
 Johnson, C.C. (101) 239  
  
 Johnson, D.C. (105) 9, (105) 25, (106) 1  
 Johnson, R.N. (107) 59  
 Jonckheer, M. (103) 409  
 Jonsen, J. (107) 211  
 Jordan, J. (109) 393  
 Jordanov, N. (104) 161  
 Jørgensen, S.S. (104) 279  
 Joshi, B.D. (104) 113  
 Joshi, D.P. (104) 153  
 Jost, C. (103) 21  
 Jungreis, E. (106) 141  
 Journey, E.T. (110) 339  
 Jütte, B.A.H.G. (110) 345  
  
 Kabanova, O.L. (102) 91  
 Kaberline, S.L. (103) 417  
 Kai, M. (106) 89  
 Kajihara, M. (101) 131  
 Kakehi, K. (105) 153, (108) 421  
 Kamata, S. (108) 385  
 Kamiura, T. (110) 117  
 Kane, J.S. (106) 325  
 Kaneda, M. (104) 145  
 Kantor, T. (102) 15  
 Kapsa, P. (107) 391  
 Karber, L.G. (108) 193  
 Kargosha, K. (107) 231  
 Kariya, R. (109) 115  
 Karlberg, B. (104) 21  
 Karube, I. (105) 429, (106) 243, (106) 369,  
 (109) 33, (109) 39  
 Kateman, G. (103) 1, (103) 11  
 Kato, T. (106) 59  
 Katoh, M. (109) 107  
 Katsura, T. (106) 95  
 Kawahara, A. (110) 321  
 Kawamura, S. (102) 225  
 Kawashima, T. (106) 355  
 Ke, P.J. (106) 279  
 Keliher, P.N. (105) 335, (109) 373  
 Kenis, P.R. (104) 337  
 Keown, S.R. (107) 339  
 Khalighie, J. (107) 191  
 Khalique, A. (101) 117  
 Kimura, A. (107) 395  
 King, A.F. (104) 85  
 Kiriyama, T. (101) 207  
 Kitagawa, K. (109) 241, (110) 291  
 Kitami, M. (106) 95  
 Klier, M. (103) 29  
 Knauer, G.A. (105) 233  
 Kobayashi, H. (105) 289, (105) 383  
 Kobayashi, S. (101) 375, (104) 173  
 Koch, O.G. (107) 373  
 Koemmerer, C. (109) 411  
 Koenitzer, H. (103) 21  
 Koeva, M. (104) 161  
 Koh, H. (101) 423  
 Koh, T. (109) 107  
 Kohashi, K. (108) 297  
 Kojima, T. (101) 273  
 Koliňová, D. (105) 263, (105) 271  
 Komárek, J. (101) 367  
 Komarek, J. (106) 285  
 Korenaga, T. (104) 369

- Korkisch, J. (104) 337, (108) 63, (109) 181  
 Kostenbauder, H.B. (105) 139  
 Koster, H.A. (101) 359  
 Kounaves, S.P. (109) 327  
 Koupparis, M.A. (107) 91  
 Kowalczyk, E. (108) 261  
 Kowalski, B.R. (103) 201, (107) 13  
 Koyama, T. (109) 241  
 Kozuma, Y. (106) 355  
 Kramer, J.R. (106) 113  
 Krug, F.J. (101) 17, (104) 279, (107) 309, (109) 45  
 Kruidhof, H. (102) 177  
 Krull, U.J. (106) 51  
 Kublik, Z. (104) 55  
 Kubo, T. (109) 33  
 Kudo, K. (110) 75  
 Kudo, S. (110) 157  
 Kuga, K. (101) 199  
 Kuleff, I. (108) 371  
 Kulys, J.J. (109) 55  
 Kunert, I. (106) 285  
 Kuroda, R. (101) 207  
 Kurotaki, K. (102) 225  
 Kusaka, Y. (108) 103  
 Kushneriuk, S.A. (102) 61  
  
 Laitinen, H.A. (108) 119  
 Lam, G. (106) 81  
 Lamathe, J. (104) 307  
 Lan-Chun-Fung, Y.L. (104) 153  
 Langmyhr, F.J. (107) 211, (110) 285  
 Lansaat, P.H. (108) 389  
 Lanza, P. (104) 139, (105) 53, (106) 137  
 Larkin, M.J. (108) 425  
 Lash, R.P. (108) 405  
 Lazarou, L.A. (108) 375  
 Ledent, R. (107) 383  
 Lee, Y.-C. (106) 373  
 Leis, F. (109) 73  
 Lely, J.A. (108) 309  
 Lengton, W. (108) 309  
 Lengyel, Z. (101) 261  
 LeRoy Blank, C. (104) 29  
 Lester, J.N. (106) 309  
 Lewandowski, R. (110) 197  
 Lewenstam, A. (107) 121, (110) 197  
 Libergott, E.K. (101) 229  
 Limonard, C.B.G. (103) 133, (103) 253  
 Littlejohn, D. (107) 139  
 Lo, V.S.K. (106) 161  
 Locke, J. (104) 225, (104) 233  
 Lockhart, K.R. (106) 251, (108) 363  
 Long, G.D. (107) 339  
 Longino, G. (103) 469  
 Loomis, C.W. (106) 155  
 Lowe, P.R. (104) 11  
 Lowry, S.R. (103) 109, (103) 213  
 Lund, W. (102) 211, (107) 37, (110) 279  
 Lundberg, E. (104) 67, (104) 75, (108) 75  
 Lunde, G. (108) 137  
 Lyle, S.J. (108) 267, (108) 437  
 Lynn, K.R. (110) 175  
 Lytle, F.E. (107) 273  
  
 MacDonald, A.S. (110) 153  
 McDonald, C. (102) 241  
 McGaughey, J.F. (107) 75  
 McGlynn, A. (108) 205  
 Machtinger, M. (107) 349  
 Mackenzie, I. (103) 401  
 McMeeking, R.F. (103) 73  
 Magrone, R. (102) 233  
 Mahenc, J. (106) 131  
 Maj-Zurawska, M. (107) 121  
 Makhija, R. (105) 375  
 Malát, M. (109) 191  
 Malinowski, E.R. (103) 339  
 Malissa, H. (109) 279  
 Manson, A. (102) 157  
 Marczenko, Z. (108) 261, (109) 123  
 Mareva, S. (104) 161  
 Marsh, S.F. (105) 439  
 Martin, J.H. (105) 233  
 Martin, J.M. (107) 391  
 Martinez-Lozano, C. (104) 397  
 Marx, G. (110) 145  
 Mašin, V. (101) 413  
 Massart, D.L. (103) 409, (106) 271  
 Masschelein, W.J. (107) 383  
 Massoumi, A. (108) 351  
 Matsuda, Y. (108) 421  
 Matsumoto, K. (105) 429  
 Matsunaga, T. (109) 39  
 Matsushita, T. (104) 145  
 Matthees, D.P. (109) 61, (109) 161  
 Mauras, Y. (110) 271  
 Means, G.E. (107) 405  
 Medeiros, J.X. (101) 9  
 Meiners, W. (107) 301  
 Mentasti, E. (108) 441  
 Messerschmidt, J. (107) 177  
 Meyer-Grall, F. (104) 355  
 Michailidis, M.S. (108) 233  
 Michel, L. (105) 109  
 Michel, S. (104) 129  
 Miller, J.A. (103) 141  
 Miller, J.N. (106) 395  
 Milne, G.W.A. (103) 141  
 Milner, B.A. (109) 165  
 Milosavljević, E.B. (107) 359  
 Mindegaard, J. (104) 185  
 Mino, Y. (107) 253  
 Miyazaki, A. (107) 395  
 Mizoguchi, T. (101) 423  
 Moody, G.J. (108) 385  
 Moore, C.E. (105) 353  
 Moore, D.C.A. (101) 401  
 Moore, W.M. (105) 99  
 Morelli, B. (106) 73  
 Morgan, P.H. (103) 175  
 Mori, S. (108) 325  
 Moriguchi, Y. (105) 391, (105) 397  
 Morishige, K. (106) 67  
 Moss, S.D. (101) 239, (108) 161  
 Motojima, K. (106) 405  
 Motomizu, S. (101) 169, (104) 369, (110) 329  
 Motonaka, J. (105) 417  
 Müller, H.-R. (103) 189  
 Mullings, L.R. (107) 327

- Munk, M.E. (103) 121, (103) 245  
 Murakami, N. (106) 95  
 Musha, S. (101) 375, (104) 173, (110) 203  
 Müskens, P.J.W.M. (103) 1, (103) 11, (103) 445
- Nadjafi, A. (109) 129  
 Nagy, G. (101) 261, (109) 1  
 Naik, D.V. (106) 147  
 Nakahara, T. (101) 375, (104) 99, (104) 173  
 Nakano, K. (107) 129  
 Nakano, S. (106) 355  
 Naldrett, A.J. (102) 157  
 Nambara, T. (101) 111  
 Naranjit, D. (110) 307  
 Narasaki, H. (104) 393  
 Narita, R. (110) 291  
 Nayak, A.N. (108) 277  
 Nishikawa, Y. (106) 67  
 Noller, B.N. (109) 157  
 Nonaka, J. (109) 181  
 Nordén, B. (103) 429  
 Norris, J.D. (104) 85, (104) 385  
 Norwitz, G. (105) 335, (109) 373
- Oehme, M. (107) 67, (109) 195  
 Ohkura, Y. (106) 89, (108) 297, (110) 335  
 Ohta, K. (104) 293, (107) 245, (108) 69, (110) 49  
 Ohtsubo, K. (110) 335  
 Okada, Y. (110) 335  
 Onoue, Y. (106) 67  
 Oostervink, R. (101) 419, (108) 169  
 Ota, N. (107) 253  
 Otruba, V. (101) 367  
 Ottaway, J.M. (107) 139  
 Ouziel, E. (102) 99  
 Overvoll, P.A. (102) 211  
 Owens, J.W. (104) 121
- Pacey, G.E. (105) 353  
 Pahlavanpour, B. (109) 251  
 Pantel, S. (101) 187, (104) 205, (109) 351  
 Pápay, M.K. (109) 279  
 Páris, M.R. (104) 299, (110) 219, (110) 227  
 Parsons, J.W. (109) 431  
 Parveen, S. (110) 171  
 Pastor, T.J. (106) 347  
 Patel, B.M. (104) 113  
 Patriarche, G.J. (102) 215, (107) 83, (108) 149  
 Patterson, J.E. (107) 201  
 Paulik, F. (101) 409  
 Paulik, J. (101) 409  
 Paus, P.E. (107) 169  
 Pawar, M.M. (104) 113  
 Pegon, Y. (101) 385  
 Pelizzetti, E. (108) 441  
 Perez-Bendito, D. (109) 401  
 Pérez-Ruiz, T. (104) 397  
 Perry, R. (106) 309  
 Persson, B. (102) 121  
 Persy, K. (109) 279  
 Peter, F. (104) 177  
 Pethö, G. (107) 113  
 Phelps, D.J. (105) 409  
 Phillip, J.D. (101) 333, (110) 245  
 Pijpers, F.W. (103) 253
- Pik, A.J. (110) 61  
 Pille, P. (104) 11  
 Pilosof, D. (106) 141  
 Pino, F. (109) 401  
 Pitombo, L.R.M. (101) 177  
 Plankey, F.W. (101) 89  
 Ploegmakers, H.H.J.L. (102) 141  
 Poitrenaud, C. (102) 167, (108) 333  
 Poldoski, J.E. (101) 79  
 Pollard, B.D. (108) 351  
 Polo-Diez, L. (108) 39  
 Pólos, L. (109) 279  
 Pool, K.H. (109) 149  
 Porthault, M. (102) 113  
 Portzer, R.M. (101) 89  
 Posta, J. (102) 185  
 Potter, N.M. (102) 201, (110) 29  
 Price, W.J. (109) 165  
 Price, W.P. Jr. (108) 227  
 Pritchard, J.G. (104) 153  
 Prue, D.G. (107) 59  
 Pryor, W.A. (108) 255  
 Pugh, D.C. (107) 279  
 Pulford, I.D. (106) 319  
 Pungor, E. (101) 261, (102) 15, (102) 85, (107) 101,  
 (109) 1, (109) 279  
 Purdy, W.C. (102) 41, (105) 409, (109) 61,  
 (109) 161  
 Püschel, P. (105) 263, (105) 271
- Quimby, B.D. (101) 99
- Racz, W.J. (106) 155  
 Radziuk, B. (105) 255, (108) 31, (110) 1  
 Rakiás, F. (102) 85  
 Rama Bhat, S. (108) 293  
 Ramanathan, P.S. (101) 157  
 Ramappa, P.G. (108) 277  
 Ramstad, T. (102) 229  
 Rasmussen, G.T. (103) 213  
 Ratsimandresy, Y. (104) 345  
 Rechnitz, G.A. (101) 125, (109) 25  
 Rechsteiner, C.E. Jr. (103) 167  
 Reis, B.F. (101) 9, (101) 17, (104) 279, (107) 309,  
 (109) 45  
 Renaud, R.H. (103) 175  
 Rhodes, R.K. (110) 185  
 Richardson, D.E. (109) 157  
 Rigali, L. (106) 385  
 Riley, J.P. (107) 1  
 Ritter, G.L. (103) 213  
 Rodriguez, A.R. (102) 167  
 Roggendorf, P. (110) 35  
 Roman, R.V. (103) 121, (103) 245  
 Roquette Pinto, C.L.S. (101) 229  
 Roseboom, H. (101) 359, (108) 401  
 Rosenberg, L.S. (106) 81  
 Rosenfarb, J. (108) 119  
 Rotter, H. (103) 61  
 Rubel, S. (104) 215, (109) 67  
 Růžicka, J. (106) 207  
 Ryan, D.E. (105) 185, (110) 9
- Saccone, P. (102) 233  
 Saeed, K. (110) 285

- Sakamoto, M. (106) 261  
 Salas, A. (103) 263  
 Salin, E.D. (104) 267  
 Samuelsson, R. (102) 133, (108) 213  
 Sánchez-Pedreño, C. (104) 397  
 Sandbu, O. (103) 389  
 Sanders, J.T. (108) 119  
 Sanke Gowda, H. (108) 277  
 Sanz-Medel, A. (104) 85, (104) 385  
 Sanzolone, R.F. (105) 247, (108) 357  
 Sasa, S. (104) 29  
 Sato, A. (108) 429  
 Satoh, I. (105) 429, (106) 243, (106) 369  
 Saxberg, B.E.H. (103) 201  
 Scarano, E. (110) 95  
 Schainbaum, J. (103) 469  
 Scharff, J.P. (104) 299  
 Scharff, O. (109) 291  
 Schouten, A. (109) 419  
 Schubiger, P.A. (106) 103  
 Schulman, S.G. (105) 311, (106) 81, (107) 411,  
 (108) 249  
 Seiyo, H. (105) 429  
 Seiler, W. (110) 35  
 Semersky, F.E. (106) 233  
 Seo, Y. (101) 273  
 Shafiqul Alam, A.M. (102) 113, (107) 391  
 Shamaev, V.I. (104) 327, (106) 333  
 Shelley, C.A. (103) 121, (103) 245  
 Shelly, D.C. (109) 361  
 Shibata, S. (102) 225  
 Shimomura, S. (107) 253  
 Shiraishi, K. (105) 289  
 Shiramizu, B. (108) 161  
 Sholkovitz, E.R. (110) 61  
 Shono, T. (104) 145  
 Silberman, D. (106) 299  
 Simona, M.G. (104) 319  
 Singh, R.B. (104) 191  
 Singh, R.P. (104) 191  
 Sjöström, M. (103) 429  
 Skar, G.T. (101) 333  
 Skogerboe, R.K. (101) 437  
 Slemr, F. (110) 35  
 Sloim-Bombard, M. (107) 349  
 Slovák, Z. (110) 301  
 Smalldon, K.W. (104) 233, (107) 327  
 Smet, T. (101) 45  
 Smit, H.C. (103) 43  
 Smith, C.J. (104) 245  
 Snider, B.G. (105) 9, (105) 25, (106) 1  
 Sokol, H.A. (105) 413  
 Somidevamma, G. (108) 417  
 Sommer, L. (101) 367, (106) 285  
 Soundar Rajan, S.C. (102) 237  
 Srdanović, M.K. (107) 359  
 Starner, J.W. (104) 121  
 Stefani, A. (105) 147  
 Steffan, I. (104) 337, (108) 63, (109) 181  
 Steinnes, E. (108) 137  
 Stephen, W.I. (101) 117  
 Stephens, R. (110) 9  
 Stifel, D.N. (106) 233  
 Still, E. (107) 105, (107) 377  
 Stöver, D. (110) 81  
 Stover, F.S. (101) 231, (109) 259  
 Strandberg, M. (103) 379, (103) 489, (109) 425  
 Strijckmans, K. (108) 127  
 Strohl, A.N. (108) 379  
 Strunc, G. (104) 177  
 Stuart, D.C. (101) 429, (106) 411  
 Stubley, E.A. (104) 195  
 Sullivan, J.V. (102) 25, (105) 213, (108) 347  
 Suzuki, M. (104) 293, (104) 389, (106) 59,  
 (107) 245, (108) 69, (110) 49  
 Suzuki, S. (105) 429, (106) 243, (106) 369,  
 (109) 33, (109) 39  
 Švirmickas, G.-J.S. (109) 55  
 Sychra, V. (105) 263, (105) 271  
 Szydłowski, F.J. (105) 445, (106) 121  
 Tagawa, H. (107) 365  
 Takada, T. (107) 129  
 Takai, Y. (105) 153  
 Takamura, K. (106) 261  
 Takeshita, H. (102) 225  
 Taketatsu, T. (108) 429  
 Takeuchi, T. (109) 241, (110) 291  
 Takitani, S. (106) 59  
 Tamizi, M. (108) 267, (108) 437  
 Tan, B. (105) 361, (105) 369, (106) 39, (107) 319,  
 (109) 393  
 Tanaka, M. (110) 117  
 Tanaka, N. (105) 417, (110) 157  
 Tanaka, T. (110) 321  
 Tardy, R. (101) 145  
 Tarutani, T. (109) 115  
 Taylor, H.E. (101) 437  
 Terao, M. (108) 421  
 Terashima, S. (101) 25, (108) 113  
 Ternero, M. (109) 401  
 Thelander, S. (104) 21  
 Thomas, I.L. (105) 177  
 Thomas, J.D.R. (108) 385  
 Thomassen, Y. (105) 255, (108) 31, (110) 1,  
 (110) 285, (110) 307  
 Thompson, M. (104) 195, (106) 51, (109) 251  
 Thompson, R. (102) 33  
 Ting, G. (106) 373  
 Tjioe, P.S. (109) 139  
 Tōei, K. (101) 169, (104) 369, (110) 329  
 Tōgō, T. (105) 289  
 Tominaga, M. (110) 55  
 Tóth, K. (101) 261, (102) 85, (107) 101, (109) 1,  
 (109) 279  
 Toullec, J. (109) 187  
 Townshend, A. (105) 433  
 Traini, A. (104) 379  
 Trémillon, B. (107) 47, (107) 349  
 Trojánek, A. (110) 161  
 Tsuji, H. (108) 103  
 Tsujii, K. (101) 199  
 Tuell, T.M. (108) 351  
 Tzeng, J.-H. (101) 71  
 Uchida, H. (108) 87  
 Uchida, T. (108) 87  
 Uden, P.C. (101) 99, (101) 117  
 Ueno, K. (105) 289, (105) 383  
 Ullman, A.H. (108) 351

- Umezaki, Y. (107) 395, (110) 55  
 Underberg, W.J.M. (105) 311, (107) 411, (108) 249  
 Upadhyaya, K.N. (110) 179  
 Ure, A.M. (102) 195, (105) 163, (107) 191  
  
 Vajgand, V.J. (106) 347  
 Valcarcel, M. (109) 401  
 Valero, A. (103) 263  
 Valladon, M. (104) 129, (109) 411  
 Van Bennekom, W.P. (101) 283  
 Van Dalen, J.P.J. (108) 433  
 Van den Berg, C.M.G. (106) 113  
 Van der Houwen, O.A.G.J. (105) 139  
 Van der Linden, W.E. (101) 419, (108) 169  
 Van Eenbergen, A. (109) 419  
 Van Grieken, R. (103) 223, (108) 93  
 Van Loon, J.C. (102) 25, (102) 157, (105) 255,  
 (108) 31, (110) 1, (110) 307  
 Van Oort, W.J. (102) 141, (108) 389  
 Van Rinsvelt, H.A. (108) 119  
 Van 't Dack, L. (108) 93  
 Van 't Klooster, H.A. (103) 313  
 Van Veen-Blaauw, A.M.W. (109) 145  
 Van Wijk, R. (103) 483  
 Vandecasteele, C. (101) 63, (108) 127, (108) 367  
 Vandenbalck, J.L. (108) 149  
 Vanderborght, B. (103) 223  
 Varmuza, K. (103) 61  
 Varnes, A.W. (101) 393  
 Vechernish, L. (108) 45  
 Veličković, Z. (106) 347  
 Velinov, G. (101) 139, (110) 183  
 Venkateswarlu, C. (107) 415  
 Verbeek, A.A. (102) 195  
 Verbeke, P. (109) 85  
 Vergnano, P.A. (107) 339  
 Veselsky, J.C. (104) 345  
 Vijan, P.N. (101) 33  
 Viriot, M.L. (105) 297  
 Viswanath, S.G. (108) 417  
 Vittori, O. (102) 113  
 Vo-Dinh, T. (107) 261  
 Volkens, K.J. (109) 139  
 Vyskočilová, O. (105) 263, (105) 271  
  
 Wacker, W.E.C. (104) 389  
 Wade, A.L. (105) 91  
 Waldo, R.A. (110) 29  
 Walg, H.L. (103) 43  
 Walker, J. (105) 403  
 Wang, J. (101) 1, (102) 99  
 Ward, N.I. (105) 185, (110) 9  
 Warner, I.M. (109) 361  
 Wartel, M. (110) 211  
 Watanabe, T. (105) 429  
 Watkinson, J.H. (105) 319, (105) 451  
 Watson, B. (106) 233  
 Weber, R. (102) 233  
 Weber, S.G. (102) 41  
 Wegmann, D. (103) 21  
 Weimann, B. (103) 289  
 Weiss, H.V. (104) 337  
 Weisz, H. (101) 187, (107) 301, (109) 351  
 Wells, D.E. (104) 253  
 Welsch, E.P. (108) 357  
  
 West, T.S. (104) 85, (104) 385, (107) 191  
 White, E.L. (101) 89  
 Whiteside, P.J. (109) 165  
 Wiese, G. (108) 401  
 Wilkins, C.L. (103) 417  
 Willars, M.J. (101) 401  
 Williams, H.P. (105) 91  
 Williams, K.L. (110) 61  
 Willis, J.E. (106) 175  
 Willmott, F.W. (103) 401  
 Wilson, A.C. (109) 149  
 Wilson, M.I. (107) 339  
 Winefordner, J.D. (101) 319, (102) 1, (108) 351,  
 (109) 229  
 Winicov, H. (103) 469  
 Wittick, J.J. (108) 233  
 Wojciechowski, M. (104) 215, (109) 67  
 Wold, S. (103) 429  
 Wolfe, F.H. (107) 399  
 Wong, P.Y. (102) 61  
 Woodruff, H.B. (103) 109  
 Worsfold, P.J. (104) 195  
 Woyewoda, A.D. (106) 279  
 Wu, C.Y. (108) 233  
 Wyttenbach, A. (106) 103  
  
 Yahaya, A.H. (110) 139  
 Yamaguchi, M. (108) 297  
 Yamaya, K. (110) 233  
 Yano, T. (105) 289  
 Yao, T. (110) 203  
 Yarnitzky, C. (102) 99  
 Yasuda, T. (109) 33  
 Yates, K. (106) 51  
 Yokosu, H. (110) 329  
 Yoshida, I. (105) 289  
 Yoshida, M. (106) 95  
 Yoshida, Z. (106) 405  
 Yoshimatsu, T. (105) 397  
 Yoshimura, K. (109) 115  
 Yudelevich, I.G. (108) 45  
 Yutani, Y. (108) 297  
  
 Zagatto, E.A.G. (101) 9, (101) 17, (104) 279,  
 (107) 309, (109) 45  
 Zaitso, K. (110) 335  
 Zatka, A. (105) 109  
 Zeitlin, H. (101) 71  
 Zelentsova, L.V. (108) 45  
 Ziegler, E. (103) 237  
 Zielinski, C.A. (101) 89  
 Zirino, A. (109) 327  
 Zupan, J. (103) 141, (103) 273

## SUBJECT INDEX

## VOLUMES 101-110

*The volume number is placed in parentheses before the page number*

## A

**Acetic acid**

Amperometry; Flow system; Microbial sensor; Trichosporon brassicae; Fermentation broths (109) 33

**Acetylglycine**

Chromatography; Detection on paper; Acetyl-glycylglycine; Acetylglycylglycylglycine (105) 413

**Acid-base**

Potentiometry; Flow system; Single-point titrations (105) 67

Titrimetry; ISFET (109) 145

**Acid-base equilibria**

Titrimetry; Dimethylsulphoxide-water; Carboxylic acids (101) 139

Titrimetry; Dimethylsulphoxide-water; Carboxylic acids; Correction (110) 183

**Acidity**

Thermom. analysis; Titrimetry; Petroleum bitumens; Catalytic (109) 129

**Acidity constants**

Fluorimetry; Naphthoic acid; Anthroic acid (105) 311

**Acidity functions**

Diff. pulse polarography; Trifluoroacetic acid; Trifluoromethanesulphonic acid; Hexafluoro-propanediol (106) 51

**Acid mixtures**

Potentiometry; Titrimetry (102) 211

**Acridone**

Fluorimetry; pH dependence (107) 411

**Acrylic fibres**

Thermogravimetry-mass spectrometry; Alkyd paints; Computer-generated mass thermograms; Interface (107) 327

**Adsorption colloid flotation**

Spectrophotometry; Selenium; Sea water (101) 71

**Air**

At. abs. spectrometry; Gas chromatography; Electrotherm. atomization; Alkyllead; Sources (105) 255

At. abs. spectrometry; Mercury; Gold-coated collector (106) 405

At. abs. spectrometry; Mercury compounds; Preconcentration (107) 159

At. abs. spectrometry; Electrotherm. atomization; Lead compounds; Inorganic, organic; Simultaneous determination (108) 11

At. abs. spectrometry; Mercury, total; Background level; Gold-coated quartz wool (110) 35

Gas chromatography; Mass spectrometry; Polynuclear aromatic hydrocarbons; Computer-controlled (105) 119

Ring oven; Lead; Rhodizonate (101) 225

Spectrophotometry; Amperometry; Chlorine traces; Comparison (104) 355

Spectrophotometry; Ozone; Specific (108) 255

Polychlorobiphenyls; High-volume sampling (110) 129

**Air filters**

At. fluor. spectrometry; Multielement analysis; Furnace-flame, non-dispersive (110) 1

**Air particulates**

At. abs. spectrometry; Electrotherm. atomization; Beryllium; Manganese (105) 219

Emission spectrometry; Trace elements; D.c. arc; Low-volume sampler (108) 103

H.p.l.c.; Spectrophotometry; Nitrate; Method comparison (110) 117

**Albumin**

Flow system; Spectrophotometry; Multi-injection analysis (104) 185

Flow system; Fluorimetry; Glycine (106) 395



**Aldehydes**

Fluorimetry; Aromatic; Dithiobisamino-naphthalene (110) 335

Gas chromatography; Periodate oxidation; Oligoglycosides (105) 153

**Aliphatic amines**

Emission spectrometry; Molecular emission cavity analysis; Amino acids (105) 433

**Aliphatic esters**

Mass spectrometry; Mass-analyzed ion kinetic energy spectra; Chemical ionization; Collision-induced (105) 129

**Alkaloids**

Enthalpimetry; Enzymatic inhibition; Cholinesterase (106) 39

Spectrophotometry; Organic bases; Surfactants; Extraction; With metallochromic indicators (109) 191

Drugs, basic; Ion-pair extraction; Diethylhexyl-phosphoric acid (106) 271

**Alkyd paints**

Thermogravimetry-mass spectrometry; Acrylic fibres; Computer-generated mass thermograms; Interface (107) 327

**Alkylammonium ions, aryl-substituted**

Fluorimetry; Dissociation constant; Drugs (108) 249

**Alkyllead**

At. abs. spectrometry; Gas chromatography; Electrotherm. atomization; Air; Sources (105) 255

**Alloys**

At. abs. spectrometry; Electrotherm. atomization; Lead; Antimony; Steels; Solid sampling (104) 67

At. abs. spectrometry; Electrotherm. atomization; Lead; Steels; Solid sampling (104) 75

X-ray fluore. spectrometry; Ceramics; Matrix effect corrections (102) 177

**Alumina**

Thermom. analysis; Automatic; Caustic soda; Bayer liquors (102) 233

**Aluminium**

Activ. analysis; Carbon; Deuteron (108) 367

At. abs. spectrometry; Electrotherm. atomization; Biological fluids (101) 385

Emission spectrometry; Iron; Silicon; Titanium; Flame; Vapor-phase sampling; Chlorides (101) 89

Flow system; Spectrophotometry; Plants; Soils; Merging zones (107) 309

Spectrophotometry; Lanthanum; Beryllium; Effect of poly(vinylbenzyltriphényl-phosphonium chloride) (104) 145

**Aluminium alloys**

At. abs. spectrometry; Trace elements; Dissolution procedure (109) 165

**Aluminium-silicon alloys**

Activ. analysis; Phosphorus; Helium-4 (101) 63

**Amines, aromatic**

Fluorimetry; Dissociation constant; Hydroxy compounds; Sparingly soluble (106) 81

**Amino acid enantiomers**

H.p.l.c.; Derivatization (101) 111

**Amino acids**

Emission spectrometry; Molecular emission cavity analysis; Aliphatic amines (105) 433

**Aminophenol**

Diff. pulse polarography; Indophenol derivatization; Ammonia; Sulphanilamide (101) 211

**Aminopyridines**

Fluorimetry; Diaminopyridines; Comparative study (107) 291

**Ammonia**

Diff. pulse polarography; Indophenol derivatization; Aminophenol; Sulphanilamide (101) 211

**Ammonium**

Autocorrelation analysis; Sampling frequency; Waters; Quality control; Nitrate; Nitrite (103) 445

**Amphotericin B**

Biosensors; Antibiotics; Nystatin; Electrochemical (104) 195

**Analytical atomic spectroscopy**

Review; CSIRO Australia (106) 175

**Animal feeds**

Fluorimetry; Automatic; Selenium (105) 445

**Anode slimes**

Tellurium; Se-Te separation (107) 415

**Anthroic acid**

Fluorimetry; Acidity constants; Naphthoic acid (105) 311

**Antibiotics**

Flow system; Potentiometry; Cephalosporins; Bacterial reactor (105) 429

Potentiometry; Rubidium-selective electrode; Nystatin assay; Polyene (105) 77

Titrimetry; Penicillins; Iodate titrant (105) 361

Biosensors; Amphotericin B; Nystatin; Electrochemical (104) 195

Cephalosporins; Iodate titrant (105) 369

**Antimony**

At. abs. spectrometry; Rocks; Automatic; Hydride generation (101) 33

At. abs. spectrometry; Electrotherm. atomization; Lead; Alloys; Steels; Solid sampling (104) 67

At. fluor. spectrometry; Hydride generation; Non-dispersive (101) 375

Emission spectrometry; Chemiluminescence, gas-phase; Arsenic; Hydride formation (109) 229

Spectrophotometry; With ferroin; Speciation (108) 417

Polyurethane foam extraction (106) 161

#### **Arc-nebulization**

At. abs. spectrometry; Lead; Cadmium; Zinc; Copper (102) 15

#### **Argon plasma**

Emission spectrometry; H.p.l.c.; Diketonates; Ketoamines; Diethyldithiocarbamates; Metal-specific detection (101) 99

#### **Arsenic**

At. abs. spectrometry; Mercury; Fish tissues; Automatic (101) 193

At. abs. spectrometry; Electrotherm. atomization; Urine; Automatic (104) 177

At. abs. spectrometry; Electrotherm. atomization; Rocks; Soils; Hydride generation (108) 357

At. fluor. spectrometry; Waters; Hydride generation (104) 173

At. fluor. spectrometry; At. abs. spectrometry; Spectral lamp; Selenium; Controlled temperature-gradient (108) 347

Emission spectrometry; Sediments; D.c. plasma (107) 395

Emission spectrometry; Chemiluminescence, gas-phase; Antimony; Hydride formation (109) 229

Titrimetry; Amperometry; Iodine; Hydrazine; Isonicotinic acid hydrazide; Uric acid; Photosensitized generation; Rose Bengal (104) 397

#### **Arsenic profiles**

Diff. pulse polarography; Silicon slices (106) 137

#### **Ascorbic acid**

Kinetic analysis; Uric acid; Mixtures (108) 441

Spectrophotometry; Titrimetry; Ferricinium reaction (106) 379

#### **Atom collection**

At. abs. spectrometry; Copper; Cooled tube (107) 191

#### **Atomic acoustic spectrometry**

Sodium (106) 361

#### **Autocorrelation analysis**

Time series; Quality control; Missing values (103) 133

Time series; Quality control; Analysis of variance; Comparison (103) 253

Sampling frequency; Waters; Quality control; Ammonium; Nitrate; Nitrite (103) 445

#### **Automated**

Activ. analysis; Multielement analysis; Extraction system (106) 103

Flow system; Diff. pulse polarography; Square-wave; Dropping mercury electrode (102) 99

#### **Automated chemical synthesis**

Simplex optimization (103) 469

#### **Automated partial structure expansion**

Computer program (103) 121

#### **Automated spectra evaluation**

Mass spectrometry; Computer program; Spark-source (103) 223

#### **Automatic**

At. abs. spectrometry; Antimony; Rocks; Hydride generation (101) 33

At. abs. spectrometry; Mercury; Arsenic; Fish tissues (101) 193

At. abs. spectrometry; Electrotherm. atomization; Arsenic; Urine (104) 177

At. abs. spectrometry; Waters; Sediments; Mercury, total (104) 285

Fluorimetry; Selenium; Biological materials; Benzopiazselenol (105) 319

Fluorimetry; Selenium; Animal feeds (105) 445

Fluorimetry; Selenium; Phase-separating device (105) 451

Kinetic analysis; Formaldehyde; Hexamethylenetetramine; Cyanide-selective electrode (107) 91

Potentiometry; Stripping analysis; Mercury (105) 33

Thermom. analysis; Caustic soda; Alumina; Bayer liquors (102) 233

#### **Automotive catalyst material**

At. abs. spectrometry; Electrotherm. atomization; Platinum (110) 29

## **B**

#### **Background monitoring device**

At. abs. spectrometry (109) 177

#### **Bacterial membrane electrode**

Potentiometry; Cysteine; Proteus morganii (101) 125

**Bacterial reactor**

Flow system; Potentiometry; Cephalosporins; Antibiotics (105) 429

**Barbiturates**

Gas chromatography; Pentobarbital; Blood; Butylation methods (105) 139

**Barium**

Emission spectrometry; Waters; Biological fluids; Inductively-coupled plasma (110) 271

**Benzidine**

Fluorimetry; Polynuclear aromatic hydrocarbons; Computer decomposition of spectra; Dibenzochrysene; Quantitative (103) 167

**Benzodiazolinone fluorophore**

Fluorimetry; Domperidone; Pharmaceuticals (110) 261

**Benzophenone oxime extractants**

Potentiometry; Titrimetry; LIX reagents; Nonaqueous (105) 83

**Benzolalpyrene**

Chromatography; Reflectance spectrometry; Oil shale; Retort waters (101) 333

**Beryllium**

At. abs. spectrometry; Electrotherm. atomization; Manganese; Air particulates (105) 219

Spectrophotometry; Lanthanum; Aluminium; Effect of poly(vinylbenzyltriphenylphosphonium chloride) (104) 145

**Bile acids**

H.p.l.c.; Naphthylidazoalkanes as derivatizing agents (109) 161

**Bioassay**

Amperometry; Nystatin; Microbial electrode; Yeast (109) 39

**Biological fluids**

At. abs. spectrometry; Electrotherm. atomization; Aluminium (101) 385

Emission spectrometry; Barium; Waters; Inductively-coupled plasma (110) 271

**Biological materials**

Activ. analysis; Chlorine; Bromine; Iodine; Waters; Organically bound; Contamination problems (108) 137

At. abs. spectrometry; Cobalt (104) 389

Fluorimetry; Selenium; Automatic; Benzopiaz-selenol (105) 319

**Biological tissues**

At. abs. spectrometry; Dithizone extraction; Sea water; Trace metals (110) 21

**Bio-Rad AG**

Ion exchange; Distribution coefficients; Effect of organic solvents (102) 167

**Biosensors**

Antibiotics; Amphotericin B; Nystatin; Electrochemical (104) 195

**Bismuth**

At. abs. spectrometry; Electrotherm. atomization; Nickel-base alloys; Hydride generation; Solid samples; Induction furnace (102) 33

At. abs. spectrometry; Electrotherm. atomization; Rocks (106) 325

At. abs. spectrometry; Electrotherm. atomization; Silver; Cadmium; Zinc; Steels; Solids autosampler (108) 75

**Blind assay**

Gas chromatography; Pattern recognition; Whiskies (103) 201

**Blood**

Activ. analysis; Multielement analysis; SLOWPOKE reactor (105) 185

Activ. analysis; Electrotherm. atomization; At. abs. spectrometry; Trace elements; Method comparison (110) 9

Amperometry; Galactose; Urine; Enzymatic (104) 47

Amperometry; Flow system; Glycerol; Triglycerides; Tubular carbon electrode; Enzymatic (106) 225

Amperometry; Phosphatidyl choline; Immobilized phospholipase-choline oxidase (106) 243

At. abs. spectrometry; Electrotherm. atomization; Selenium; Stabilization in ashing (110) 285

Flow system; Enzymatic analysis; Injection analysis; Glucose; Merging zones (106) 207

Gas chromatography; Pentobarbital; Barbiturates; Butylation methods (105) 139

Gas chromatography; Warfarin (106) 155

Gas chromatography; Xanthinol (108) 401

H.p.l.c.; Nitrofurantoin; Urine; Related drugs (101) 359

**Boron**

At. abs. spectrometry; Electrotherm. atomization; Waters (106) 121

Emission spectrometry; Waters; Trace metals; Plasmas; High salt concentration (109) 73

Spectrophotometry; Waters; Rocks; Sephadex G-25 sorption (109) 115

**Brines**

Spectrophotometry; Chlorophenols; Aminoantipyrene (102) 229

**Bromide-selective electrode**

Potentiometry; Response mechanism; Hg<sub>2</sub>Br<sub>2</sub>-HgS-Ag<sub>2</sub>S membranes (110) 197

**Bromine**

Activ. analysis; Chlorine; Iodine; Waters; Biological materials; Organically bound; Contamination problems (108) 137

**Bromine-containing compounds**

Gas chromatography; Potentiometry; Chlorine-containing compounds; Hydrogenation; Dual electrode detector (101) 273

**Bromine generation**

Coulometry; Acetic acid medium (106) 347

**Buffer systems**

Multicomponent two-phase (107) 359

**Butyl phosphate**

Gas chromatography; Dibutyl phosphate; In tributyl phosphate (106) 373

**C****Cadmium**

Anod. stripping voltammetry; Flow system; Rotating disc electrode; Lead; Copper (101) 1

Anod. stripping voltammetry; Mercury film electrode; Lead; Copper; Waters; Baseline concentrations (101) 79

Anod. stripping voltammetry; Semidifferential electroanalysis; Lead; Thallium (101) 131

Anod. stripping voltammetry; Lead; Thallium; Learning machine method (103) 151

Anod. stripping voltammetry; Computer-controlled; Lead; Copper; Parameter evaluation (107) 13

Anod. stripping voltammetry; Lead; Copper; Urine; Sample treatment (107) 37

At. abs. spectrometry; Lead; Zinc; Copper; Arc-nebulization (102) 15

At. abs. spectrometry; Electrotherm. atomization; Chromium; Cobalt; In uranium (104) 113

At. abs. spectrometry; Rice; Low-temperature ashing; Extraction (104) 393

At. abs. spectrometry; Electrotherm. atomization; Copper; Zinc; Nickel; Sea water; Sampling methods; Dithiocarbamate extraction; Chelex (105) 233

At. abs. spectrometry; Gel perm. chromatography; Copper; Zinc; Saliva; Distribution (107) 211

At. abs. spectrometry; Electrotherm. atomization; Silver; Bismuth; Zinc; Steels; Solids autosampler (108) 75

At. fluor. spectrometry; Electrotherm. atomization; Trace metals; Carbon filament (104) 85

Emission spectrometry; Discharge lamp; Heated-electrode (110) 291

Ion exchange; Lead; Hafnium phosphate cation exchanger; Photoelectron study; Separation (104) 319

Potentiometry; Stripping analysis; Zinc; Lead; Copper; Sea water; Mercury film electrode (107) 29

Detection; Pyruvylidinediazinobenzothiazole (101) 229

Computer-controlled; Charging current correction; Pseudo-derivative (101) 309

Computerized Kalousek polarography; Potassium; Lithium (103) 367

**Cadmium-ethylenediamine complex formation**

Computer-assisted; Stripping polarography; Sea water (109) 327

**Cadmium-selective electrode**

Potentiometry; Mercury-selective electrode; Metal sulphide membranes; Complexing agents (108) 169

**Calcium**

Amperometry; Titrimetry; In alkali metal salts; Triethylenetetraminehexaacetic acid (109) 67

Emission spectrometry; Sodium; Potassium; Lithium; Computer program; High concentrations (107) 201

Flow system; Emission spectrometry; At. abs. spectrometry; Magnesium; Potassium; Plants; Merging zones (104) 279

Kinetic analysis; Flow system; Magnesium; Differential; Cryptates; Phthalein complexone (108) 241

Potentiometry; Hydrogen ion; Potassium; ISFET (101) 239

**Calcium ion buffers**

Potentiometry; Measured and calculated concentrations (109) 291

**Calcium-selective electrode**

Potentiometry; PVC membrane; Bistetra-methylbutyldinitrophenoxide (108) 385

**Calibration in quantitative analysis**

Theory (108) 315

**Carbaryl**

Fluorimetry; Naphthylmethylcarbamate; Naphthol (108) 425

**Carbohydrates, reducing**

Fluorimetry; With malonamide (108) 421

**Carbon**

Activ. analysis; In refractory metals; Deuteron (108) 127

Activ. analysis; Aluminium; Deuteron (108) 367

Activ. analysis; Nitrogen; Hydrogen; Prompt  $\gamma$ -ray; Environmental materials (110) 339

I.r. spectrometry; Sulphur; Rocks; Combustion (101) 25

I.r. spectrometry; Carbonate; Geological materials; Rocks; Non-carbonate (108) 113

#### **Carbon, activated**

Silicic acid, dispersed; Multielement preconcentration; Comparison (107) 177

#### **Carbonate**

I.r. spectrometry; Carbon; Geological materials; Rocks; Non-carbonate (108) 113

#### **Carbon disulphide**

Diff. pulse polarography; Waters (107) 387

#### **Carbon electrode**

Flow system; Cyclic voltammetry; H.p.l.c.; Hexacyanoferrate; Dianisidine; Drugs (102) 41

pH response; Reticulated vitreous (108) 379

Lead dioxide-coated (108) 395

#### **Carbonic acid dehydration kinetics**

Flow system; Mixer design (106) 73

#### **Carbositil electrode**

Anod. stripping voltammetry; Chronopotentiometry; Copper (102) 91

#### **Carboxylic acids**

Titrimetry; Acid-base equilibria; Dimethylsulphoxide-water (101) 139

Titrimetry; Acid-base equilibria; Dimethylsulphoxide-water; Correction (110) 183

#### **Carboxymethylcysteine**

Manganese; Nickel; Copper; Lead; Complex formation (104) 299

#### **Carotenoids**

H.p.l.c.; Phytoplankton pigments; Chlorophylls; Marine particulate matter (107) 1

#### **Catecholamines**

Phosphorimetry; Related compounds; Analytical characteristics (108) 297

#### **Caustic soda**

Thermom. analysis; Automatic; Alumina; Bayer liquors (102) 233

#### **Cephalexin degradation study**

Diff. pulse polarography (110) 107

#### **Cephalosporins**

Diff. pulse polarography; Degradation products (108) 205

Flow system; Potentiometry; Bacterial reactor; Antibiotics (105) 429

Antibiotics; Iodate titrant (105) 369

#### **Ceramics**

X-ray fluores. spectrometry; Alloys; Matrix effect corrections (102) 177

#### **Cerium**

Gravimetry; Titrimetry; As phosphate (101) 413

#### **Cesium**

Gravimetry; Tetrathienylborates; Quaternary ammonium salts; Synthesis (105) 353

Isotope dilut. analysis; Substoichiometric concentration; Theory (104) 327

#### **Cesium-137**

Sea water; Sorption on copper hexacyanoferrate (102) 225

#### **Chemical shifts**

N.m.r. spectrometry; Computer program; Retrieval system; Carbon-13 (103) 141

#### **Chemiluminescence, gas-phase**

Emission spectrometry; Arsenic; Antimony; Hydride formation (109) 229

#### **Chloride**

Potentiometry; Single-point titrations; Silver; Sulphate (107) 101

ISFET; Iodide; Polyfluorinated polyphosphazene membranes; Silver salts (108) 161

#### **Chlorindazone DS**

Spectrophotometry; Metal ions; Reagent evaluation (106) 141

#### **Chlorine**

Activ. analysis; Bromine; Iodine; Waters; Biological materials; Organically bound; Contamination problems (108) 137

Potentiometry; Titrimetry; Organic materials; Sodium biphenyl (101) 221

#### **Chlorine-containing compounds**

Gas chromatography; Potentiometry; Bromine-containing compounds; Hydrogenation; Dual electrode detector (101) 273

#### **Chlorine traces**

Spectrophotometry; Amperometry; Air; Comparison (104) 355

#### **Chlorite traces**

Pulse polarography (107) 383

#### **Chloroalkanes**

Gas chromatography; Mass spectrometry; Negative-ion counting (107) 335

#### **Chlorophenols**

Spectrophotometry; Brines; Aminoantipyrine (102) 229

#### **Chlorophylls**

H.p.l.c.; Phytoplankton pigments; Carotenoids; Marine particulate matter (107) 1

#### **Cholinesterase activity**

Enthalpimetry; Serum; Direct injection (109) 393

#### **Chromate**

Gravimetry; Sulphate; Vanadate; Stepwise precipitation (110) 179

Potentiometry; Titrimetry; Fluoride; Sulphate; Molybdate; Tungstate; Oxalate; Phosphate; Hexacyanoferrate; Fluoride-selective electrode; Lead titrant (109) 319

**Chromium**

At. abs. spectrometry; Electrotherm. atomization; Cadmium; Cobalt; In uranium (104) 113

**Chromium losses**

Activ. analysis; Liver tissue lyophilization; Trace element losses (109) 139

**Chromium speciation**

Ion exchange; At. abs. spectrometry; Welding fumes (110) 307

**Chronopotentiometry**

Anod. stripping voltammetry; Copper; Carbosital electrode (102) 91

**Citric acid**

Potentiometry; Kinetic analysis; Perbromate-selective electrode (108) 375

**Coal fly ash**

At. abs. spectrometry; Trace metals; Room-temperature dissolution (106) 299

**Cobalt**

Anod. stripping voltammetry; Mercury film electrode (109) 157

At. abs. spectrometry; Electrotherm. atomization; Cadmium; Chromium; In uranium (104) 113

At. abs. spectrometry; Biological materials (104) 389

At. abs. spectrometry; Nickel; Copper; Rocks; Matrix masking; Dithiocarbamate extraction (105) 247

At. abs. spectrometry; Electrotherm. atomization; Ion-exchanger suspensions; Mercury; Nickel; Molybdenum; Direct sampling (110) 301

Flow system; Spectrophotometry; Nickel; Computer-processed; Photodiode-array spectrophotometer (109) 425

Ion exchange; Copper; Nickel; Uranyl; Stability constants; Sulphosalicylate complexes; Distribution diagrams (108) 333

Potentiometry; Coulometry; Steels; Picolinic acid media (110) 227

Spectrophotometry; Dipyrildylpyrimidyl-hydrazone (104) 191

**Cobalt(III)/cobalt(II) system**

Steels; Current-voltage curves; Picolinic acid media (110) 219

**Cobalt-selective electrode**

Potentiometry; Coated wire; Benzalkonium ion pair (107) 113

**Codeine**

Flow system; Spectrophotometry; Extraction device; Acetylsalicylic acid tablets (104) 21

**Complement fixation test**

Potentiometry; Immunoassay; Serum antibodies; Trimethylphenylammonium-selective electrodes (109) 25

**Computer-aided interpretation**

I.r. spectrometry; Information theory; Numerical taxonomy; Feature selection (103) 313

Mass spectrometry; Steroids; Pattern recognition; Binary classifiers (103) 61

**Computer-aided structure elucidation**

Unique naming (103) 245

**Computer-assisted**

Cadmium-ethylenediamine complex formation; Stripping polarography; Sea water (109) 327

**Computer-based system**

Diff. pulse polarography; Molybdenum; Microcomputer; Interfacing (108) 155

**Computer-calculated rate constants**

Spectrophotometry; Halogenopentamine-chromium(III) perchlorate; Aquation kinetics (107) 279

**Computer-controlled**

Anod. stripping voltammetry; Cadmium; Lead; Copper; Parameter evaluation (107) 13

At. abs. spectrometry; Microcomputer (103) 401

Gas chromatography; Mass spectrometry; Polynuclear aromatic hydrocarbons; Air (105) 119

Spectrophotometry; Photometric analyzer; Lidocaine; Microcomputer (103) 489

Cadmium; Charging current correction; Pseudo-derivative (101) 309

**Computer-controlled laboratory system**

(103) 459  
Pharmaceuticals; Quality control; Hierarchical (103) 483

**Computer decomposition of spectra**

Fluorimetry; Polynuclear aromatic hydrocarbons; Benzidine; Dibenzochrysene; Quantitative (103) 167

Parameter refinement (103) 263

**Computer deconvolution of spectral data**

Transition metal compounds; Least-squares fitting (103) 73

**Computer-generated mass thermograms**

Thermogravimetry-mass spectrometry; Acrylic fibres; Alkyd paints; Interface (107) 327

**Computerized data processing**

Gas chromatography; Microwave plasma detector; Selectivity improvement; Four-channel calculations (103) 29

N.m.r. spectrometry; HOSE; Substructure code (103) 355

**Computerized data system**

I.r. spectrometry; Minicomputer; Dispersive (103) 303

I.r. spectrometry; Industrial applications; Dispersive; Minicomputer (103) 323

**Computerized Kalousek polarography**

Cadmium; Potassium; Lithium (103) 367

**Computer-processed**

Flow system; Spectrophotometry; Nickel; Cobalt; Photodiode-array spectrophotometer (109) 425

**Computer program**

Emission spectrometry; Sodium; Potassium; Calcium; Lithium; High concentrations (107) 201

E.s.r.; Spectra simulation; Fourier transform; Morphamquat (103) 175

Mass spectrometry; Text search system; Spectral library (103) 109

Mass spectrometry; Automated spectra evaluation; Spark-source (103) 223

N.m.r. spectrometry; Chemical shifts; Retrieval system; Carbon-13 (103) 141

Fourier spectral analysis; Multipurpose (103) 43

Automated partial structure expansion (103) 121

**Computer-readable spectra libraries**

Mass spectrometry; N.m.r. spectrometry; I.r. spectrometry; Spectrophotometry; Compilation (103) 21

**Computer system**

Mass spectrometry; N.m.r. spectrometry; Graphical reproduction; Structure input (103) 237

**Conductivity detector**

Flow system; Potassium chloride; Non-intrusive very high-frequency (110) 325

**Copper**

Activ. analysis; At. abs. spectrometry; Manganese; Sea water; Comparison; Co-crystallization; Extraction (104) 337

Anod. stripping voltammetry; Flow system; Rotating disc electrode; Lead; Cadmium (101) 1

Anod. stripping voltammetry; Mercury film electrode; Cadmium; Lead; Waters; Baseline concentrations (101) 79

Anod. stripping voltammetry; Waters; Iron interference (101) 437

Anod. stripping voltammetry; Chronopotentiometry; Carbonsital electrode (102) 91

Anod. stripping voltammetry; Computer-controlled; Cadmium; Lead; Parameter evaluation (107) 13

Anod. stripping voltammetry; Cadmium; Lead; Urine; Sample treatment (107) 37

At. abs. spectrometry; Electrotherm. atomization; Zeeman splitting; Molybdenum (101) 367

At. abs. spectrometry; Lead; Cadmium; Zinc; Arc-nebulization (102) 15

At. abs. spectrometry; Electrotherm. atomization; Gasoline (102) 201

At. abs. spectrometry; Electrotherm. atomization; Cadmium; Zinc; Nickel; Sea water; Sampling methods; Dithiocarbamate extraction; Chelex (105) 233

At. abs. spectrometry; Cobalt; Nickel; Rocks; Matrix masking; Dithiocarbamate extraction (105) 247

At. abs. spectrometry; Atom collection; Cooled tube (107) 191

At. abs. spectrometry; Gel perm. chromatography; Cadmium; Zinc; Saliva; Distribution (107) 211

At. abs. spectrometry; Electrotherm. atomization; Gallium; Silver; Signal depression (109) 97

Ion exchange; Nickel; Cobalt; Uranyl; Stability constants; Sulphosalicylate complexes; Distribution diagrams (108) 333

Potentiometry; Kinetic analysis; pH-stat method; Molybdenum; Zirconium; Vanadium (104) 205

Potentiometry; Stripping analysis; Zinc; Cadmium; Lead; Sea water; Mercury film electrode (107) 29

Spectrophotometry; Tetraphenylporphine (101) 423

X-ray fluores. spectrometry; Zinc; Lead; Manganese; Phosphate-containing matrices (109) 419

Manganese; Nickel; Lead; Carboxymethylcysteine; Complex formation (104) 299

**Copper complexes**

Gas chromatography; Ketoamines; Quantitative (101) 117

**Copper, electrolytic**

Anod. stripping voltammetry; Selenium; Tellurium; Gold film electrode (110) 87

**Copper-nitritotriacetic acid ternary complexes**  
Potentiometry; Stability constants (107) 105**Copper-selective electrode**

Potentiometry; Flow system (101) 419

Potentiometry; Chloride interference; Mechanism (105) 53

Potentiometry; Ion-selective electrodes; Surface morphology (109) 279

**Correction constants**

X-ray fluores. spectrometry; Multivariate least-squares method (104) 1

**Corticosteroids**

Coulometry; Diff. pulse voltammetry; Diff. pulse polarography; Electroproperties (102) 161

Diff. pulse polarography; Pharmaceuticals; Single component (108) 389

**Coumaric acid**

H.p.l.c.; Scopoletin; Umbelliferone; Ferulic acid; Isomers; Optimization strategy (108) 227

**Cyanide-selective electrode**

Potentiometry; Effect of pH (102) 85

**Cysteine**

Amperometry; Flow system; H.p.l.c.; Cystine; Penicillamine (101) 253

Potentiometry; Bacterial membrane electrode; *Proteus morgani* (101) 125

**Cystine**

Amperometry; Flow system; H.p.l.c.; Cysteine; Penicillamine (101) 253

**D****Diaminopyridines**

Fluorimetry; Aminopyridines; Comparative study (107) 291

**Dianisidine**

Flow system; Cyclic voltammetry; H.p.l.c.; Carbon electrode; Hexacyanoferrate; Drugs (102) 41

**Dibenzochrysenes**

Fluorimetry; Polynuclear aromatic hydrocarbons; Computer decomposition of spectra; Benzidine; Quantitative (103) 167

**Dibutyl phosphate**

Gas chromatography; Butyl phosphate; In tributyl phosphate (106) 373

**Diethyldithiocarbamates**

Emission spectrometry; H.p.l.c.; Argon plasma; Diketonates; Ketoamines; Metal-specific detection (101) 99

**Diethyldithiocarbamic acid**

Liquid-liquid extraction; Optimization (105) 281

**Dihaloquinolinols**

Fluorimetry; Quinolinol; Simultaneous (106) 67

**Dihydroxyphenylalanine**

H.p.l.c.; Fluorimetry; Pharmaceuticals; Hydrazinomethyl-dihydroxyphenylpropanoic acid (105) 403

**Diketonates**

Emission spectrometry; H.p.l.c.; Argon plasma; Ketoamines; Diethyldithiocarbamates; Metal-specific detection (101) 99

**Dimethylsulphoxide-water**

Titrimetry; Acid-base equilibria; Carboxylic acids (101) 139

Titrimetry; Acid-base equilibria; Carboxylic acids; Correction (110) 183

**Dinitrogen tetroxide**

Potentiometry; Dissociation constant; Nitrosyl chloride; Silver-silver chloride electrode; Sulpholane media (110) 211

**Diocetyl tin stabilizers**

At. abs. spectrometry; Electrotherm. atomization; Food-simulating solvents (101) 393

**Discharge lamp**

Emission spectrometry; Cadmium; Heated-electrode (110) 291

**Disodium cromoglycate**

Diff. pulse polarography; Urine (102) 205

**Dissociation constant**

Fluorimetry; Amines, aromatic; Hydroxy compounds; Sparingly soluble (106) 81

Fluorimetry; Alkylammonium ions, aryl-substituted; Drugs (108) 249

Potentiometry; Nitrosyl chloride; Dinitrogen tetroxide; Silver-silver chloride electrode; Sulpholane media (110) 211

**Distribution coefficients**

Ion exchange; Metals; Thiocyanates (101) 207

Ion exchange; Bio-Rad AG; Effect of organic solvents (102) 167

**Disulphide**

Emission spectrometry; Sulphur, total; Polysulphide; Petroleum products; Reduction method (107) 231

**Dithizone extraction**

At. abs. spectrometry; Sea water; Biological tissues; Trace metals (110) 21

**Domperidone**

Fluorimetry; Pharmaceuticals; Benzodiazolin-one fluorophore (110) 261

**Dopamine**

H.p.l.c.; Norepinephrine; Serotonin; Brain tissue; Electrochemical detection (104) 29

**Drugs, basic**

Alkaloids; Ion-pair extraction; Diethylhexyl-phosphoric acid (106) 271

**E****EDTA**

Spectrophotometry; Niobium; Pyrocatechol ternary complex; NTA contamination (108) 433



**Enzymatic analysis**

Flow system; Injection analysis; Blood;  
Glucose; Merging zones (106) 207

**Enzymatic inhibition**

Enthalpimetry; Alkaloids; Cholinesterase  
(106) 39

**Enzyme determinations**

Spectrophotometry; U.V.-absorptiostat;  
Catalase; Ascorbate oxidase; Peroxidase;  
Sorbitol dehydrogenase; Lactate  
dehydrogenase (109) 351

**Enzyme reactor**

Potentiometry; Flow system; Glucose; Protein  
removal (105) 43

**Enzyme sensors**

Amperometry; Lactate; Cytochrome (109) 55

**Ethanediol solvent**

Spectrophotometry; pH scale (104) 181

**Ethanol**

Voltammery; Lactic acid; Enzymatic; Linear-  
sweep; NAD-modified carbon paste electrode  
(110) 203

**Ethylenediaminetetraacetic acid**

Spectrophotometry; Titrimetry; Manganese;  
Nickel; Catalytic; Dihydroxyphthalimide dithio-  
semicarbazone oxidation (109) 401

**Eulan WA New**

Gas chromatography; Mass spectrometry; Fish  
tissues; Polychloro(chloromethylsulphonamide)-  
diphenyl ether isomers; Identification;  
Metabolites (104) 253

**Europium**

Fluorimetry; Samarium; Thenoyltrifluoro-  
acetone-trioctylphosphine oxide (108) 429

**Extraction**

Flow system; Spectrophotometry;  
Molybdenum; Plants; Thiocyanate (101) 9

Spectrophotometry; Palladium; Nitrosodiethyl-  
aminophenol (101) 169

Spectrophotometry; Tin; Diphenyl-  
phenanthroline (104) 363

Spectrophotometry; Iron; Waters; Pyrogallol  
red; Zephramine; Removal of extracted  
reagent (104) 369

**Extraction device**

Flow system; Spectrophotometry; Codeine;  
Acetylsalicylic acid tablets (104) 21

**Extraction system**

Activ. analysis; Automated; Multielement  
analysis (106) 103

**F****Fatty acids**

H.p.l.c.; Naphthyl diazoalkanes as derivatizing  
agents; Edible oils (109) 61

**Ferulic acid**

H.p.l.c.; Scopoletin; Umbelliferone; Coumaric  
acid; Isomers; Optimization strategy (108) 227

**Fire assay**

Activ. analysis; Platinum group elements;  
Gold; Rocks; Ores (102) 157

**Fish**

At. abs. spectrometry; Methylmercury (102) 189

At. abs. spectrometry; Mercury; Hair (108) 13

Gas chromatography; At. abs. spectrometry;  
Mercury compounds; Extraction procedure  
(107) 169

**Fish oils**

Spectrophotometry; Thiobarbituric acid values  
(106) 279

**Fish tissues**

At. abs. spectrometry; Mercury; Arsenic;  
Automatic (101) 193

Gas chromatography; Mass spectrometry;  
Eulan WA New; Polychloro(chloromethyl-  
sulphonamide)diphenyl ether isomers;  
Identification; Metabolites (104) 253

**Fluoride**

Potentiometry; Titrimetry; Sulphate;  
Chromate; Molybdate; Tungstate; Oxalate;  
Phosphate; Hexacyanoferrate; Fluoride-  
selective electrode; Lead titrant (109) 319

Spectrophotometry; Potentiometry; Distillation  
with hexamethyldisiloxane (106) 95

**Fluoride-selective electrode**

Potentiometry; Dynamic response (102) 61

**Fly ash**

Potentiometry; Titrimetry; Sulphur; Waters;  
Irons; Steels; Cadmium sulphide electrode;  
Hydrogen sulphide generation (109) 307

**Food-simulating solvents**

At. abs. spectrometry; Electrotherm. atomiz-  
ation; Dioctyltin stabilizers (101) 393

**Formaldehyde**

Kinetic analysis; Hexamethylenetetramine;  
Automatic; Cyanide-selective electrode (107) 91

**Formation constants**

Spectrophotometry; Molar absorptivity;  
Continuous variations curves (101) 157

**Fourier spectral analysis**

Computer program; Multipurpose (103) 43

**Fourier transform**

E.s.r.; Spectra simulation; Computer program;  
Morphamquat (103) 175

**Furosemide**

Spectrophotometry; Phloroglucinol (106) 151

**G****Galactose**

Amperometry; Blood; Urine; Enzymatic  
(104) 47

**Gallium**

At. abs. spectrometry; Electrotherm. atomiz-  
ation; Rhenium; Silicon; Trace metals (108) 45

At. abs. spectrometry; Electrotherm. atomiz-  
ation; Copper; Silver; Signal depression  
(109) 97

Ion exchange; At. abs. spectrometry;  
Manganese nodules; Rocks (109) 181

**Gasoline**

At. abs. spectrometry; Electrotherm. atomiz-  
ation; Copper (102) 201

**Geological materials**

I.r. spectrometry; Carbonate; Carbon; Rocks;  
Non-carbonate (108) 113

**Germanium**

A.c. polarography; Diff. pulse polarography;  
Silver-germanium alloys (102) 113

At. abs. spectrometry; Electrotherm. atomiz-  
ation; Tungsten tube; Rocks (104) 293

At. abs. spectrometry; Electrotherm. atomiz-  
ation; Interference mechanisms (107) 253

Emission spectrometry; Tin; Plasmas; Hydride  
generation (109) 251

**Glass column connector**

Gas chromatography (107) 399

**Glow discharge detector**

Gas chromatography; Silicon; Shale-derived  
liquids; Trimethylsilylation (108) 221

**Glow lamp**

Emission spectrometry; Gold; Internal  
standardization (104) 11

**Glucose**

Flow system; Enzymatic analysis; Injection  
analysis; Blood; Merging zones (106) 207

Potentiometry; Flow system; Enzyme reactor;  
Protein removal (105) 43

**Glucose analyzer**

Amperometry; Flow system; Immobilized  
glucose oxidase (106) 233

**Glycerol**

Amperometry; Flow system; Triglycerides;  
Blood; Tubular carbon electrode; Enzymatic  
(106) 225

**Glycine**

Flow system; Fluorimetry; Albumin (106) 395

**Gold**

Activ. analysis; Platinum group elements;  
Rocks; Fire assay; Ores (102) 157

Activ. analysis; Tungsten; Rocks (102) 221

Coulometry; Electrogeneration (107) 83

Emission spectrometry; Glow lamp; Internal  
standardization (104) 11

Fluorimetry; Kojic acid; Reaction study  
(106) 147

Gravimetry; Dialkyl sulphites (102) 237

**Gold film electrode**

Anod. stripping voltammetry; Selenium;  
Tellurium; Copper, electrolytic (110) 87

**Gran method**

Potentiometry; Titrimetry (107) 377

**Guanidino compounds**

Fluorimetry; Polypeptides; Benzoin-dimethyl-  
formamide (106) 89

**Gum exudates**

Polysaccharides; Degradation in  
permethylation (105) 147

**H****Hafnium**

Mass spectrometry; Lanthanides; Rocks;  
Interference effects; Spark-source (105) 163

**Hafnium phosphate cation exchanger**

Ion exchange; Lead; Cadmium; Photoelectron  
study; Separation (104) 319

**Hair**

At. abs. spectrometry; Mercury; Fish (108) 13

**Halide mixtures**

Potentiometry; Titrimetry; Iodide-selective  
electrode (105) 417

**Halogenopentamminechromium(III)  
perchlorate**

Spectrophotometry; Computer-calculated rate  
constants; Aquation kinetics (107) 279

**Heavy metals**

Anod. stripping voltammetry; Siliconization effects (107) 67

At. abs. spectrometry; Electrotherm. atomization; Ion exchange; Sea water; Selective elution; Chelex (104) 307

**Hexacyanoferrate**

Flow system; Cyclic voltammetry; H.p.l.c.; Carbon electrode; Dianisidine; Drugs (102) 41

Potentiometry; Titrimetry; Fluoride; Sulphate; Chromate; Molybdate; Tungstate; Oxalate; Phosphate; Fluoride-selective electrode; Lead titrant (109) 319

Extraction study; Aliquat-336 (105) 383

**Hexafluoropropanediol**

Diff. pulse polarography; Acidity functions; Trifluoroacetic acid; Trifluoromethane-sulphonic acid (106) 51

**Hexamethylenetetramine**

Kinetic analysis; Formaldehyde; Automatic; Cyanide-selective electrode (107) 91

**Homogeneity of solids**

Sampling; Statistical model (105) 1

Two-dimensional variance analysis (110) 145

**Hydrazide**

Coulometry; Titrimetry; Hydrazine (102) 215

**Hydrazine**

Coulometry; Titrimetry; Hydrazide (102) 215

Titrimetry; Amperometry; Iodine; Isonicotinic acid hydrazide; Uric acid; Arsenic; Photosensitized generation; Rose Bengal (104) 397

**Hydrazinomethylidihydroxyphenylpropanoic acid**

H.p.l.c.; Fluorimetry; Pharmaceuticals; Dihydroxyphenylalanine (105) 403

**Hydride generation**

At. abs. spectrometry; Antimony; Rocks; Automatic (101) 33

At. abs. spectrometry; Electrotherm. atomization; Bismuth; Nickel-base alloys; Solid samples; Induction furnace (102) 33

At. fluor. spectrometry; Tin (101) 199

At. fluor. spectrometry; Antimony; Non-dispersive (101) 375

At. fluor. spectrometry; Arsenic; Waters (104) 173

Emission spectrometry; Tin; Germanium; Plasmas (109) 251

**Hydrogen**

Activ. analysis; Nitrogen; Carbon; Prompt  $\gamma$ -ray; Environmental materials (110) 339

**Hydrogen chloride traces**

Coulometry; Standard source; Gaseous reference mixtures (110) 95

**Hydrogen ion**

Potentiometry; Potassium; Calcium; ISFET (101) 239

**Hydrogen peroxide**

Amperometry; Catalytic electrode (110) 157

**Hydroxy compounds**

Fluorimetry; Dissociation constant; Amines, aromatic; Sparingly soluble (106) 81

**Hypoxanthine**

Diff. pulse voltammetry; Polyinosinic acid; Oxidation at PGE (108) 193

**I****Indophenol derivatization**

Diff. pulse polarography; Ammonia; Aminophenol; Sulphanilamide (101) 211

**Information theory**

I.r. spectrometry; Computer-aided interpretation; Numerical taxonomy; Feature selection (103) 313

**Injection analysis**

Flow system; Enzymatic analysis; Blood; Glucose; Merging zones (106) 207

**Injection techniques**

Flow system; Potentiometry; Voltammetry; Ion-selective electrodes; Voltammetric detectors; Mixing chambers; Theory (109) 1

**Iodide**

Enthalpimetry; Enzymatic method (108) 363

ISFET; Chloride; Polyfluorinated polyphosphazene membranes; Silver salts (108) 161

**Iodide-selective electrode**

Potentiometry; Theory; Low iodide concentrations (107) 121

**Iodine**

Activ. analysis; Chlorine; Bromine; Waters; Biological materials; Organically bound; Contamination problems (108) 137

Titrimetry; Amperometry; Hydrazine; Isonicotinic acid hydrazide; Uric acid; Arsenic; Photosensitized generation; Rose Bengal (104) 397

**Ion chromatography**

Chromatography; Waters; Multielement analysis; Evaluation; Geothermal (108) 405

**Ion counting-multichannel analyser**

Mass spectrometry; Quadrapole (104) 167

**Ion-exchanger suspensions**

At. abs. spectrometry; Electrotherm. atomization; Mercury; Cobalt; Nickel; Molybdenum; Direct sampling (110) 301

**Ion-selective electrodes**

Flow system; Potentiometry; Voltammetry; Injection techniques; Voltammetric detectors; Mixing chambers; Theory (109) 1

Potentiometry; Liquid ion-exchange membranes; Time constants; Method comparison (109) 259

Potentiometry; Copper-selective electrode; Surface morphology (109) 279

Potentiometry; Silver sulphide electrode; Interfacial properties; Impedance measurements (110) 185

**Ion-selective field effect transistors**

see ISFET

**Iron**

At. abs. spectrometry; Electrotherm. atomization; Magnetite electrode (101) 401

At. abs. spectrometry; Electrotherm. atomization; Internal standardization; Dual-channel system (107) 129

Emission spectrometry; Aluminium; Silicon; Titanium; Flame; Vapor-phase sampling; Chlorides (101) 89

Spectrophotometry; Extraction; Waters; Pyrogallol red; Zephiramine; Removal of extracted reagent (104) 369

Spectrophotometry; Catalytic; Anisidine-dimethylaniline reaction (106) 355

**Iron(II)-iron(III) determination**

Voltammetry; Rocks; Vitamin tablets (105) 99

**Irons**

Potentiometry; Titrimetry; Sulphur; Waters; Steels; Fly ash; Cadmium sulphide electrode; Hydrogen sulphide generation (109) 307

**ISFET**

Potentiometry; Hydrogen ion; Potassium; Calcium (101) 239

Potentiometry; Reference electrode (101) 247

Titrimetry; Acid-base (109) 145

Chloride; Iodide; Polyfluorinated polyphosphazene membranes; Silver salts (108) 161

**Isonicotinic acid hydrazide**

Ring oven; In tablets (110) 171

Titrimetry; Amperometry; Iodine; Hydrazine; Uric acid; Arsenic; Photosensitized generation; Rose Bengal (104) 397

**K****Karl Fischer titration**

Water content; Muscovites; High fluorine content (110) 233

**Ketoamines**

Emission spectrometry; H.p.l.c.; Argon plasma; Diketonates; Diethyldithiocarbamates; Metal-specific detection (101) 99

Gas chromatography; Copper complexes; Quantitative (101) 117

**Kojic acid**

Fluorimetry; Gold; Reaction study (106) 147

**L****Lactate**

Amperometry; Enzyme sensors; Cytochrome (109) 55

Flow system; Amperometry; Continuous assay (106) 131

**Lactic acid**

Voltammetry; Ethanol; Enzymatic; Linear-sweep; NAD-modified carbon paste electrode (110) 203

**Lanthanides**

Mass spectrometry; Hafnium; Rocks; Interference effects; Spark-source (105) 163

Spectrophotometry; Calmagite (106) 401

Titrimetry; Magnetic susceptibility measurements; Binary mixtures (108) 309

**Lanthanum**

Spectrophotometry; Beryllium; Aluminium; Effect of poly(vinylbenzyltriphenylphosphonium chloride) (104) 145

**Lanthanum complexes**

N.m.r. spectrometry; Stability constants; Potassium hydroxotrifluoroborate demasking reactions; EDTA; NTA (105) 391

Potassium hydroxotrifluoroborate demasking reactions; Selective demasking; EDTA (105) 397

**Lead**

Anod. stripping voltammetry; Flow system; Rotating disc electrode; Cadmium; Copper (101) 1

Anod. stripping voltammetry; Mercury film electrode; Cadmium; Copper; Waters; Baseline concentrations (101) 79

Anod. stripping voltammetry; Semidifferential electroanalysis; Cadmium; Thallium (101) 131

Anod. stripping voltammetry; Cadmium; Thallium; Learning machine method (103) 151

Anod. stripping voltammetry; Computer-controlled; Cadmium; Copper; Parameter evaluation (107) 13

Anod. stripping voltammetry; Cadmium; Copper; Urine; Sample treatment (107) 37

At. abs. spectrometry; Cadmium; Zinc; Copper; Arc-nebulization (102) 15

At. abs. spectrometry; Electrotherm. atomization; Antimony; Alloys; Steels; Solid sampling (104) 67

At. abs. spectrometry; Electrotherm. atomization; Steels; Alloys; Solid sampling (104) 75

At. abs. spectrometry; At. fluor. spectrometry; Gas chromatography; Detectors; Alkyllead compounds (108) 31

At. abs. spectrometry; Lubricants; Emulsion nebulization (108) 39

Ion exchange; Cadmium; Hafnium phosphate cation exchanger; Photoelectron study; Separation (104) 319

Potentiometry; Stripping analysis; Urine; Mercury film electrode (106) 15

Potentiometry; Stripping analysis; Zinc; Cadmium; Copper; Sea water; Mercury film electrode (107) 29

Ring oven; Air; Rhodizonate (101) 225

X-ray fluores. spectrometry; Zinc; Copper; Manganese; Phosphate-containing matrices (109) 419

Manganese; Nickel; Copper; Carboxymethyl-cysteine; Complex formation (104) 299

#### **Lead compounds**

At. abs. spectrometry; Electrotherm. atomization; Air; Inorganic, organic; Simultaneous determination (108) 21

#### **Learning machine method**

Anod. stripping voltammetry; Cadmium; Lead; Thallium (103) 151

#### **Lidocaine**

Spectrophotometry; Computer-controlled; Photometric analyzer; Microcomputer (103) 489

#### **Ligand complexing capacity**

Waters; Stability constants; Copper complexes (106) 113

#### **Lipids**

Flow system; Potentiometry; Immobilized lipase (106) 369

#### **Liquid ion-exchange membranes**

Potentiometry; Selectivity coefficients; Digital simulation (101) 231

Potentiometry; Ion-selective electrodes; Time constants; Method comparison (109) 259

#### **Liquid-liquid extraction**

Diethyldithiocarbamic acid; Optimization (105) 281

#### **Lithium**

Emission spectrometry; Sodium; Potassium; Calcium; Computer program; High concentrations (107) 201

Computerized Kalousek polarography; Cadmium; Potassium (103) 367

#### **Liver tissue**

At. abs. spectrometry; Trace metals; Destruction procedures (104) 225

Mass spectrometry; At. abs. spectrometry; Multielement analysis; Spark-source (104) 233

#### **Liver tissue lyophilization**

Activ. analysis; Chromium losses; Trace element losses (109) 139

#### **LIX reagents**

Potentiometry; Titrimetry; Benzophenone oxime extractants; Nonaqueous (105) 83

#### **Lubricant additives**

Diff. pulse polarography; Zinc dialkyldithiophosphate (107) 391

#### **Lubricants**

At. abs. spectrometry; Lead; Emulsion nebulization (108) 39

At. abs. spectrometry; At. fluor. spectrometry; Trace metals; Comparison of standards (108) 351

#### **Lysine**

Ion exchange; Pharmaceuticals (108) 411

## **M**

#### **Magnesium**

Flow system; Emission spectrometry; At. abs. spectrometry; Calcium; Potassium; Plants; Merging zones (104) 279

Kinetic analysis; Flow system; Strontium; Differential; DCTA complexes (105) 327

Kinetic analysis; Flow system; Calcium; Differential; Cryptates; Phthalein complexone (108) 241

**Magnetic susceptibility measurements**

Titrimetry; Lanthanides; Binary mixtures (108) 309

**Magnetite electrode**

At. abs. spectrometry; Electrotherm. atomization; Iron (101) 401

**Manganese**

Activ. analysis; At. abs. spectrometry; Copper; Sea water; Comparison; Co-crystallization; Extraction (104) 337

At. abs. spectrometry; Electrotherm. atomization; Beryllium; Air particulates (105) 219

Emission spectrometry; Plasmas; Four-line correction method; Inter-element effects; Torch symmetry (109) 241

Spectrophotometry; Titrimetry; Ethylenediaminetetraacetic acid; Nickel; Catalytic; Dihydroxyphthalimide dithiosemicarbazone oxidation (109) 401

X-ray fluores. spectrometry; Zinc; Copper; Lead; Phosphate-containing matrices (109) 419

Nickel; Copper; Lead; Carboxymethylcysteine; Complex formation (104) 299

**Manganese nodules**

Ion exchange; At. abs. spectrometry; Nickel (108) 63

Ion exchange; At. abs. spectrometry; Gallium; Rocks (109) 181

**Mass-analyzed ion kinetic energy spectra**

Mass spectrometry; Aliphatic esters; Chemical ionization; Collision-induced (105) 129

**Matrix correction**

X-ray fluores. spectrometry; Dead-time (105) 177

**Mercury**

At. abs. spectrometry; Arsenic; Fish tissues; Automatic (101) 193

At. abs. spectrometry; Simple apparatus (101) 203

At. abs. spectrometry; Radiotracer study (101) 429

At. abs. spectrometry; Electrotherm. atomization; Amalgamation methods (106) 285

At. abs. spectrometry; Air; Gold-coated collector (106) 405

At. abs. spectrometry; Peak shapes (106) 411

At. abs. spectrometry; Mercury compounds; Gases; Manganese dioxide collection; Activated carbon collection; Reference method (108) 1

At. abs. spectrometry; Fish; Hair (108) 13

At. abs. spectrometry; Electrotherm. atomization; Ion-exchanger suspensions; Cobalt; Nickel; Molybdenum; Direct sampling (110) 301

Potentiometry; Stripping analysis; Automatic (105) 33

Spectrophotometry; Waters; Dual-wavelength; Copper(II) dithizonate (105) 289

**Mercury compounds**

At. abs. spectrometry; Air; Preconcentration (107) 159

At. abs. spectrometry; Mercury; Gases; Manganese dioxide collection; Activated carbon collection; Reference method (108) 1

Gas chromatography; At. abs. spectrometry; Fish; Extraction procedure (107) 169

**Mercury film electrode**

Anod. stripping voltammetry; Cadmium; Lead; Copper; Waters; Baseline concentrations (101) 79

Potentiometry; Stripping analysis; Lead; Urine (106) 15

**Mercury-selective electrode**

Potentiometry; Cadmium-selective electrode; Metal sulphide membranes; Complexing agents (108) 169

**Mercury solution storage**

Effect of gold(III) (101) 433

Oxidizing preservatives; Container material (110) 313

**Mercury, total**

At. abs. spectrometry; Automatic; Waters; Sediments (104) 285

At. abs. spectrometry; Waters; Reference methods (109) 209

At. abs. spectrometry; Air; Background level; Gold-coated quartz wool (110) 35

**Metal ions**

Spectrophotometry; Chlorindazone DS; Reagent evaluation (106) 141

**Metal (oxide)-on-silica catalysts**

At. abs. spectrometry; Rapid analysis (110) 345

**Metals**

Ion exchange; Distribution coefficients; Thiocyanates (101) 207

**Metal-specific detection**

Emission spectrometry; H.p.l.c.; Argon plasma; Diketonates; Ketoamines; Diethylthio-carbamates (101) 99

**Methylbenzimidazolylpyridylethyl sulphide**

Polarography; Pharmaceuticals; Methylbenzimidazolylpyridylethyl sulphoxide; Methylbenzimidazolylpyridyloxideethyl sulphone (102) 121

**Methylbenzimidazolylpyridylethyl sulphoxide**

Polarography; Pharmaceuticals; Methylbenzimidazolylpyridylethyl sulphide; Methylbenzimidazolylpyridyloxideethyl sulphone (102) 121

**Methylbenzimidazolypyridyloxideethyl sulphone**

Polarography; Pharmaceuticals; Methylbenzimidazolypyridylethyl sulphide; Methylbenzimidazolypyridylethyl sulphoxide (102) 121

**Methylmercury**

At. abs. spectrometry; Fish (102) 189

**Microbial electrode**

Amperometry; Bioassay; Nystatin; Yeast (109) 39

**Microbial sensor**

Amperometry; Flow system; Acetic acid; Trichosporon brassicae; Fermentation broths (109) 33

**Microwave plasma detector**

Gas chromatography; Computerized data processing; Selectivity improvement; Four-channel calculations (103) 29

**Millipore filters**

Impurity levels (102) 241

**Mining effluents**

Titrimetry; Sulphate; Thiosulphate; Polythionates (105) 375

**Molar absorptivity**

Spectrophotometry; Formation constants; Continuous variations curves (101) 157

**Molecular emission cavity analysis**

Emission spectrometry; Aliphatic amines; Amino acids (105) 433

**Molybdate**

Potentiometry; Titrimetry; Fluoride; Sulphate; Chromate; Tungstate; Oxalate; Phosphate; Hexacyanoferrate; Fluoride-selective electrode; Lead titrant (109) 319

**Molybdenum**

At. abs. spectrometry; Electrotherm. atomization; Zeeman splitting; Copper (101) 367

At. abs. spectrometry; Electrotherm. atomization; Sea water (104) 99

At. abs. spectrometry; Electrotherm. atomization; Ion-exchanger suspensions; Mercury; Cobalt; Nickel; Direct sampling (110) 301

Diff. pulse polarography; Cathode ray polarography; Catalytic wave (108) 149

Diff. pulse polarography; Computer-based system; Microcomputer; Interfacing (108) 155

Flow system; Spectrophotometry; Extraction; Plants; Thiocyanate (101) 9

Potentiometry; Kinetic analysis; pH-stat method; Copper; Zirconium; Vanadium (104) 205

**Morphamquat**

E.s.r.; Spectra simulation; Fourier transform; Computer program (103) 175

**Morphine**

H.p.l.c.; Poppy straw (108) 233

**Multicomponent analysis**

Phosphorimetry; Second-derivative method; Room-temperature (107) 261

**Multielement analysis**

Activ. analysis; Rocks; Group separation (101) 45

Activ. analysis; Blood; SLOWPOKE reactor (105) 185

Activ. analysis; Automated; Extraction system (106) 103

Activ. analysis; Tea leaves; Single comparator method (110) 75

At. fluor. spectrometry; Time-multiplex multiple slit design (104) 267

At. fluor. spectrometry; Air filters; Furnace-flame, non-dispersive (110) 1

Chromatography; Ion chromatography; Waters; Evaluation; Geothermal (108) 405

Mass spectrometry; At. abs. spectrometry; Liver tissue; Spark-source (104) 233

X-ray fluores. spectrometry; Rocks; Soils; Energy-dispersive; Sample preparation (109) 85

X-ray fluores. spectrometry; Waters; Coprecipitation with molybdenum-APDC (110) 61

**Multielement preconcentration**

Silicic acid, dispersed; Carbon, activated; Comparison (107) 177

**Multi-injection analysis**

Flow system; Spectrophotometry; Albumin (104) 185

**Multiparametric curve-fitting**

Number of parameters (101) 215

**Muscovites**

Water content; Karl Fischer titration; High fluorine content (110) 233

**N****Naphthoic acid**

Fluorimetry; Acidity constants; Anthroic acid (105) 311

**Naphthol**

Fluorimetry; Carbaryl; Naphthylmethyl-carbamate (108) 425

**Naphthylidazoalkanes as derivatizing agents**

H.p.l.c.; Fatty acids; Edible oils (109) 61

H.p.l.c.; Bile acids (109) 161

**Naphthylmethylcarbamate**

Fluorimetry; Carbaryl; Naphthol (108) 425

**Nickel**

Activ. analysis; Trace elements; Thermal neutron; Purity control (101) 145

At. abs. spectrometry; Effect of acids (102) 181

At. abs. spectrometry; Electrotherm. atomization; Copper; Cadmium; Zinc; Sea water; Sampling methods; Dithiocarbamate extraction; Chelex (105) 233

At. abs. spectrometry; Cobalt; Copper; Rocks; Matrix masking; Dithiocarbamate extraction (105) 247

At. abs. spectrometry; Electrotherm. atomization; Ion-exchanger suspensions; Mercury; Cobalt; Molybdenum; Direct sampling (110) 301

Flow system; Spectrophotometry; Cobalt; Computer-processed; Photodiode-array spectrophotometer (109) 425

Ion exchange; At. abs. spectrometry; Manganese nodules (108) 63

Ion exchange; Copper; Cobalt; Uranyl; Stability constants; Sulphosalicylate complexes; Distribution diagrams (108) 333

Spectrophotometry; Titrimetry; Ethylenediaminetetraacetic acid; Manganese; Catalytic; Dihydroxyphthalimide dithiosemicarbazone oxidation (109) 401

Spectrophotometry; Extraction; Chloronitrosophthalol; Crystal violet (110) 329

Manganese; Copper; Lead; Carboxymethylcysteine; Complex formation (104) 299

**Nickel-base alloys**

At. abs. spectrometry; Electrotherm. atomization; Bismuth; Hydride generation; Solid samples; Induction furnace (102) 33

**Niobium**

Spectrophotometry; EDTA; Pyrocatechol ternary complex; NTA contamination (108) 433

Spectrophotometry; Steels; With sulphochlorophenol S (109) 381

**Nitrate**

Flow system; Spectrophotometry; Nitrite; Copper-coated cadmium reductor (110) 123

H.p.l.c.; Spectrophotometry; Air particulates; Method comparison (110) 117

Spectrophotometry; Organic interferences; Xylenol (105) 335

Spectrophotometry; Plants; Soil extracts; Waters; Phenol (108) 285

Spectrophotometry; Improved 2,4-xylenol method (109) 373

Autocorrelation analysis; Sampling frequency; Waters; Quality control; Ammonium; Nitrite (103) 445

**Nitrate-selective electrode**

Potentiometry; Bipyridine derivatives (106) 341

**Nitric oxide**

Coulometry; Nitrous acid; Nitrogen dioxide; Platinum flow-through electrode; Reaction study; Acidic halide media (105) 25

Voltammetry; Nitrous acid; Nitrogen dioxide; Reduction at platinum electrodes (105) 9

**Nitrides**

Nitrogen types; Steels; Extraction with hydrogen (107) 339

**Nitrite**

Flow system; Spectrophotometry; Nitrate; Copper-coated cadmium reductor (110) 123

Autocorrelation analysis; Sampling frequency; Waters; Quality control; Ammonium; Nitrate (103) 445

**Nitrobenzene**

H.p.l.c.; D.c. polarography; Nitrophenol; Electrochemical detector; Dropping mercury electrode (105) 109

**Nitrofurantoin**

H.p.l.c.; Blood; Urine; Related drugs (101) 359

**Nitrofurazone**

Spectrophotometry; With phloroglucinol (107) 401

**Nitrogen**

Activ. analysis; Reaction study; In zirconium; Deuteron (109) 411

Activ. analysis; Carbon; Hydrogen; Prompt  $\gamma$ -ray; Environmental materials (110) 339**Nitrogen dioxide**

Coulometry; Nitric oxide; Nitrous acid; Platinum flow-through electrode; Reaction study; Acidic halide media (105) 25

Voltammetry; Nitric oxide; Nitrous acid; Reduction at platinum electrodes (105) 9

**Nitrogen isotope ratio**

Mass spectrometry; Gas preparative system (104) 245

**Nitrogen, Kjeldahl**

Flow system; Spectrophotometry; Phosphorus, total; Optimization (103) 189

**Nitrogen, total**

Flow system; Spectrophotometry; Plants; Isothermal distillation (109) 45

**Nitrogen types**

Steels; Nitrides; Extraction with hydrogen (107) 339



**Nitroimidazoles**

Spectrophotometry; Nitrite formation (106) 389

**Nitrophenol**

H.p.l.c.; D.c. polarography; Nitrobenzene; Electrochemical detector; Dropping mercury electrode (105) 109

**Nitrosamines**

Diff. pulse polarography; Nitrosodiphenylamine; Nitrosodibutylamine; Extraction (108) 213

Flow system; Amperometry; Photo-electroanalyzer; Nitrosodipropylamine; Flow-through platinum electrode (106) 1

**Nitrosodiethanolamines**

Diff. pulse polarography; Grinding fluids (102) 133

**Nitrosodipropylamine**

Flow system; Amperometry; Photo-electroanalyzer; Nitrosamines; Flow-through platinum electrode (106) 1

**Nitrosyl chloride**

Potentiometry; Dissociation constant; Dinitrogen tetroxide; Silver-silver chloride electrode; Sulpholane media (110) 211

**Nitrous acid**

Coulometry; Nitric oxide; Nitrogen dioxide; Platinum flow-through electrode; Reaction study; Acidic halide media (105) 25

Voltammetry; Nitric oxide; Nitrogen dioxide; Reduction at platinum electrodes (105) 9

**Nitrous oxide-acetylene flame**

At. abs. spectrometry; Improved precision (102) 195

**Noble metals**

Activ. analysis; Photon; Black concentrates (104) 129

**Nomenclature**

Trace analysis (107) 373

**Norepinephrine**

H.p.l.c.; Dopamine; Serotonin; Brain tissue; Electrochemical detection (104) 29

**Nuclear reactor fuels**

Ion exchange; Activ. analysis; Silver fission product (110) 81

**Nystatin**

Amperometry; Bioassay; Microbial electrode; Yeast (109) 39

Biosensors; Antibiotics; Amphotericin B; Electrochemical (104) 195

**Nystatin assay**

Potentiometry; Rubidium-selective electrode; Antibiotics; Polyene (105) 77

**O****Oil shale**

Chromatography; Reflectance spectrometry; Benzolalpyrene; Retort waters (101) 333

**Oligoglycosides**

Gas chromatography; Periodate oxidation; Aldehydes (105) 153

**Ores**

Activ. analysis; Platinum group elements; Gold; Rocks; Fire assay (102) 157

Fluorimetry; Uranium; Quenching effects (104) 345

**Organic bases**

Spectrophotometry; Alkaloids; Surfactants; Extraction; With metallochromic indicators (109) 191

**Organic ligands**

Ultrafiltration; Waters; Fractionation (101) 339

**Organic materials**

Potentiometry; Titrimetry; Chlorine; Sodium biphenyl (101) 221

**Osmium**

Spectrophotometry; Ruthenium; Extraction; Thiocyanate complexes (109) 123

**Oxalate**

Potentiometry; Titrimetry; Fluoride; Sulphate; Chromate; Molybdate; Tungstate; Phosphate; Hexacyanoferrate; Fluoride-selective electrode; Lead titrant (109) 319

**Oxygen**

Gravimetry; Uranium oxides (107) 365

**Oxyphenbutazone**

Voltammetry; Diff. pulse voltammetry; Phenylbutazone (109) 341

**Ozone**

Spectrophotometry; Air; Specific (108) 255

**P****Palladium**

At. abs. spectrometry; Electrotherm. atomization; Carbon filament (104) 385

Spectrophotometry; Extraction; Nitrosodiethylaminophenol (101) 169

Spectrophotometry; Stability constants; Thioglycolic acid derivatives (101) 177

X-ray fluores. spectrometry; Titanium alloys; Extraction-filtration concentration (110) 67

#### **Pareptide**

Diff. pulse polarography; Pharmaceuticals; Prolylmethylleucylglycinamide sulphate; Spectroscopic study; Nitroso derivative (107) 59

#### **Pattern recognition**

Gas chromatography; Blind assay; Whiskies (103) 201

Mass spectrometry; Computer-aided interpretation; Steroids; Binary classifiers (103) 61

Mass spectrometry; Simplex optimization; Super-modified (103) 417

N.m.r. spectrometry; Trace metals; Steels; Classification in 4 levels (103) 429

#### **Penicillamine**

Amperometry; Flow system; H.p.l.c.; Cystine; Cysteine (101) 253

#### **Penicillins**

Enthalpimetry; Enzymatic method (107) 319

Titrimetry; Antibiotics; Iodate titrant (105) 361

#### **Pentachlorophenol**

Diff. pulse polarography; Diff. pulse voltammetry (105) 91

#### **Pentobarbital**

Gas chromatography; Barbiturates; Blood; Butylation methods (105) 139

#### **Perchlorate-selective electrode**

Potentiometry; Urushi membrane; Liquid ion-exchanger (110) 321

#### **Periodate oxidation**

Gas chromatography; Aldehydes; Oligoglycosides (105) 153

#### **Peroxidase activity**

Enthalpimetry; Potentiometry; Iodide substrate (106) 251

#### **Petroleum bitumens**

Thermom. analysis; Titrimetry; Acidity; Catalytic (109) 129

#### **Petroleum products**

Emission spectrometry; Sulphur, total; Disulphide; Polysulphide; Reduction method (107) 231

#### **pH scale**

Spectrophotometry; Ethanediol solvent (104) 181

#### **pH-stat method**

Potentiometry; Kinetic analysis; Copper; Molybdenum; Zirconium; Vanadium (104) 205

#### **Pharmaceuticals**

Diff. pulse polarography; Pareptide; Prolylmethylleucylglycinamide sulphate; Spectroscopic study; Nitroso derivative (107) 59

Diff. pulse polarography; Corticosteroids; Single component (108) 389

Fluorimetry; Domperidone; Benzodiazolinone fluorophore (110) 261

H.p.l.c.; Fluorimetry; Dihydroxyphenylalanine; Hydrazinomethyl-dihydroxyphenylpropanoic acid (105) 403

Ion exchange; Lysine (108) 411

Phosphorimetry; Room-temperature (101) 319

Polarography; Methylbenzimidazolylpyridyl-ethyl sulphide; Methylbenzimidazolylpyridyl-ethyl sulphoxide; Methylbenzimidazolylpyridyl-oxideethyl sulphone (102) 121

Spectrophotometry; Phenothiazines; Molybdophosphoric acid (108) 277

Voltammetry; Phenolic analgesics (105) 423

Computer-controlled laboratory system; Quality control; Hierarchical (103) 483

#### **Phenolic analgesics**

Voltammetry; Pharmaceuticals (105) 423

#### **Phenols**

Fluorimetry; Synchronous excitation; Increased sensitivity (105) 297

#### **Phenothiazines**

Spectrophotometry; Pharmaceuticals; Molybdophosphoric acid (108) 277

#### **Phenylbutazone**

Voltammetry; Diff. pulse voltammetry; Oxyphenbutazone (109) 341

#### **Phosphatases, acid**

Kinetic analysis; Spectrophotometry (110) 175

#### **Phosphate**

Flow system; Plants; Merging zones; Double proportional injector (101) 17

Potentiometry; Titrimetry; Fluoride; Sulphate; Chromate; Molybdate; Tungstate; Oxalate; Hexacyanoferrate; Fluoride-selective electrode; Lead titrant (109) 319

#### **Phosphate-selective electrode**

Potentiometry; Tris(thiourea)copper monohydrogenphosphate (109) 149

#### **Phosphatidyl choline**

Amperometry; Blood; Immobilized phospholipase-choline oxidase (106) 243

#### **Phosphorus**

Activ. analysis; Aluminium-silicon alloys; Helium-4 (101) 63

#### **Phosphorus profiles**

Spectrophotometry; Silicon slices (104) 139

#### **Phosphorus, total**

Flow system; Spectrophotometry; Nitrogen, Kjeldahl; Optimization (103) 189

**Photodiode-array spectrophotometer**

Flow system; Spectrophotometry; Nickel; Cobalt; Computer-processed (109) 425

**Photo-electroanalyzer**

Flow system; Amperometry; Nitrosamines; Nitrosodipropylamine; Flow-through platinum electrode (106) 1

**Photometric analyzer**

Spectrophotometry; Computer-controlled; Lidocaine; Microcomputer (103) 489

**Phthalate ester plasticizers**

H.p.l.c.; Plastic bottles; Solution contamination (108) 325

**Phytoplankton pigments**

H.p.l.c.; Chlorophylls; Carotenoids; Marine particulate matter (107) 1

**Piperazinedione**

H.p.l.c.; In reaction mixtures (105) 409

**Plants**

Flow system; Spectrophotometry; Extraction; Molybdenum; Thiocyanate (101) 9

Flow system; Phosphate; Merging zones; Double proportional injector (101) 17

Flow system; Emission spectrometry; At. abs. spectrometry; Calcium; Magnesium; Potassium; Merging zones (104) 279

Flow system; Spectrophotometry; Aluminium; Soils; Merging zones (107) 309

Flow system; Spectrophotometry; Nitrogen, total; Isothermal distillation (109) 45

Spectrophotometry; Nitrate; Soil extracts; Waters; Phenol (108) 285

Sulphuric-perchloric acid digestion; Contamination sources (109) 431

**Plasmas**

Emission spectrometry; Manganese; Four-line correction method; Inter-element effects; Torch symmetry (109) 241

Emission spectrometry; Tin; Germanium; Hydride generation (109) 251

**Plastic bottles**

H.p.l.c.; Phthalate ester plasticizers; Solution contamination (108) 325

**Platinum**

At. abs. spectrometry; Electrotherm. atomization; Automotive catalyst material (110) 29

**Platinum flow-through electrode**

Coulometry; Nitric oxide; Nitrous acid; Nitrogen dioxide; Reaction study; Acidic halide media (105) 25

**Platinum group elements**

Activ. analysis; Gold; Rocks; Fire assay; Ores (102) 157

**Platinum tetrammine chloride**

Thermal decomposition (101) 409

**Platinum thin films**

Activ. analysis; Rutherford back-scattering; Non-destructive (108) 119

**Polarographic current sampling**

Polarography; Without drop synchronization (101) 161

**Polychlorobiphenyls**

Air; High-volume sampling (110) 129

**Polychloro(chloromethylsulphonamide)-diphenyl ether isomers**

Gas chromatography; Mass spectrometry; Fish tissues; Eulan WA New; Identification; Metabolites (104) 253

**Polyfluorinated polyphosphazene membranes**

ISFET; Chloride; Iodide; Silver salts (108) 161

**Polyinosinic acid**

Diff. pulse voltammetry; Hypoxanthine; Oxidation at PGE (108) 193

**Polyuclear aromatic hydrocarbons**

Chromatography; Fluorimetry; Shale oil; Densitometry (110) 245

Diff. pulse voltammetry; Rapid-scan (110) 255

Fluorimetry; Computer decomposition of spectra; Benzidine; Dibenzochrysenes; Quantitative (103) 167

Gas chromatography; Mass spectrometry; Computer-controlled; Air (105) 119

Phosphorimetry; Room-temperature; Heavy atom effect (102) 1

**Polypeptides**

Fluorimetry; Guanidino compounds; Benzoin-dimethylformamide (106) 89

**Polysaccharides**

Gum exudates; Degradation in permethylation (105) 147

**Polysulphide**

Emission spectrometry; Sulphur, total; Disulphide; Petroleum products; Reduction method (107) 231

**Polythionates**

Titrimetry; Sulphate; Thiosulphate; Mining effluents (105) 375

**Polyurethane foam extraction**

Antimony (106) 161

**Polyvinyl alcohol**

Spectrophotometry; Complex formation (104) 153

**Poppy straw**

H.p.l.c.; Morphine (108) 233

**Potassium**

Emission spectrometry; Sodium; Calcium; Lithium; Computer program; High concentrations (107) 201

Flow system; Emission spectrometry; At. abs. spectrometry; Calcium; Magnesium; Plants; Merging zones (104) 279

Potentiometry; Hydrogen ion; Calcium; ISFET (101) 239

Computerized Kalousek polarography; Cadmium; Lithium (103) 367

#### **Potassium chloride**

Flow system; Conductivity detector; Non-intrusive very high-frequency (110) 325

**Potassium hydrogenphthalate reference buffer**  
Redetermination of pH(S) (108) 179

#### **Potassium hydroxotrifluoroborate demasking reactions**

N.m.r. spectrometry; Lanthanum complexes; Stability constants; EDTA; NTA (105) 391

Lanthanum complexes; Selective demasking; EDTA (105) 397

#### **Principal component analysis**

I.r. spectrometry; Gas chromatography; Mixtures (103) 213

#### **Prolylmethylleucylglycinamide sulphate**

Diff. pulse polarography; Pharmaceuticals; Pareptide; Spectroscopic study; Nitroso derivative (107) 59

#### **Proteus morgani**

Potentiometry; Bacterial membrane electrode; Cysteine (101) 125

## Q

#### **Quality control**

Time series; Autocorrelation analysis; Missing values (103) 133

Autocorrelation analysis; Time series; Analysis of variance; Comparison (103) 253

Autocorrelation analysis; Sampling frequency; Waters; Ammonium; Nitrate; Nitrite (103) 445

Computer-controlled laboratory system; Pharmaceuticals; Hierarchical (103) 483

#### **Quaternary ammonium salts**

Gravimetry; Tetrathienylborates; Cesium; Synthesis (105) 353

#### **Quinolinol**

Fluorimetry; Dihaloquinolinols; Simultaneous (106) 67

## R

#### **Reaction rates on paper**

Ring oven; Semiquantitative analysis (101) 187

#### **Reference electrode**

Potentiometry; ISFET (101) 247

#### **Review**

Spectral data retrieval systems (103) 273

Analytical atomic spectroscopy; CSIRO Australia (106) 175

#### **Rhenium**

At. abs. spectrometry; Electrotherm. atomization; Gallium; Silicon; Trace metals (108) 45

#### **Rhodium**

Spectrophotometry; With malachite green (108) 261

#### **Rice**

At. abs. spectrometry; Cadmium; Low-temperature ashing; Extraction (104) 393

#### **Rocks**

Activ. analysis; Multielement analysis; Group separation (101) 45

Activ. analysis; Platinum group elements; Gold; Fire assay; Ores (102) 157

Activ. analysis; Gold; Tungsten (102) 221

Activ. analysis; Uranium; Thorium; Epithelial (104) 121

Activ. analysis; Uranium; Tellurium fission product (108) 371

At. abs. spectrometry; Antimony; Automatic; Hydride generation (101) 33

At. abs. spectrometry; Electrotherm. atomization; Germanium; Tungsten tube (104) 293

At. abs. spectrometry; Cobalt; Nickel; Copper; Matrix masking; Dithiocarbamate extraction (105) 247

At. abs. spectrometry; Electrotherm. atomization; Bismuth (106) 325

At. abs. spectrometry; Electrotherm. atomization; Vanadium; Tungsten tube (108) 69

At. abs. spectrometry; Electrotherm. atomization; Arsenic; Soils; Hydride generation (108) 357

At. abs. spectrometry; Electrotherm. atomization; Silver; Extraction (109) 171

Ion exchange; At. abs. spectrometry; Manganese nodules; Gallium (109) 181

I.r. spectrometry; Carbon; Sulphur; Combustion (101) 25

I.r. spectrometry; Carbonate; Carbon; Geological materials; Non-carbonate (108) 113

Mass spectrometry; Hafnium; Lanthanides; Interference effects; Spark-source (105) 163

Spectrophotometry; Boron; Waters; Sephadex G-25 sorption (109) 115

Voltammetry; Iron(II)-iron(III) determination; Vitamin tablets (105) 99

X-ray fluores. spectrometry; Soils; Trace elements; Thin-film energy-dispersive (108) 93

X-ray fluores. spectrometry; Multielement analysis; Soils; Energy-dispersive; Sample preparation (109) 85

#### **Rotating disc electrode**

Anod. stripping voltammetry; Flow system; Lead; Cadmium; Copper (101) 1

#### **Rubidium-selective electrode**

Potentiometry; Antibiotics; Nystatin assay; Polyene (105) 77

#### **Ruthenium**

At. abs. spectrometry; Ionic interferences (102) 185

Spectrophotometry; Osmium; Extraction; Thiocyanate complexes (109) 123

## **S**

#### **Salicylideneaminophenolates**

Fluorimetry; Kinetic analysis; Atomic number effects; Group IIIA metals (107) 273

#### **Saliva**

At. abs. spectrometry; Gel perm. chromatography; Cadmium; Copper; Zinc; Distribution (107) 211

#### **Samarium**

Fluorimetry; Europium; Thenoyltrifluoroacetone-trioctylphosphine oxide (108) 429

#### **Sampling**

At. abs. spectrometry; Snow; Trace elements; Contamination problems (106) 127

Internally correlated lots; Theory; Gross sample reproducibility (103) 1

Internally correlated lots; Practical analysis; Gross sample reproducibility (103) 11

Homogeneity of solids; Statistical model (105) 1

#### **Sampling frequency**

Autocorrelation analysis; Waters; Quality control; Ammonium; Nitrate; Nitrite (103) 445

#### **Sampling methods**

At. abs. spectrometry; Electrotherm. atomization; Copper; Cadmium; Zinc; Nickel; Sea water; Dithiocarbamate extraction; Chelex (105) 233

#### **Scanning fluorimeter**

Fluorimetry; Design considerations; Two-dimensional (109) 361

#### **Scopoletin**

H.p.l.c.; Umbelliferone; Coumaric acid; Ferulic acid; Isomers; Optimization strategy (108) 227

#### **Sea water**

Activ. analysis; At. abs. spectrometry; Copper; Manganese; Comparison; Co-crystallization; Extraction (104) 337

Anod. stripping voltammetry; Diff. pulse voltammetry; Trace metals (106) 23

At. abs. spectrometry; Electrotherm. atomization; Molybdenum (104) 99

At. abs. spectrometry; Electrotherm. atomization; Ion exchange; Heavy metals; Selective elution; Chelex (104) 307

At. abs. spectrometry; Electrotherm. atomization; Copper; Cadmium; Zinc; Nickel; Sampling methods; Dithiocarbamate extraction; Chelex (105) 233

At. abs. spectrometry; Dithizone extraction; Biological tissues; Trace metals (110) 21

Potentiometry; Stripping analysis; Zinc; Cadmium; Lead; Copper; Mercury film electrode (107) 29

Spectrophotometry; Selenium; Adsorption colloid flotation (101) 71

Cesium-137; Sorption on copper hexacyanoferrate (102) 225

Cadmium-ethylenediamine complex formation; Computer-assisted; Stripping polarography (109) 327

#### **Sediments**

At. abs. spectrometry; Automatic; Waters; Mercury, total (104) 285

At. abs. spectrometry; Electrotherm. atomization; Tin; Waters; Effect of organic compounds (110) 55

Emission spectrometry; Arsenic; D.c. plasma (107) 395

#### **Selectivity coefficients**

Potentiometry; Liquid ion-exchange membranes; Digital simulation (101) 231

#### **Selenium**

Anod. stripping voltammetry; Tellurium; Gold film electrode; Copper, electrolytic (110) 87

At. abs. spectrometry; Electrochemical preconcentration; High chloride content (110) 279

**At. abs. spectrometry; Electrotherm. atomization; Blood; Stabilization in ashing (110) 285**

**At. fluor. spectrometry; At. abs. spectrometry; Spectral lamp; Arsenic; Controlled temperature-gradient (108) 347**

**Enthalpimetry; Titrimetry; With thiosulphate (110) 139**

**Fluorimetry; Biological materials; Automatic; Benzopiazselenol (105) 319**

**Fluorimetry; Automatic; Animal feeds (105) 445**

**Fluorimetry; Automatic; Phase-separating device (105) 451**

**Ion exchange; At. abs. spectrometry; Electrotherm. atomization; In pyrite (110) 153**

**Spectrophotometry; Sea water; Adsorption colloid flotation (101) 71**

#### **Semidifferential electroanalysis**

**Anod. stripping voltammetry; Cadmium; Lead; Thallium (101) 131**

#### **Semiquantitative analysis**

**Ring oven; Reaction rates on paper (101) 187**

#### **Serotonin**

**H.p.l.c.; Norepinephrine; Dopamine; Brain tissue; Electrochemical detection (104) 29**

#### **Serum antibodies**

**Potentiometry; Immunoassay; Complement fixation test; Trimethylphenylammonium-selective electrodes (109) 25**

#### **Sewage sludge**

**At. abs. spectrometry; Electrotherm. atomization; Trace metals; Pretreatment comparison (106) 309**

#### **Shale-derived liquids**

**Gas chromatography; Glow discharge detector; Silicon; Trimethylsilylation (108) 221**

#### **Shale oil**

**Chromatography; Fluorimetry; Polynuclear aromatic hydrocarbons; Densitometry (110) 245**

#### **Silicates**

**Emission spectrometry; Trace elements; Inductively coupled plasma; Major elements (108) 87**

#### **Silicic acid, dispersed**

**Carbon, activated; Multielement preconcentration; Comparison (107) 177**

#### **Silicon**

**At. abs. spectrometry; Electrotherm. atomization; Gallium; Rhenium; Trace metals (108) 45**

**Emission spectrometry; Aluminium; Iron; Titanium; Flame; Vapor-phase sampling; Chlorides (101) 89**

**Gas chromatography; Glow discharge detector; Shale-derived liquids; Trimethylsilylation (108) 221**

#### **Siliconization effects**

**Anod. stripping voltammetry; Heavy metals (107) 67**

#### **Silicon slices**

**Diff. pulse polarography; Arsenic profiles (106) 137**

**Spectrophotometry; Phosphorus profiles (104) 139**

#### **Silver**

**At. abs. spectrometry; Electrotherm. atomization; Bismuth; Cadmium; Zinc; Steels; Solids autosampler (108) 75**

**At. abs. spectrometry; Electrotherm. atomization; Copper; Gallium; Signal depression (109) 97**

**At. abs. spectrometry; Electrotherm. atomization; Rocks; Extraction (109) 171**

**Potentiometry; Single-point titrations; Chloride; Sulphate (107) 101**

**Spectrophotometry; Dicyanoargentate; Extraction; Methylene blue (109) 107**

#### **Silver complexes**

**Potentiometry; Stability constants; Organic ligands (107) 349**

#### **Silver fission product**

**Ion exchange; Activ. analysis; Nuclear reactor fuels (110) 81**

#### **Silver-germanium alloys**

**A.c. polarography; Diff. pulse polarography; Germanium (102) 113**

#### **Silver sulphide electrode**

**Potentiometry; Ion-selective electrodes; Interfacial properties; Impedance measurements (110) 185**

#### **Simplex optimization**

**Mass spectrometry; Pattern recognition; Super-modified (103) 417**

**Automated chemical synthesis (103) 469**

#### **Single-point titrations**

**Potentiometry; Flow system; Acid-base (105) 67**

**Potentiometry; Silver; Chloride; Sulphate (107) 101**

#### **Snow**

**At. abs. spectrometry; Sampling; Trace elements; Contamination problems (106) 127**

#### **Sodium**

**Emission spectrometry; Potassium; Calcium; Lithium; Computer program; High concentrations (107) 201**

**Atomic acoustic spectrometry (106) 361**

#### **Soil extracts**

**At. abs. spectrometry; Electrotherm. atomization; Trace metals; Dithizone extraction (106) 319**

Spectrophotometry; Nitrate; Plants; Waters; Phenol (108) 285

### Soils

At. abs. spectrometry; Electrotherm. atomization; Arsenic; Rocks; Hydride generation (108) 357

Flow system; Spectrophotometry; Aluminium; Plants; Merging zones (107) 309

X-ray fluores. spectrometry; Rocks; Trace elements; Thin-film energy-dispersive (108) 93

X-ray fluores. spectrometry; Multielement analysis; Rocks; Energy-dispersive; Sample preparation (109) 85

### Spectral coding

Mass spectrometry; SISCOM; Library search (103) 289

### Spectral data retrieval systems

Review (103) 273

### Spectral lamp

At. fluor. spectrometry; Boosted-output; Interchangeable cathode (105) 213

At. fluor. spectrometry; At. abs. spectrometry; Arsenic; Selenium; Controlled temperature-gradient (108) 347

### Spectral lamp, demountable

At. abs. spectrometry; At. fluor. spectrometry (102) 25

### Spectra simulation

E.s.r.; Fourier transform; Computer program; Morphamquat (103) 175

### Stability constants

Ion exchange; Copper; Nickel; Cobalt; Uranyl; Sulphosalicylate complexes; Distribution diagrams (108) 333

N.m.r. spectrometry; Lanthanum complexes; Potassium hydroxotrihydroborate demasking reactions; EDTA; NTA (105) 391

Potentiometry; Silver complexes; Organic ligands (107) 349

Spectrophotometry; Palladium; Thioglycolic acid derivatives (101) 177

Waters; Ligand complexing capacity; Copper complexes (106) 113

### Statistical approach

Dual parameter blends (103) 477

### Statistical linear discriminant analysis

Thyroid disease diagnosis; Feature selection (103) 409

### Steels

At. abs. spectrometry; Electrotherm. atomization; Lead; Antimony; Alloys; Solid sampling (104) 67

At. abs. spectrometry; Electrotherm. atomization; Lead; Alloys; Solid sampling (104) 75

At. abs. spectrometry; Electrotherm. atomization; Silver; Bismuth; Cadmium; Zinc; Solids autosampler (108) 75

N.m.r. spectrometry; Pattern recognition; Trace metals; Classification in 4 levels (103) 429

Potentiometry; Titrimetry; Sulphur; Waters; Irons; Fly ash; Cadmium sulphide electrode; Hydrogen sulphide generation (109) 307

Potentiometry; Coulometry; Cobalt; Picolinic acid media (110) 227

Spectrophotometry; Niobium; With sulphochlorophenol S (109) 381

Nitrogen types; Nitrides; Extraction with hydrogen (107) 339

Cobalt(III)/cobalt(II) system; Current-voltage curves; Picolinic acid media (110) 219

### Steroids

Mass spectrometry; Computer-aided interpretation; Pattern recognition; Binary classifiers (103) 61

### Stripping analysis

Potentiometry; Microcomputer system (103) 379

Potentiometry; Mercury; Automatic (105) 33

Potentiometry; Lead; Urine; Mercury film electrode (106) 15

Potentiometry; Zinc; Cadmium; Lead; Copper; Sea water; Mercury film electrode (107) 29

### Stripping polarography

Cadmium-ethylenediamine complex formation; Computer-assisted; Sea water (109) 327

### Strontium

Kinetic analysis; Flow system; Magnesium; Differential; DCTA complexes (105) 327

### Substoichiometric concentration

Isotope dilut. analysis; Cesium; Theory (104) 327

### Substoichiometric preconcentration

Isotope dilut. analysis (106) 333

### Sulphaganidine

Spectrophotometry; Diff. pulse polarography (106) 365

### Sulphanilamide

Diff. pulse polarography; Indophenol derivatization; Ammonia; Aminophenol (101) 211

### Sulphate

Gravimetry; Chromate; Vanadate; Stepwise precipitation (110) 179

Potentiometry; Single-point titrations; Silver; Chloride (107) 101

Potentiometry; Titrimetry; Fluoride; Chromate; Molybdate; Tungstate; Oxalate; Phosphate;

Hexacyanoferrate; Fluoride-selective electrode;  
Lead titrant (109) 319

Titrimetry; Thiosulphate; Polythionates;  
Mining effluents (105) 375

### Sulphide

Kinetic analysis; Spectrophotometry;  
Thermom. analysis; Thiosulphate;  
Simultaneous indication (107) 301

Spectrophotometry; Waters; Sulphite;  
Extraction; Dimethylphenanthrolinecopper  
reagent (108) 293

### Sulphite

Spectrophotometry; Waters; Sulphide;  
Extraction; Dimethylphenanthrolinecopper  
reagent (108) 293

Titrimetry; Dimethyl sulphoxide medium;  
Cerium(IV) (104) 379

### Sulphur

I.r. spectrometry; Carbon; Rocks; Combustion  
(101) 25

Potentiometry; Titrimetry; Waters; Irons;  
Steels; Fly ash; Cadmium sulphide electrode;  
Hydrogen sulphide generation (109) 307

### Sulphuric acid

Diff. pulse polarography; Acetonitrile media  
(107) 75

### Sulphur, total

Coulometry; Waters; Traces (110) 167

Emission spectrometry; Disulphide;  
Polysulphide; Petroleum products; Reduction  
method (107) 231

### Surfactants

Spectrophotometry; Organic bases; Alkaloids;  
Extraction; With metallochromic indicators  
(109) 191

### Surfactants, nonionic

At. abs. spectrometry; Waters (104) 93

### Synchronous excitation

Fluorimetry; Phenols; Increased sensitivity  
(105) 297

## T

### Target factor analysis

Mass spectrometry; N.m.r. spectrometry;  
Theory of error (103) 339

### Tea leaves

Activ. analysis; Multielement analysis; Single  
comparator method (110) 75

### Technetium

Cyclic voltammetry; Coulometry; D.c. polarog-  
raphy; Electrochemical study (107) 47

### Tellurium

Anod. stripping voltammetry; Selenium; Gold  
film electrode; Copper, electrolytic (110) 87

At. abs. spectrometry; Electrotherm. atomiz-  
ation; Molybdenum tube (110) 49

Anode slimes; Se-Te separation (107) 415

### Tetrahydroborate

Spectrophotometry; With trinitrobenzene-  
sulphonic acid (107) 405

### Tetrathienylborates

Gravimetry; Cesium; Quaternary ammonium  
salts; Synthesis (105) 353

### Thallium

Anod. stripping voltammetry; Semidifferential  
electroanalysis; Cadmium; Lead (101) 131

Anod. stripping voltammetry; Cadmium; Lead;  
Learning machine method (103) 151

### Thermogravimetry-mass spectrometry

Acrylic fibres; Alkyd paints; Computer-  
generated mass thermograms; Interface  
(107) 327

### Thiobarbituric acid values

Spectrophotometry; Fish oils (106) 279

### Thiocyanates

Ion exchange; Distribution coefficients; Metals  
(101) 207

### Thiosulphate

Kinetic analysis; Spectrophotometry;  
Thermom. analysis; Sulphide; Simultaneous  
indication (107) 301

Titrimetry; Sulphate; Polythionates; Mining  
effluents (105) 375

### Thorium

Activ. analysis; Uranium; Rocks; Epithermal  
(104) 121

Spectrophotometry; Waters; Aliquot extraction  
(106) 385

### Thyroid disease diagnosis

Statistical linear discriminant analysis;  
Feature selection (103) 409

### Time series

Autocorrelation analysis; Quality control;  
Missing values (103) 133

Autocorrelation analysis; Quality control;  
Analysis of variance; Comparison (103) 253

### Tin

At. abs. spectrometry; Electrotherm. atomiz-  
ation; Molybdenum tube (107) 245

At. abs. spectrometry; Electrotherm. atomiz-  
ation; Waters; Sediments; Effect of organic  
compounds (110) 55



At. fluor. spectrometry; Hydride generation (101) 199

Cyclic voltammetry; Anod. stripping voltammetry; Pyrogallol medium (104) 55

Emission spectrometry; Germanium; Plasmas; Hydride generation (109) 251

Spectrophotometry; Extraction; Diphenylphenanthroline (104) 363

Extraction mechanism; Benzoylphenylhydroxylamine (104) 161

#### **Titanium**

Emission spectrometry; Aluminium; Iron; Silicon; Flame; Vapor-phase sampling; Chlorides (101) 89

#### **Titanium alloys**

X-ray fluores. spectrometry; Palladium; Extraction-filtration concentration (110) 67

#### **Trace analysis**

Nomenclature (107) 373

Wet ashing unit (109) 195

#### **Trace element losses**

Activ. analysis; Liver tissue lyophilization; Chromium losses (109) 139

#### **Trace elements**

Activ. analysis; Nickel; Thermal neutron; Purity control (101) 145

Activ. analysis; Electrotherm. atomization; At. abs. spectrometry; Blood; Method comparison (110) 9

At. abs. spectrometry; Sampling; Snow; Contamination problems (106) 127

At. abs. spectrometry; Aluminium alloys; Dissolution procedure (109) 165

Emission spectrometry; Silicates; Inductively coupled plasma; Major elements (108) 87

Emission spectrometry; Air particulates; D.c. arc; Low-volume sampler (108) 103

X-ray fluores. spectrometry; Rocks; Soils; Thin-film energy-dispersive (108) 93

#### **Trace metals**

Anod. stripping voltammetry; Diff. pulse voltammetry; Sea water (106) 23

At. abs. spectrometry; Liver tissue; Destruction procedures (104) 225

At. abs. spectrometry; Optimization of instrumental variables (105) 199

At. abs. spectrometry; Electrotherm. atomization; Tungsten tube; Design (105) 263

At. abs. spectrometry; Electrotherm. atomization; Tungsten tube; Atom formation processes (105) 271

At. abs. spectrometry; Coal fly ash; Room-temperature dissolution (106) 299

At. abs. spectrometry; Electrotherm. atomization; Sewage sludge; Pretreatment comparison (106) 309

At. abs. spectrometry; Electrotherm. atomization; Soil extracts; Dithizone extraction (106) 319

At. abs. spectrometry; Waters; APDC, DDTC comparison (107) 219

At. abs. spectrometry; Electrotherm. atomization; Gallium; Rhenium; Silicon (108) 45

At. abs. spectrometry; Electrotherm. atomization; Signal enhancement; Metal-oxygen reactions (108) 53

At. abs. spectrometry; At. fluor. spectrometry; Lubricants; Comparison of standards (108) 351

At. abs. spectrometry; Dithizone extraction; Sea water; Biological tissues (110) 21

At. fluor. spectrometry; Electrotherm. atomization; Cadmium; Carbon filament (104) 85

Emission spectrometry; Boron; Waters; Plasmas; High salt concentration (109) 73

N.m.r. spectrometry; Pattern recognition; Steels; Classification in 4 levels (103) 429

#### **Transition metal compounds**

Computer deconvolution of spectral data; Least-squares fitting (103) 73

#### **Triangle-programmed titration**

Flow system; Coulometry; Titrimetry; Automatic evaluation (101) 261

#### **Trichothecene mycotoxins**

Spectrophotometry; Fluorimetry; Formaldehyde formation (106) 59

#### **Triethylenetetraaminehexaacetic acid**

D.c. polarography; Pulse polarography; Reaction study (104) 215

#### **Trifluoroacetic acid**

Diff. pulse polarography; Acidity functions; Trifluoromethanesulphonic acid; Hexafluoropropanediol (106) 51

#### **Trifluoromethanesulphonic acid**

Diff. pulse polarography; Acidity functions; Trifluoroacetic acid; Hexafluoropropanediol (106) 51

#### **Triglycerides**

Amperometry; Flow system; Glycerol; Blood; Tubular carbon electrode; Enzymatic (106) 225

#### **Trimethylphenylammonium-selective electrodes**

Potentiometry; Immunoassay; Serum antibodies; Complement fixation test (109) 25

#### **Tungstate**

Potentiometry; Titrimetry; Fluoride; Sulphate; Chromate; Molybdate; Oxalate; Phosphate; Hexacyanoferrate; Fluoride-selective electrode; Lead titrant (109) 319

**Tungsten**

Activ. analysis; Gold; Rocks (102) 221

**Tungsten tube**

At. abs. spectrometry; Electrotherm. atomization; Germanium; Rocks (104) 293

At. abs. spectrometry; Electrotherm. atomization; Trace metals; Design (105) 263

At. abs. spectrometry; Electrotherm. atomization; Trace metals; Atom formation processes (105) 271

At. abs. spectrometry; Electrotherm. atomization; Vanadium; Rocks (108) 69

**U****Ultrafiltration**

Organic ligands; Waters; Fractionation (101) 339

**Umbelliferone**

H.p.l.c.; Scopoletin; Coumaric acid; Ferulic acid; Isomers; Optimization strategy (108) 227

**Uranium**

Activ. analysis; Thorium; Rocks; Epithermal (104) 121

Activ. analysis; Rocks; Tellurium fission product (108) 371

Fluorimetry; Ores; Quenching effects (104) 345

Spectrophotometry; Extraction; Benzoyl-trifluoroacetone (105) 439

Spectrophotometry; Trialkylamine extracts; Bromopyridylazodiethylaminophenol (108) 267

Spectrophotometry; Trialkylamine extracts; With dibenzoylmethane (108) 437

**Uranium oxides**

Gravimetry; Oxygen (107) 365

**Uranyl**

Ion exchange; Copper; Nickel; Cobalt; Stability constants; Sulphosalicylate complexes; Distribution diagrams (108) 333

**Uric acid**

Kinetic analysis; Ascorbic acid; Mixtures (108) 441

Titrimetry; Amperometry; Iodine; Hydrazine; Isonicotinic acid hydrazide; Arsenic; Photosensitized generation; Rose Bengal (104) 397

**Urine**

Amperometry; Galactose; Blood; Enzymatic (104) 47

Anod. stripping voltammetry; Cadmium; Lead; Copper; Sample treatment (107) 37

At. abs. spectrometry; Electrotherm. atomization; Arsenic; Automatic (104) 177

Diff. pulse polarography; Disodium cromoglycate (102) 205

H.p.l.c.; Nitrofurantoin; Blood; Related drugs (101) 359

Potentiometry; Stripping analysis; Lead; Mercury film electrode (106) 15

**U.V.-absorptiostat**

Spectrophotometry; Enzyme determinations; Catalase; Ascorbate oxidase; Peroxidase; Sorbitol dehydrogenase; Lactate dehydrogenase (109) 351

**V****Vanadate**

Gravimetry; Sulphate; Chromate; Stepwise precipitation (110) 179

**Vanadium**

At. abs. spectrometry; Electrotherm. atomization; Tungsten tube; Rocks (108) 69

Potentiometry; Kinetic analysis; pH-stat method; Copper; Molybdenum; Zirconium (104) 205

**Viscometry**

High-precision; Microprocessor operated (103) 389

**Vitamins K**

D.c. polarography; Thiols reaction study (106) 261

**Vitamin tablets**

Voltammetry; Iron(II)-iron(III) determination; Rocks (105) 99

**Voltammetric detectors**

Flow system; Potentiometry; Voltammetry; Injection techniques; Ion-selective electrodes; Mixing chambers; Theory (109) 1

# W

## Warfarin

Gas chromatography; Blood (106) 155

## Water content

Muscovites; Karl Fischer titration; High fluorine content (110) 233

## Waters

Activ. analysis; Chlorine; Bromine; Iodine; Biological materials; Organically bound; Contamination problems (108) 137

Anod. stripping voltammetry; Mercury film electrode; Cadmium; Lead; Copper; Baseline concentrations (101) 79

Anod. stripping voltammetry; Copper; Iron interference (101) 437

At. abs. spectrometry; Surfactants, nonionic (104) 93

At. abs. spectrometry; Automatic; Sediments; Mercury, total (104) 285

At. abs. spectrometry; Electrotherm. atomization; Boron (106) 121

At. abs. spectrometry; Trace metals; APDC, DDTC comparison (107) 219

At. abs. spectrometry; Mercury, total; Reference methods (109) 209

At. abs. spectrometry; Electrotherm. atomization; Tin; Sediments; Effect of organic compounds (110) 55

At. fluor. spectrometry; Arsenic; Hydride generation (104) 173

Chromatography; Ion chromatography; Multielement analysis; Evaluation; Geothermal (108) 405

Coulometry; Sulphur, total; Traces (110) 167

Diff. pulse polarography; Carbon disulphide (107) 387

Emission spectrometry; Boron; Trace metals; Plasmas; High salt concentration (109) 73

Emission spectrometry; Barium; Biological fluids; Inductively-coupled plasma (110) 271

Potentiometry; Titrimetry; Sulphur; Irons; Steels; Fly ash; Cadmium sulphide electrode; Hydrogen sulphide generation (109) 307

Spectrophotometry; Extraction; Iron; Pyrogallol red; Zephiramine; Removal of extracted reagent (104) 369

Spectrophotometry; Mercury; Dual-wavelength; Copper(II) dithizonate (105) 289

Spectrophotometry; Thorium; Aliquat extraction (106) 385

Spectrophotometry; Nitrate; Plants; Soil extracts; Phenol (108) 285

Spectrophotometry; Sulphide; Sulphite; Extraction; Dimethylphenanthrolinecopper reagent (108) 293

Spectrophotometry; Boron; Rocks; Sephadex G-25 sorption (109) 115

X-ray fluores. spectrometry; Multielement analysis; Coprecipitation with molybdenum-APDC (110) 61

Ultrafiltration; Organic ligands; Fractionation (101) 339

Autocorrelation analysis; Sampling frequency; Quality control; Ammonium; Nitrate; Nitrite (103) 445

Stability constants; Ligand complexing capacity; Copper complexes (106) 113

## Water traces

Spectrophotometry; In acidic methanol (109) 187

## Welding fumes

Ion exchange; At. abs. spectrometry; Chromium speciation (110) 307

## Wet ashing unit

Trace analysis (109) 195

## Whiskies

Gas chromatography; Pattern recognition; Blind assay (103) 201

# X

## Xanthinol

Gas chromatography; Blood (108) 401

# Z

## Zeeman splitting

At. abs. spectrometry; Electrotherm. atomization; Copper; Molybdenum (101) 367

## Zinc

At. abs. spectrometry; Lead; Cadmium; Copper; Arc-nebulization (102) 15

At. abs. spectrometry; Electrotherm. atomization; Copper; Cadmium; Nickel; Sea water; Sampling methods; Dithiocarbamate extraction; Chelex (105) 233

At. abs. spectrometry; Gel perm. chromatography; Cadmium; Copper; Saliva; Distribution (107) 211

At. abs. spectrometry; Electrotherm. atomization; Silver; Bismuth; Cadmium; Steels; Solids autosampler (108) 75

Potentiometry; Stripping analysis; Cadmium; Lead; Copper; Sea water; Mercury film electrode (107) 29

X-ray fluores. spectrometry; Copper; Lead; Manganese; Phosphate-containing matrices (109) 419

**Zinc dialkyldithiophosphate**

Diff. pulse polarography; Lubricant additives (107) 391

**Zirconium**

Potentiometry; Kinetic analysis; pH-stat method; Copper; Molybdenum; Vanadium (104) 205

## TECHNIQUE INDEX

## VOLUMES 101-110

*The volume number is placed in parentheses before the page number*

**Activation analysis**

Rocks; Multielement analysis; Group separation (101) 45

Phosphorus; Aluminium-silicon alloys; Helium-4 (101) 63

Trace elements; Nickel; Thermal neutron; Purity control (101) 145

Platinum group elements; Gold; Rocks; Fire assay; Ores (102) 157

Gold; Tungsten; Rocks (102) 221

Uranium; Thorium; Rocks; Epithermal (104) 121

Noble metals; Photon; Black concentrates (104) 129

At. abs. spectrometry; Copper; Manganese; Sea water; Comparison; Co-crystallization; Extraction (104) 337

Multielement analysis; Blood; SLOWPOKE reactor (105) 185

Automated; Multielement analysis; Extraction system (106) 103

Platinum thin films; Rutherford back-scattering; Non-destructive (108) 119

Carbon; In refractory metals; Deuteron (108) 127

Chlorine; Bromine; Iodine; Waters; Biological materials; Organically bound; Contamination problems (108) 137

Carbon; Aluminium; Deuteron (108) 367

Uranium; Rocks; Tellurium fission product (108) 371

Liver tissue lyophilization; Chromium losses; Trace element losses (109) 139

Nitrogen; Reaction study; In zirconium; Deuteron (109) 411

Electrotherm. atomization; At. abs. spectrometry; Trace elements; Blood; Method comparison (110) 9

Multielement analysis; Tea leaves; Single comparator method (110) 75

Ion exchange; Silver fission product; Nuclear reactor fuels (110) 81

Nitrogen; Carbon; Hydrogen; Prompt  $\gamma$ -ray; Environmental materials (110) 339

**A.c. polarography**

Diff. pulse polarography; Silver-germanium alloys; Germanium (102) 113

**Amperometry**

Flow system; H.p.l.c.; Cystine; Cysteine; Penicillamine (101) 253

Galactose; Blood; Urine; Enzymatic (104) 47

Spectrophotometry; Chlorine traces; Air; Comparison (104) 355

Titrimetry; Iodine; Hydrazine; Isonicotinic acid hydrazide; Uric acid; Arsenic; Photosensitized generation; Rose Bengal (104) 397

Flow system; Photo-electroanalyzer; Nitrosamines; Nitrosodipropylamine; Flow-through platinum electrode (106) 1

Flow system; Lactate; Continuous assay (106) 131

Flow system; Glycerol; Triglycerides; Blood; Tubular carbon electrode; Enzymatic (106) 225

Flow system; Glucose analyzer; Immobilized glucose oxidase (106) 233

Phosphatidyl choline; Blood; Immobilized phospholipase-choline oxidase (106) 243

Flow system; Acetic acid; Microbial sensor; Trichosporon brassicae; Fermentation broths (109) 33

Bioassay; Nystatin; Microbial electrode; Yeast (109) 39

Lactate; Enzyme sensors; Cytochrome (109) 55

Titrimetry; Calcium; In alkali metal salts; Triethylenetetraminehexaacetic acid (109) 67

Hydrogen peroxide; Catalytic electrode (110) 157

**Anodic stripping voltammetry**

Flow system; Rotating disc electrode; Lead; Cadmium; Copper (101) 1

- Mercury film electrode; Cadmium; Lead; Copper; Waters; Baseline concentrations (101) 79
- Semidifferential electroanalysis; Cadmium; Lead; Thallium (101) 131
- Copper; Waters; Iron interference (101) 437
- Chronopotentiometry; Copper; Carboxital electrode (102) 91
- Cadmium; Lead; Thallium; Learning machine method (103) 151
- Cyclic voltammetry; Tin; Pyrogallol medium (104) 55
- Diff. pulse voltammetry; Sea water; Trace metals (106) 23
- Computer-controlled; Cadmium; Lead; Copper; Parameter evaluation (107) 13
- Cadmium; Lead; Copper; Urine; Sample treatment (107) 37
- Heavy metals; Siliconization effects (107) 67
- Cobalt; Mercury film electrode (109) 157
- Selenium; Tellurium; Gold film electrode; Copper, electrolytic (110) 87
- Atomic absorption spectrometry**
- Antimony; Rocks; Automatic; Hydride generation (101) 33
- Mercury; Arsenic; Fish tissues; Automatic (101) 193
- Mercury; Simple apparatus (101) 203
- Electrotherm. atomization; Zeeman splitting; Copper; Molybdenum (101) 367
- Electrotherm. atomization; Aluminium; Biological fluids (101) 385
- Electrotherm. atomization; Diocetyl tin stabilizers; Food-simulating solvents (101) 393
- Electrotherm. atomization; Iron; Magnetite electrode (101) 401
- Mercury; Radiotracer study (101) 429
- Lead; Cadmium; Zinc; Copper; Arc-nebulization (102) 15
- At. fluor. spectrometry; Spectral lamp, demountable (102) 25
- Electrotherm. atomization; Bismuth; Nickel-base alloys; Hydride generation; Solid samples; Induction furnace (102) 33
- Nickel; Effect of acids (102) 181
- Ruthenium; Ionic interferences (102) 185
- Methylmercury; Fish (102) 189
- Nitrous oxide-acetylene flame; Improved precision (102) 195
- Electrotherm. atomization; Copper; Gasoline (102) 201
- Computer-controlled; Microcomputer (103) 401
- Electrotherm. atomization; Lead; Antimony; Alloys; Steels; Solid sampling (104) 67
- Electrotherm. atomization; Lead; Steels; Alloys; Solid sampling (104) 75
- Surfactants, nonionic; Waters (104) 93
- Electrotherm. atomization; Molybdenum; Sea water (104) 99
- Electrotherm. atomization; Cadmium; Chromium; Cobalt; In uranium (104) 113
- Electrotherm. atomization; Arsenic; Urine; Automatic (104) 177
- Liver tissue; Trace metals; Destruction procedures (104) 225
- Mass spectrometry; Multielement analysis; Liver tissue; Spark-source (104) 233
- Flow system; Emission spectrometry; Calcium; Magnesium; Potassium; Plants; Merging zones (104) 279
- Automatic; Waters; Sediments; Mercury, total (104) 285
- Electrotherm. atomization; Germanium; Tungsten tube; Rocks (104) 293
- Electrotherm. atomization; Ion exchange; Heavy metals; Sea water; Selective elution; Chelex (104) 307
- Activ. analysis; Copper; Manganese; Sea water; Comparison; Co-crystallization; Extraction (104) 337
- Electrotherm. atomization; Palladium; Carbon filament (104) 385
- Cobalt; Biological materials (104) 389
- Cadmium; Rice; Low-temperature ashing; Extraction (104) 393
- Trace metals; Optimization of instrumental variables (105) 199
- Electrotherm. atomization; Beryllium; Manganese; Air particulates (105) 219
- Electrotherm. atomization; Copper; Cadmium; Zinc; Nickel; Sea water; Sampling methods; Dithiocarbamate extraction; Chelex (105) 233
- Cobalt; Nickel; Copper; Rocks; Matrix masking; Dithiocarbamate extraction (105) 247
- Gas chromatography; Electrotherm. atomization; Alkyllead; Air; Sources (105) 255
- Electrotherm. atomization; Trace metals; Tungsten tube; Design (105) 263
- Electrotherm. atomization; Tungsten tube; Trace metals; Atom formation processes (105) 271
- Electrotherm. atomization; Boron; Waters (106) 121

- Sampling; Snow; Trace elements; Contamination problems (106) 127
- Electrotherm. atomization; Mercury; Amalgamation methods (106) 285
- Coal fly ash; Trace metals; Room-temperature dissolution (106) 299
- Electrotherm. atomization; Sewage sludge; Trace metals; Pretreatment comparison (106) 309
- Electrotherm. atomization; Soil extracts; Trace metals; Dithizone extraction (106) 319
- Electrotherm. atomization; Bismuth; Rocks (106) 325
- Mercury; Air; Gold-coated collector (106) 405
- Mercury; Peak shapes (106) 411
- Electrotherm. atomization; Iron; Internal standardization; Dual-channel system (107) 129
- Mercury compounds; Air; Preconcentration (107) 159
- Gas chromatography; Mercury compounds; Fish; Extraction procedure (107) 169
- Atom collection; Copper; Cooled tube (107) 191
- Gel perm. chromatography; Cadmium; Copper; Zinc; Saliva; Distribution (107) 211
- Trace metals; Waters; APDC, DDTC comparison (107) 219
- Electrotherm. atomization; Tin; Molybdenum tube (107) 245
- Electrotherm. atomization; Germanium; Interference mechanisms (107) 253
- Mercury; Mercury compounds; Gases; Manganese dioxide collection; Activated carbon collection; Reference method (108) 1
- Mercury; Fish; Hair (108) 13
- Electrotherm. atomization; Air; Lead compounds; Inorganic, organic; Simultaneous determination (108) 21
- At. fluor. spectrometry; Gas chromatography; Lead; Detectors; Alkyllead compounds (108) 31
- Lead; Lubricants; Emulsion nebulization (108) 39
- Electrotherm. atomization; Gallium; Rhenium; Silicon; Trace metals (108) 45
- Electrotherm. atomization; Trace metals; Signal enhancement; Metal-oxygen reactions (108) 53
- Ion exchange; Manganese nodules; Nickel (108) 63
- Electrotherm. atomization; Vanadium; Tungsten tube; Rocks (108) 69
- Electrotherm. atomization; Silver; Bismuth; Cadmium; Zinc; Steels; Solids autosampler (108) 75
- At. fluor. spectrometry; Spectral lamp; Arsenic; Selenium; Controlled temperature-gradient (108) 347
- At. fluor. spectrometry; Trace metals; Lubricants; Comparison of standards (108) 351
- Electrotherm. atomization; Arsenic; Rocks; Soils; Hydride generation (108) 357
- Electrotherm. atomization; Copper; Gallium; Silver; Signal depression (109) 97
- Aluminium alloys; Trace elements; Dissolution procedure (109) 165
- Electrotherm. atomization; Silver; Rocks; Extraction (109) 171
- Background monitoring device (109) 177
- Ion exchange; Manganese nodules; Gallium; Rocks (109) 181
- Mercury, total; Waters; Reference methods (109) 209
- Activ. analysis; Electrotherm. atomization; Trace elements; Blood; Method comparison (110) 9
- Dithizone extraction; Sea water; Biological tissues; Trace metals (110) 21
- Electrotherm. atomization; Platinum; Automotive catalyst material (110) 29
- Air; Mercury, total; Background level; Gold-coated quartz wool (110) 35
- Electrotherm. atomization; Tellurium; Molybdenum tube (110) 49
- Electrotherm. atomization; Tin; Waters; Sediments; Effect of organic compounds (110) 55
- Ion exchange; Electrotherm. atomization; Selenium; In pyrite (110) 153
- Selenium; Electrochemical preconcentration; High chloride content (110) 279
- Electrotherm. atomization; Selenium; Blood; Stabilization in ashing (110) 285
- Electrotherm. atomization; Ion-exchanger suspensions; Mercury; Cobalt; Nickel; Molybdenum; Direct sampling (110) 301
- Ion exchange; Chromium speciation; Welding fumes (110) 307
- Metal (oxide)-on-silica catalysts; Rapid analysis (110) 345
- Atomic fluorescence spectrometry**  
Tin; Hydride generation (101) 199
- Antimony; Hydride generation; Non-dispersive (101) 375

At. abs. spectrometry; Spectral lamp, demountable (102) 25

Electrotherm. atomization; Trace metals; Cadmium; Carbon filament (104) 85

Arsenic; Waters; Hydride generation (104) 173

Multielement analysis; Time-multiplex multiple slit design (104) 267

Spectral lamp; Boosted-output; Interchangeable cathode (105) 213

At. abs. spectrometry; Gas chromatography; Lead; Detectors; Alkyllead compounds (108) 31

At. abs. spectrometry; Spectral lamp; Arsenic; Selenium; Controlled temperature-gradient (108) 347

At. abs. spectrometry; Trace metals; Lubricants; Comparison of standards (108) 351

Multielement analysis; Air filters; Furnace-flame, non-dispersive (110) 1

**Chromatography**  
see also Gas chromatography, Gel permeation chromatography, High-performance liquid chromatography, Thin-layer chromatography

Reflectance spectrometry; Benzofalpyrene; Oil shale; Retort waters (101) 333

Acetylglycine; Detection on paper; Acetylglycylglycine; Acetylglycylglycylglycine (105) 413

Ion chromatography; Waters; Multielement analysis; Evaluation; Geothermal (108) 405

Fluorimetry; Polynuclear aromatic hydrocarbons; Shale oil; Densitometry (110) 245

**Coulometry**  
Flow system; Titrimetry; Triangle-programmed titration; Automatic evaluation (101) 261

Diff. pulse voltammetry; Diff. pulse polarography; Corticosteroids; Electroproperties (102) 141

Titrimetry; Hydrazine; Hydrazide (102) 215

Nitric oxide; Nitrous acid; Nitrogen dioxide; Platinum flow-through electrode; Reaction study; Acidic halide media (105) 25

Bromine generation; Acetic acid medium (106) 347

Cyclic voltammetry; D.c. polarography; Technetium; Electrochemical study (107) 47

Gold; Electrogeneration (107) 83

Hydrogen chloride traces; Standard source; Gaseous reference mixtures (110) 95

Waters; Sulphur, total; Traces (110) 167

Potentiometry; Cobalt; Steels; Picolinic acid media (110) 227

## Cyclic voltammetry

Flow system; H.p.l.c.; Carbon electrode; Hexacyanoferrate; Dianisidine; Drugs (102) 41

Anod. stripping voltammetry; Tin; Pyrogallol medium (104) 55

Coulometry; D.c. polarography; Technetium; Electrochemical study (107) 47

**Differential pulse polarography**  
Indophenol derivatization; Ammonia; Aminophenol; Sulphanilamide (101) 211

Pulse polarography; High-performance; Instrumental considerations (101) 283

Flow system; Automated; Square-wave; Dropping mercury electrode (102) 99

A.c. polarography; Silver-germanium alloys; Germanium (102) 113

Nitrosodiethanolamines; Grinding fluids (102) 133

Coulometry; Diff. pulse voltammetry; Corticosteroids; Electroproperties (102) 141

Disodium cromoglycate; Urine (102) 205

Diff. pulse voltammetry; Pentachlorophenol (105) 91

Acidity functions; Trifluoroacetic acid; Trifluoromethanesulphonic acid; Hexafluoropropanediol (106) 51

Arsenic profiles; Silicon slices (106) 137

Spectrophotometry; Sulphaganidine (106) 365

Pharmaceuticals; Pareptide; Prolylmethyl-leucylglycinamide sulphate; Spectroscopic study; Nitroso derivative (107) 59

Sulphuric acid; Acetonitrile media (107) 75

Carbon disulphide; Waters (107) 387

Lubricant additives; Zinc dialkyldithiophosphate (107) 391

Molybdenum; Cathode ray polarography; Catalytic wave (108) 149

Computer-based system; Molybdenum; Microcomputer; Interfacing (108) 155

Cephalosporins; Degradation products (108) 205

Nitrosamines; Nitrosodiphenylamine; Nitrosodibutylamine; Extraction (108) 213

Corticosteroids; Pharmaceuticals; Single component (108) 389

Cephalexin degradation study (110) 107

**Differential pulse voltammetry**  
Coulometry; Diff. pulse polarography; Corticosteroids; Electroproperties (102) 141

Diff. pulse polarography; Pentachlorophenol (105) 91



Anod. stripping voltammetry; Sea water; Trace metals (106) 23

Polyinosinic acid; Hypoxanthine; Oxidation at PGE (108) 193

Voltammetry; Phenylbutazone; Oxyphenbutazone (109) 341

Polynuclear aromatic hydrocarbons; Rapid-scan (110) 255

### **D.c. polarography**

Pulse polarography; Triethylenetetraamine-hexaacetic acid; Reaction study (104) 215

H.p.l.c.; Nitrophenol; Nitrobenzene; Electrochemical detector; Dropping mercury electrode (105) 109

Vitamins K; Thiols reaction study (106) 261

Cyclic voltammetry; Coulometry; Technetium; Electrochemical study (107) 47

### **Electron spin resonance**

Spectra simulation; Fourier transform; Computer program; Morphamquat (103) 175

### **Electrothermal atomization**

At. abs. spectrometry; Zeeman splitting; Copper; Molybdenum (101) 367

At. abs. spectrometry; Aluminium; Biological fluids (101) 385

At. abs. spectrometry; Dioctyltin stabilizers; Food-simulating solvents (101) 393

At. abs. spectrometry; Iron; Magnetite electrode (101) 401

At. abs. spectrometry; Bismuth; Nickel-base alloys; Hydride generation; Solid samples; Induction furnace (102) 33

At. abs. spectrometry; Copper; Gasoline (102) 201

At. abs. spectrometry; Lead; Antimony; Alloys; Steels; Solid sampling (104) 67

At. abs. spectrometry; Lead; Steels; Alloys; Solid sampling (104) 75

At. fluor. spectrometry; Trace metals; Cadmium; Carbon filament (104) 85

At. abs. spectrometry; Molybdenum; Sea water (104) 99

At. abs. spectrometry; Cadmium; Chromium; Cobalt; In uranium (104) 113

At. abs. spectrometry; Arsenic; Urine; Automatic (104) 177

At. abs. spectrometry; Germanium; Tungsten tube; Rocks (104) 293

At. abs. spectrometry; Ion exchange; Heavy metals; Sea water; Selective elution; Chelex (104) 307

At. abs. spectrometry; Palladium; Carbon filament (104) 385

At. abs. spectrometry; Beryllium; Manganese; Air particulates (105) 219

At. abs. spectrometry; Copper; Cadmium; Zinc; Nickel; Sea water; Sampling methods; Dithiocarbamate extraction; Chelex (105) 233

At. abs. spectrometry; Gas chromatography; Alkyllead; Air; Sources (105) 255

At. abs. spectrometry; Trace metals; Tungsten tube; Design (105) 263

At. abs. spectrometry; Tungsten tube; Trace metals; Atom formation processes (105) 271

At. abs. spectrometry; Boron; Waters (106) 121

At. abs. spectrometry; Mercury; Amalgamation methods (106) 285

At. abs. spectrometry; Sewage sludge; Trace metals; Pretreatment comparison (106) 309

At. abs. spectrometry; Soil extracts; Trace metals; Dithizone extraction (106) 319

At. abs. spectrometry; Bismuth; Rocks (106) 325

At. abs. spectrometry; Iron; Internal standardization; Dual-channel system (107) 129

Emission spectrometry; Carbon furnace; Temperature optimization (107) 139

At. abs. spectrometry; Tin; Molybdenum tube (107) 245

At. abs. spectrometry; Germanium; Interference mechanisms (107) 253

At. abs. spectrometry; Air; Lead compounds; Inorganic, organic; Simultaneous determination (108) 21

At. abs. spectrometry; Gallium; Rhenium; Silicon; Trace metals (108) 45

At. abs. spectrometry; Trace metals; Signal enhancement; Metal-oxygen reactions (108) 53

At. abs. spectrometry; Vanadium; Tungsten tube; Rocks (108) 69

At. abs. spectrometry; Silver; Bismuth; Cadmium; Zinc; Steels; Solids autosampler (108) 75

At. abs. spectrometry; Arsenic; Rocks; Soils; Hydride generation (108) 357

At. abs. spectrometry; Copper; Gallium; Silver; Signal depression (109) 97

At. abs. spectrometry; Silver; Rocks; Extraction (109) 171

Activ. analysis; At. abs. spectrometry; Trace elements; Blood; Method comparison (110) 9

At. abs. spectrometry; Platinum; Automotive catalyst material (110) 29

At. abs. spectrometry; Tellurium; Molybdenum tube (110) 49

At. abs. spectrometry; Tin; Waters; Sediments; Effect of organic compounds (110) 55

Ion exchange; At. abs. spectrometry; Selenium; In pyrite (110) 153

At. abs. spectrometry; Selenium; Blood; Stabilization in ashing (110) 285

At. abs. spectrometry; Ion-exchanger suspensions; Mercury; Cobalt; Nickel; Molybdenum; Direct sampling (110) 301

### Emission spectrometry

Aluminium; Iron; Silicon; Titanium; Flame; Vapor-phase sampling; Chlorides (101) 89

H.p.l.c.; Argon plasma; Diketonates; Ketoamines; Diethylthiocarbamates; Metal-specific detection (101) 99

Gold; Glow lamp; Internal standardization (104) 11

Flow system; At. abs. spectrometry; Calcium; Magnesium; Potassium; Plants; Merging zones (104) 279

Molecular emission cavity analysis; Aliphatic amines; Amino acids (105) 433

Electrotherm. atomization; Carbon furnace; Temperature optimization (107) 139

Sodium; Potassium; Calcium; Lithium; Computer program; High concentrations (107) 201

Sulphur, total; Disulphide; Polysulphide; Petroleum products; Reduction method (107) 231

Arsenic; Sediments; D.c. plasma (107) 395

Silicates; Trace elements; Inductively coupled plasma; Major elements (108) 87

Trace elements; Air particulates; D.c. arc; Low-volume sampler (108) 103

Boron; Waters; Trace metals; Plasmas; High salt concentration (109) 73

Chemiluminescence, gas-phase; Arsenic; Antimony; Hydride formation (109) 229

Plasmas; Manganese; Four-line correction method; Inter-element effects; Torch symmetry (109) 241

Tin; Germanium; Plasmas; Hydride generation (109) 251

Barium; Waters; Biological fluids; Inductively-coupled plasma (110) 271

Discharge lamp; Cadmium; Heated-electrode (110) 291

### Enthalpimetry

Enzymatic inhibition; Alkaloids; Cholinesterase (106) 39

Potentiometry; Peroxidase activity; Iodide substrate (106) 251

Penicillins; Enzymatic method (107) 319

Iodide; Enzymatic method (108) 363

Cholinesterase activity; Serum; Direct injection (109) 393

Titrimetry; Selenium; With thiosulphate (110) 139

### Flow system

Anod. stripping voltammetry; Rotating disc electrode; Lead; Cadmium; Copper (101) 1

Spectrophotometry; Extraction; Molybdenum; Plants; Thiocyanate (101) 9

Plants; Phosphate; Merging zones; Double proportional injector (101) 17

Amperometry; H.p.l.c.; Cystine; Cysteine; Penicillamine (101) 253

Coulometry; Titrimetry; Triangle-programmed titration; Automatic evaluation (101) 261

Potentiometry; Copper-selective electrode (101) 419

Cyclic voltammetry; H.p.l.c.; Carbon electrode; Hexacyanoferrate; Dianisidine; Drugs (102) 41

Diff. pulse polarography; Automated; Square-wave; Dropping mercury electrode (102) 99

Spectrophotometry; Nitrogen, Kjeldahl; Phosphorus, total; Optimization (103) 189

Spectrophotometry; Extraction device; Codeine; Acetylsalicylic acid tablets (104) 21

Spectrophotometry; Multi-injection analysis; Albumin (104) 185

Emission spectrometry; At. abs. spectrometry; Calcium; Magnesium; Potassium; Plants; Merging zones (104) 279

Potentiometry; Glucose; Enzyme reactor; Protein removal (105) 43

Potentiometry; Single-point titrations; Acid-base (105) 67

Kinetic analysis; Magnesium; Strontium; Differential; DCTA complexes (105) 327

Potentiometry; Cephalosporins; Bacterial reactor; Antibiotics (105) 429

Amperometry; Photo-electroanalyzer; Nitrosamines; Nitrosodipropylamine; Flow-through platinum electrode (106) 1

Carbonic acid dehydration kinetics; Mixer design (106) 73

Amperometry; Lactate; Continuous assay (106) 131

Enzymatic analysis; Injection analysis; Blood; Glucose; Merging zones (106) 207

Amperometry; Glycerol; Triglycerides; Blood; Tubular carbon electrode; Enzymatic (106) 225

- Amperometry; Glucose analyzer; Immobilized glucose oxidase (106) 233
- Potentiometry; Lipids; Immobilized lipase (106) 369
- Fluorimetry; Glycine; Albumin (106) 395
- Spectrophotometry; Aluminium; Plants; Soils; Merging zones (107) 309
- Kinetic analysis; Magnesium; Calcium; Differential; Cryptates; Phthalein complexone (108) 241
- Potentiometry; Voltammetry; Injection techniques; Ion-selective electrodes; Voltammetric detectors; Mixing chambers; Theory (109) 1
- Amperometry; Acetic acid; Microbial sensor; Trichosporon brassicae; Fermentation broths (109) 33
- Spectrophotometry; Nitrogen, total; Plants; Isothermal distillation (109) 45
- Spectrophotometry; Nickel; Cobalt; Computer-processed; Photodiode-array spectrophotometer (109) 425
- Spectrophotometry; Nitrite; Nitrate; Copper-coated cadmium reductor (110) 123
- Conductivity detector; Potassium chloride; Non-intrusive very high-frequency (110) 325
- Fluorimetry**
- Polynuclear aromatic hydrocarbons; Computer decomposition of spectra; Benzidine; Dibenzochrysenes; Quantitative (103) 167
- Uranium; Ores; Quenching effects (104) 345
- Synchronous excitation; Phenols; Increased sensitivity (105) 297
- Acidity constants; Naphthoic acid; Anthroic acid (105) 311
- Selenium; Biological materials; Automatic; Benzopiazselenol (105) 319
- H.p.l.c.; Pharmaceuticals; Dihydroxyphenylalanine; Hydrazinomethyl-dihydroxyphenylpropanoic acid (105) 403
- Automatic; Selenium; Animal feeds (105) 445
- Selenium; Automatic; Phase-separating device (105) 451
- Spectrophotometry; Trichothecene mycotoxins; Formaldehyde formation (106) 59
- Quinolinol; Dihaloquinolinols; Simultaneous (106) 67
- Dissociation constant; Amines, aromatic; Hydroxy compounds; Sparingly soluble (106) 81
- Guanidino compounds; Polypeptides; Benzoin-dimethylformamide (106) 89
- Kojic acid; Gold; Reaction study (106) 147
- Flow system; Glycine; Albumin (106) 395
- Kinetic analysis; Salicylideneaminophenolates; Atomic number effects; Group IIIA metals (107) 273
- Diaminopyridines; Aminopyridines; Comparative study (107) 291
- Acridone; pH dependence (107) 411
- Dissociation constant; Alkylammonium ions, aryl-substituted; Drugs (108) 249
- Carbohydrates, reducing; With malonamide (108) 421
- Carbaryl; Naphthylmethylcarbamate; Naphthol (108) 425
- Europium; Samarium; Thenoyltrifluoroacetone-trioctylphosphine oxide (108) 429
- Scanning fluorimeter; Design considerations; Two-dimensional (109) 361
- Chromatography; Polynuclear aromatic hydrocarbons; Shale oil; Densitometry (110) 245
- Domperidone; Pharmaceuticals; Benzodiazolinone fluorophore (110) 261
- Aldehydes; Aromatic; Dithiobisaminonaphthalene (110) 335
- Gas chromatography**
- Copper complexes; Ketoamines; Quantitative (101) 117
- Potentiometry; Chlorine-containing compounds; Bromine-containing compounds; Hydrogenation; Dual electrode detector (101) 273
- Computerized data processing; Microwave plasma detector; Selectivity improvement; Four-channel calculations (103) 29
- Pattern recognition; Blind assay; Whiskies (103) 201
- I.r. spectrometry; Principal component analysis; Mixtures (103) 213
- Mass spectrometry; Fish tissues; Eulan WA New; Polychloro(chloromethylsulphonamide)-diphenyl ether isomers; Identification; Metabolites (104) 253
- Mass spectrometry; Polynuclear aromatic hydrocarbons; Computer-controlled; Air (105) 119
- Pentobarbital; Barbiturates; Blood; Butylation methods (105) 139
- Periodate oxidation; Aldehydes; Oligoglycosides (105) 153
- At. abs. spectrometry; Electrotherm. atomization; Alkyllead; Air; Sources (105) 255
- Warfarin; Blood (106) 155

Dibutyl phosphate; Butyl phosphate; In tributyl phosphate (106) 373

At. abs. spectrometry; Mercury compounds; Fish; Extraction procedure (107) 169

Mass spectrometry; Chloroalkanes; Negative-ion counting (107) 335

Glass column connector (107) 399

At. abs. spectrometry; At. fluor. spectrometry; Lead; Detectors; Alkyllead compounds (108) 31

Glow discharge detector; Silicon; Shale-derived liquids; Trimethylsilylation (108) 221

Xanthinol; Blood (108) 401

### **Gel permeation chromatography**

At. abs. spectrometry; Cadmium; Copper; Zinc; Saliva; Distribution (107) 211

### **Gravimetry**

Titrimetry; Cerium; As phosphate (101) 413

Gold; Dialkyl sulphites (102) 237

Tetrathienylborates; Cesium; Quaternary ammonium salts; Synthesis (105) 353

Oxygen; Uranium oxides (107) 365

Sulphate; Chromate; Vanadate; Stepwise precipitation (110) 179

### **High-performance liquid chromatography**

Emission spectrometry; Argon plasma; Diketonates; Ketoamines; Diethylthio-carbamates; Metal-specific detection (101) 99

Amino acid enantiomers; Derivatization (101) 111

Amperometry; Flow system; Cystine; Cysteine; Penicillamine (101) 253

Nitrofurantoin; Blood; Urine; Related drugs (101) 359

Flow system; Cyclic voltammetry; Carbon electrode; Hexacyanoferrate; Dianisidine; Drugs (102) 41

Norepinephrine; Dopamine; Serotonin; Brain tissue; Electrochemical detection (104) 29

D.c. polarography; Nitrophenol; Nitrobenzene; Electrochemical detector; Dropping mercury electrode (105) 109

Fluorimetry; Pharmaceuticals; Dihydroxy-phenylalanine; Hydrazinomethylidihydroxy-phenylpropanoic acid (105) 403

Piperazinedione; In reaction mixtures (105) 409

Phytoplankton pigments; Chlorophylls; Carotenoids; Marine particulate matter (107) 1

Scopoletin; Umbelliferone; Coumaric acid; Ferulic acid; Isomers; Optimization strategy (108) 227

Morphine; Poppy straw (108) 233

Plastic bottles; Phthalate ester plasticizers; Solution contamination (108) 325

Naphthylidazoalkanes as derivatizing agents; Fatty acids; Edible oils (109) 61

Naphthylidazoalkanes as derivatizing agents; Bile acids (109) 161

Spectrophotometry; Nitrate; Air particulates; Method comparison (110) 117

### **Immunoassay**

Potentiometry; Serum antibodies; Complement fixation test; Trimethylphenylammonium-selective electrodes (109) 25

### **Infrared spectrometry**

Carbon; Sulphur; Rocks; Combustion (101) 25

Mass spectrometry; N.m.r. spectrometry; Spectrophotometry; Computer-readable spectra libraries; Compilation (103) 21

Gas chromatography; Principal component analysis; Mixtures (103) 213

Computerized data system; Minicomputer; Dispersive (103) 303

Information theory; Computer-aided interpretation; Numerical taxonomy; Feature selection (103) 313

Computerized data system; Industrial applications; Dispersive; Minicomputer (103) 323

Carbonate; Carbon; Geological materials; Rocks; Non-carbonate (108) 113

### **Ion exchange**

Distribution coefficients; Metals; Thiocyanates (101) 207

Distribution coefficients; Bio-Rad AG; Effect of organic solvents (102) 167

At. abs. spectrometry; Electrotherm. atomization; Heavy metals; Sea water; Selective elution; Chelex (104) 307

Lead; Cadmium; Hafnium phosphate cation exchanger; Photoelectron study; Separation (104) 319

At. abs. spectrometry; Manganese nodules; Nickel (108) 63

Copper; Nickel; Cobalt; Uranyl; Stability constants; Sulphosalicylate complexes; Distribution diagrams (108) 333

Lysine; Pharmaceuticals (108) 411

At. abs. spectrometry; Manganese nodules; Gallium; Rocks (109) 181

Activ. analysis; Silver fission product; Nuclear reactor fuels (110) 81

At. abs. spectrometry; Electrotherm. atomization; Selenium; In pyrite (110) 153

At. abs. spectrometry; Chromium speciation;  
Welding fumes (110) 307

### Isotope dilution analysis

Substoichiometric concentration; Cesium;  
Theory (104) 327

Substoichiometric preconcentration (106) 333

### Kinetic analysis

Potentiometry; pH-stat method; Copper;  
Molybdenum; Zirconium; Vanadium (104) 205

Flow system; Magnesium; Strontium;  
Differential; DCTA complexes (105) 327

Formaldehyde; Hexamethylenetetramine;  
Automatic; Cyanide-selective electrode (107) 91

Fluorimetry; Salicylideneaminophenolates;  
Atomic number effects; Group IIIA metals  
(107) 273

Spectrophotometry; Thermom. analysis;  
Thiosulphate; Sulphide; Simultaneous  
indication (107) 301

Flow system; Magnesium; Calcium;  
Differential; Cryptates; Phthalein complexone  
(108) 241

Potentiometry; Citric acid; Perbromate-  
selective electrode (108) 375

Uric acid; Ascorbic acid; Mixtures (108) 441

Spectrophotometry; Phosphatases, acid  
(110) 175

### Mass spectrometry

N.m.r. spectrometry; I.r. spectrometry; Spectro-  
photometry; Computer-readable spectra  
libraries; Compilation (103) 21

Computer-aided interpretation; Steroids;  
Pattern recognition; Binary classifiers (103) 61

Computer program; Text search system;  
Spectral library (103) 109

Automated spectra evaluation; Computer  
program; Spark-source (103) 223

N.m.r. spectrometry; Computer system;  
Graphical reproduction; Structure input  
(103) 237

Spectral coding; SISCOM; Library search  
(103) 289

N.m.r. spectrometry; Target factor analysis;  
Theory of error (103) 339

Pattern recognition; Simplex optimization;  
Super-modified (103) 417

Ion counting-multichannel analyser;  
Quadrupole (104) 167

At. abs. spectrometry; Multielement analysis;  
Liver tissue; Spark-source (104) 233

Nitrogen isotope ratio; Gas preparative system  
(104) 245

Gas chromatography; Fish tissues; Eulan WA  
New; Polychloro(chloromethylsulphonamide)-  
diphenyl ether isomers; Identification;  
Metabolites (104) 253

Gas chromatography; Polynuclear aromatic  
hydrocarbons; Computer-controlled; Air  
(105) 119

Mass-analyzed ion kinetic energy spectra;  
Aliphatic esters; Chemical ionization;  
Collision-induced (105) 129

Hafnium; Lanthanides; Rocks; Interference  
effects; Spark-source (105) 163

Gas chromatography; Chloroalkanes; Negative-  
ion counting (107) 335

### Nuclear magnetic resonance spectrometry

Mass spectrometry; I.r. spectrometry; Spectro-  
photometry; Computer-readable spectra  
libraries; Compilation (103) 21

Chemical shifts; Computer program; Retrieval  
system; Carbon-13 (103) 141

Mass spectrometry; Computer system;  
Graphical reproduction; Structure input  
(103) 237

Mass spectrometry; Target factor analysis;  
Theory of error (103) 339

Computerized data processing; HOSE;  
Substructure code (103) 355

Pattern recognition; Trace metals; Steels;  
Classification in 4 levels (103) 429

Lanthanum complexes; Stability constants;  
Potassium hydroxotrifluoroborate demasking  
reactions; EDTA; NTA (105) 391

### Phosphorimetry

Pharmaceuticals; Room-temperature (101) 319

Polynuclear aromatic hydrocarbons; Room-  
temperature; Heavy atom effect (102) 1

Multicomponent analysis; Second-derivative  
method; Room-temperature (107) 261

Catecholamines; Related compounds;  
Analytical characteristics (108) 297

### Polarography

see also A.c. polarography, D.c. polarography,  
Differential pulse polarography, Pulse  
polarography

Pharmaceuticals; Methylbenzimidazolylpyridyl-  
ethyl sulphide; Methylbenzimidazolylpyridyl-  
ethyl sulphoxide; Methylbenzimidazolylpyridyl-  
oxideethyl sulphone (102) 121

Polarographic current sampling; Without drop  
synchronization (110) 161

### Potentiometry

Bacterial membrane electrode; Cysteine;  
Proteus morganii (101) 125

- Titrimetry; Chlorine; Organic materials; Sodium biphenyl (101) 221
- Selectivity coefficients; Liquid ion-exchange membranes; Digital simulation (101) 231
- Hydrogen ion; Potassium; Calcium; ISFET (101) 239
- ISFET; Reference electrode (101) 247
- Gas chromatography; Chlorine-containing compounds; Bromine-containing compounds; Hydrogenation; Dual electrode detector (101) 273
- Flow system; Copper-selective electrode (101) 419
- Fluoride-selective electrode; Dynamic response (102) 61
- Cyanide-selective electrode; Effect of pH (102) 85
- Titrimetry; Acid mixtures (102) 211
- Stripping analysis; Microcomputer system (103) 379
- Kinetic analysis; pH-stat method; Copper; Molybdenum; Zirconium; Vanadium (104) 205
- Stripping analysis; Mercury; Automatic (105) 33
- Flow system; Glucose; Enzyme reactor; Protein removal (105) 43
- Copper-selective electrode; Chloride interference; Mechanism (105) 53
- Flow system; Single-point titrations; Acid-base (105) 67
- Rubidium-selective electrode; Antibiotics; Nystatin assay; Polyene (105) 77
- Titrimetry; Benzophenone oxime extractants; LIX reagents; Nonaqueous (105) 83
- Titrimetry; Halide mixtures; Iodide-selective electrode (105) 417
- Flow system; Cephalosporins; Bacterial reactor; Antibiotics (105) 429
- Stripping analysis; Lead; Urine; Mercury film electrode (106) 15
- Spectrophotometry; Fluoride; Distillation with hexamethyldisiloxane (106) 95
- Enthalpimetry; Peroxidase activity; Iodide substrate (106) 251
- Nitrate-selective electrode; Bipyridine derivatives (106) 341
- Flow system; Lipids; Immobilized lipase (106) 369
- Stripping analysis; Zinc; Cadmium; Lead; Copper; Sea water; Mercury film electrode (107) 29
- Single-point titrations; Silver; Chloride; Sulphate (107) 101
- Copper-nitrioltriacetic acid ternary complexes; Stability constants (107) 105
- Cobalt-selective electrode; Coated wire; Benzalkonium ion pair (107) 113
- Iodide-selective electrode; Theory; Low iodide concentrations (107) 121
- Stability constants; Silver complexes; Organic ligands (107) 349
- Titrimetry; Gran method (107) 377
- Cadmium-selective electrode; Mercury-selective electrode; Metal sulphide membranes; Complexing agents (108) 169
- Kinetic analysis; Citric acid; Perbromate-selective electrode (108) 375
- Calcium-selective electrode; PVC membrane; Bistetramethylbutyldinitrophenoxide (108) 385
- Flow system; Voltammetry; Injection techniques; Ion-selective electrodes; Voltammetric detectors; Mixing chambers; Theory (109) 1
- Immunoassay; Serum antibodies; Complement fixation test; Trimethylphenylammonium-selective electrodes (109) 25
- Phosphate-selective electrode; Tris(thiourea)-copper monohydrogenphosphate (109) 149
- Liquid ion-exchange membranes; Ion-selective electrodes; Time constants; Method comparison (109) 259
- Ion-selective electrodes; Copper-selective electrode; Surface morphology (109) 279
- Calcium ion buffers; Measured and calculated concentrations (109) 291
- Titrimetry; Sulphur; Waters; Irons; Steels; Fly ash; Cadmium sulphide electrode; Hydrogen sulphide generation (109) 307
- Titrimetry; Fluoride; Sulphate; Chromate; Molybdate; Tungstate; Oxalate; Phosphate; Hexacyanoferrate; Fluoride-selective electrode; Lead titrant (109) 319
- Ion-selective electrodes; Silver sulphide electrode; Interfacial properties; Impedance measurements (110) 185
- Bromide-selective electrode; Response mechanism;  $Hg_2Br_2$ - $HgS$ - $Ag_2S$  membranes (110) 197
- Dissociation constant; Nitrosyl chloride; Dinitrogen tetroxide; Silver-silver chloride electrode; Sulpholane media (110) 211
- Coulometry; Cobalt; Steels; Picolinic acid media (110) 227
- Perchlorate-selective electrode; Urushi membrane; Liquid ion-exchanger (110) 321

**Pulse polarography**

Diff. pulse polarography; High-performance; Instrumental considerations (101) 283

D.c. polarography; Triethylenetetraaminehexaacetic acid; Reaction study (104) 215

Chlorite traces (107) 383

**Reflectance spectrometry**

Chromatography; Benzolapyrene; Oil shale; Retort waters (101) 333

**Ring oven**

Semiquantitative analysis; Reaction rates on paper (101) 187

Lead; Air; Rhodizonate (101) 225

Isonicotinic acid hydrazide; In tablets (110) 171

**Spectrophotometry**

Flow system; Extraction; Molybdenum; Plants; Thiocyanate (101) 9

Selenium; Sea water; Adsorption colloid flotation (101) 71

Molar absorptivity; Formation constants; Continuous variations curves (101) 157

Extraction; Palladium; Nitrosodiethylaminophenol (101) 169

Palladium; Stability constants; Thioglycolic acid derivatives (101) 177

Copper; Tetraphenylporphine (101) 423

Chlorophenols; Brines; Aminoantipyrine (102) 229

Mass spectrometry; N.m.r. spectrometry; I.r. spectrometry; Computer-readable spectra libraries; Compilation (103) 21

Flow system; Nitrogen, Kjeldahl; Phosphorus, total; Optimization (103) 189

Computer-controlled; Photometric analyzer; Lidocaine; Microcomputer (103) 489

Flow system; Extraction device; Codeine; Acetylsalicylic acid tablets (104) 21

Phosphorus profiles; Silicon slices (104) 139

Lanthanum; Beryllium; Aluminium; Effect of poly(vinylbenzyltriphenylphosphonium chloride) (104) 145

Polyvinyl alcohol; Complex formation (104) 153

pH scale; Ethanedial solvent (104) 181

Flow system; Multi-injection analysis; Albumin (104) 185

Cobalt; Dipyrityldipyrimidylhydrazone (104) 191

Amperometry; Chlorine traces; Air; Comparison (104) 355

Extraction; Tin; Diphenylphenanthroline (104) 363

Extraction; Iron; Waters; Pyrogallol red; Zephiramine; Removal of extracted reagent (104) 369

Mercury; Waters; Dual-wavelength; Copper(II) dithizonate (105) 289

Nitrate; Organic interferences; Xylenol (105) 335

Uranium; Extraction; Benzoyltrifluoroacetone (105) 439

Fluorimetry; Trichothecene mycotoxins; Formaldehyde formation (106) 59

Potentiometry; Fluoride; Distillation with hexamethyldisiloxane (106) 95

Chlorindazone DS; Metal ions; Reagent evaluation (106) 141

Furosemide; Phloroglucinol (106) 151

Thiobarbituric acid values; Fish oils (106) 279

Iron; Catalytic; Anisidine-dimethylaniline reaction (106) 355

Diff. pulse polarography; Sulphaguanidine (106) 365

Titrimetry; Ascorbic acid; Ferricinium reaction (106) 379

Thorium; Waters; Aliquat extraction (106) 385

Nitroimidazoles; Nitrite formation (106) 389

Lanthanides; Calmagite (106) 401

Halogenopentamminechromium(III) perchlorate; Computer-calculated rate constants; Aquation kinetics (107) 279

Kinetic analysis; Thermom. analysis; Thiosulphate; Sulphide; Simultaneous indication (107) 301

Flow system; Aluminium; Plants; Soils; Merging zones (107) 309

Nitrofurazone; With phloroglucinol (107) 401

Tetrahydroborate; With trinitrobenzenesulphonic acid (107) 405

Ozone; Air; Specific (108) 255

Rhodium; With malachite green (108) 261

Uranium; Trialkylamine extracts; Bromopyridylazodiethylaminophenol (108) 267

Phenothiazines; Pharmaceuticals; Molybdophosphoric acid (108) 277

Nitrate; Plants; Soil extracts; Waters; Phenol (108) 285

Waters; Sulphide; Sulphite; Extraction; Dimethylphenanthrolinecopper reagent (108) 293

Antimony; With ferroin; Speciation (108) 417

Niobium; EDTA; Pyrocatechol ternary complex; NTA contamination (108) 433

Uranium; Trialkylamine extracts; With dibenzoylmethane (108) 437

Flow system; Nitrogen, total; Plants; Isothermal distillation (109) 45

Silver; Dicyanoargentate; Extraction; Methylene blue (109) 107

Boron; Waters; Rocks; Sephadex G-25 sorption (109) 115

Osmium; Ruthenium; Extraction; Thiocyanate complexes (109) 123

Water traces; In acidic methanol (109) 187

Organic bases; Alkaloids; Surfactants; Extraction; With metallochromic indicators (109) 191

U.V.-absorptiostat; Enzyme determinations; Catalase; Ascorbate oxidase; Peroxidase; Sorbitol dehydrogenase; Lactate dehydrogenase (109) 351

Nitrate; Improved 2,4-xyleneol method (109) 373

Niobium; Steels; With sulphochlorophenol S (109) 381

Titrimetry; Ethylenediaminetetraacetic acid; Manganese; Nickel; Catalytic; Dihydroxyphthalimide dithiosemicarbazone oxidation (109) 401

Flow system; Nickel; Cobalt; Computer-processed; Photodiode-array spectrophotometer (109) 425

H.p.l.c.; Nitrate; Air particulates; Method comparison (110) 117

Flow system; Nitrite; Nitrate; Copper-coated cadmium reductor (110) 123

Kinetic analysis; Phosphatases, acid (110) 175

Nickel; Extraction; Chloronitrosophthalol; Crystal violet (110) 329

**Thermometric analysis**  
Automatic; Caustic soda; Alumina; Bayer liquors (102) 233

Kinetic analysis; Spectrophotometry; Thiosulphate; Sulphide; Simultaneous indication (107) 301

Titrimetry; Acidity; Petroleum bitumens; Catalytic (109) 129

**Titrimetry**  
Acid-base equilibria; Dimethylsulphoxide-water; Carboxylic acids (101) 139

Potentiometry; Chlorine; Organic materials; Sodium biphenyl (101) 221

Flow system; Coulometry; Triangle-programmed titration; Automatic evaluation (101) 261

Gravimetry; Cerium; As phosphate (101) 413

Potentiometry; Acid mixtures (102) 211

Coulometry; Hydrazine; Hydrazide (102) 215

Sulphite; Dimethyl sulphoxide medium; Cerium(IV) (104) 379

Amperometry; Iodine; Hydrazine; Isonicotinic acid hydrazide; Uric acid; Arsenic; Photosensitized generation; Rose Bengal (104) 397

Potentiometry; Benzophenone oxime extractants; LX reagents; Nonaqueous (105) 83

Antibiotics; Penicillins; Iodate titrant (105) 361

Sulphate; Thiosulphate; Polythionates; Mining effluents (105) 375

Potentiometry; Halide mixtures; Iodide-selective electrode (105) 417

Spectrophotometry; Ascorbic acid; Ferricinium reaction (106) 379

Potentiometry; Gran method (107) 377

Magnetic susceptibility measurements; Lanthanides; Binary mixtures (108) 309

Amperometry; Calcium; In alkali metal salts; Triethylenetetraminehexaacetic acid (109) 67

Thermom. analysis; Acidity; Petroleum bitumens; Catalytic (109) 129

ISFET; Acid-base (109) 145

Potentiometry; Sulphur; Waters; Irons; Steels; Fly ash; Cadmium sulphide electrode; Hydrogen sulphide generation (109) 307

Potentiometry; Fluoride; Sulphate; Chromate; Molybdate; Tungstate; Oxalate; Phosphate; Hexacyanoferrate; Fluoride-selective electrode; Lead titrant (109) 319

Spectrophotometry; Ethylenediaminetetraacetic acid; Manganese; Nickel; Catalytic; Dihydroxyphthalimide dithiosemicarbazone oxidation (109) 401

Enthalpimetry; Selenium; With thiosulphate (110) 139

Acid-base equilibria; Dimethylsulphoxide-water; Carboxylic acids; Correction (110) 183

**Voltammetry**  
see also Anodic stripping voltammetry, Cyclic voltammetry, Differential pulse voltammetry

Nitric oxide; Nitrous acid; Nitrogen dioxide; Reduction at platinum electrodes (105) 9

Iron(II)-iron(III) determination; Rocks; Vitamin tablets (105) 99

Phenolic analgesics; Pharmaceuticals (105) 423

Flow system; Potentiometry; Injection techniques; Ion-selective electrodes; Voltammetric detectors; Mixing chambers; Theory (109) 1

Diff. pulse voltammetry; Phenylbutazone; Oxyphenbutazone (109) 341



Ethanol; Lactic acid; Enzymatic; Linear-sweep;  
NAD-modified carbon paste electrode (110) 203

### **X-ray fluorescence spectrometry**

Ceramics; Alloys; Matrix effect corrections  
(102) 177

Correction constants; Multivariate least-  
squares method (104) 1

Matrix correction; Dead-time (105) 177

Rocks; Soils; Trace elements; Thin-film  
energy-dispersive (108) 93

Multielement analysis; Rocks; Soils; Energy-  
dispersive; Sample preparation (109) 85

Zinc; Copper; Lead; Manganese; Phosphate-  
containing matrices (109) 419

Waters; Multielement analysis; Coprecipitation  
with molybdenum-APDC (110) 61

Palladium; Titanium alloys; Extraction-  
filtration concentration (110) 67

FIRST ISSUE  
FALL 1979

ANNOUNCING A NEW JOURNAL

# SYNTHETIC METALS

An International Journal Integrating Research and Applications on Intercalation Compounds of Graphite, Transition Metal Compounds, and Quasi One-Dimensional Conductors

## EDITOR

**F. Lincoln Vogel**

University of Pennsylvania  
Philadelphia, Pennsylvania, U.S.A.  
*(Intercalation Compounds of Graphite)*

## ASSOCIATE EDITORS

**Alan J. Heeger**

University of Pennsylvania  
Philadelphia, Pennsylvania, U.S.A.  
*(Quasi One-Dimensional Conductors)*

**Wayne L. Worrell**

University of Pennsylvania  
Philadelphia, Pennsylvania, U.S.A.  
*(Transition Metal Compounds)*

## Aims and Scope

This journal is an international medium for the rapid publication of original research papers, short communications and subject reviews dealing with research on and applications of synthetic metals. The term "synthetic metals" is meant to include those chemical compounds having metallic properties but which are distinguishable from the naturally occurring elemental metals or their combinations which produce alloys.

The following types of materials are considered to be synthetic metals and therefore fall within the purview of this journal:

- intercalation compounds of graphite of either the donor or acceptor type
- transition metal compounds and transition metal layered dichalcogenides
- quasi one-dimensional conductors

## Subscription Information

1979/1980, volume 1 (4 issues) Price: SFr. 160.00, including postage.

## Specimen Copies

Requests for review and free specimen copies should be sent to the publishers.

**ELSEVIER SEQUOIA S.A.**

P.O. Box 851  
1001 Lausanne  
Switzerland



# NEW!

FIRST ISSUE: JANUARY 1980

# COLLOIDS AND SURFACES

AN INTERNATIONAL JOURNAL DEVOTED TO THE APPLICATIONS AND PRINCIPLES OF COLLOID AND INTERFACE SCIENCE

## Editor-in-Chief:

P. Somasundaran, Henry Krumb School of Mines, Columbia University, New York NY 10027, U.S.A.

## Regional Editors:

E. D. Goddard, Union Carbide Corp., Tarrytown Technical Center, Old Saw Mill River Road, Tarrytown, NY 10591, U.S.A.

T. W. Healy, Department of Physical Chemistry, University of Melbourne, Parkville Victoria 3052, Australia

G. D. Parfitt, Tioxide International, Ltd., Stockton-on-Tees, Cleveland TS18 2NQ, England

## Scope:

COLLOIDS AND SURFACES is a new international journal concerned with applications and principles of colloidal and interfacial phenomena. It is designed to encourage publication of basic colloid and surface science and, in particular, its application in engineering and applied science. In addition to research papers, the journal will contain notes, brief communications, book reviews and announcements.

Areas, topics and subjects that will be covered include emulsions, foams, aerosols, detergents and wetting, flocculation and dispersion, rheology, cosmetics, paints, foods, paper and pulp electrokinetic and electrode phenomena, friction and lubrication, thin films, liquid membranes and bilayers, biomaterials and biocolloids, polymer colloids, pharmaceutical and related health sciences, environmental and aquatic systems, water treatment and dewatering, agricultural and soil science, minerals extraction and metallurgy, precipitation and crystal growth and modification.

COLLOIDS AND SURFACES will be published in one volume per year in quarterly issues. The subscription price for 1980 - Volume 1 - is 166 Dutch guilders/US \$81.00, including postage.

Write for a sample copy to Dept. COL at one of the addresses below.



# ELSEVIER

P.O. Box 211,  
1000 AE Amsterdam  
The Netherlands

52 Vanderbilt Ave  
New York, N.Y. 10017

The Dutch guilder price is definitive. US \$ prices are subject to exchange rate fluctuations.

(continued from outside of cover)

Flame atomic absorption analysis for selenium after electrochemical preconcentration W. Lund and R. Bye (Oslo, Norway) . . . . .	276
Direct electrothermal atomic absorption spectrometric determination of selenium in serum K. Saeed, Y. Thomassen and F. J. Langmyhr (Oslo, Norway) . . . . .	285
A heated-electrode discharge lamp for trace analysis by atomic emission spectroscopy K. Kitagawa, R. Narita (Nagoya, Japan) and T. Takeuchi (Toyohashi, Japan) . . . . .	291
Direct sampling of ion-exchanger suspensions for atomic absorption spectrometry with electrothermal atomization Z. Slovák (Brno, Czechoslovakia) . . . . .	301
Development of a procedure for studies of the chromium(III) and chromium(VI) contents of welding fumes D. Naranjit, Y. Thomassen and J. C. van Loon (Toronto, Canada) . . . . .	307
Increased mercury contamination of distilled and natural water samples caused by oxidizing preservatives J. H. Cragin (Hanover, NH, U.S.A.) . . . . .	313

**Short Communications**

Perchlorate-selective electrodes with Urushi as the membrane matrix K. Hiro, A. Kawahara and T. Tanaka (Osaka, Japan) . . . . .	321
A non-intrusive very high-frequency conductivity detector for continuous flow monitoring J. F. Alder and P. K. P. Drew (London, Gt. Britain) . . . . .	325
Extraction-spectrophotometric determination of nickel with 4-chloro-2-nitroso-1-naphthol and crystal violet K. Tōei, S. Motomizu and H. Yokosu (Okayama-shi, Japan) . . . . .	329
The fluorescent reaction product in the determination of aromatic aldehydes with 2,2'-dithiobis(1-aminonaphthalene) K. Ohtsubo, Y. Okada, K. Zaitu and Y. Ohkura (Fukuoka, Japan) . . . . .	335
Simultaneous determination of nitrogen, carbon, and hydrogen by thermal neutron prompt $\gamma$ -ray spectrometry E. S. Gladney, D. B. Curtis and E. T. Journey (Los Alamos, NM, U.S.A.) . . . . .	339
Rapid accurate analysis of metal (oxide)-on-silica catalysts by atomic absorption spectrometry B. A. H. G. Jütte, A. Heikamp and J. Agterdenbos (Utrecht, The Netherlands) . . . . .	345

<b>Book Reviews</b> . . . . .	349
<b>Announcements</b> . . . . .	354
<b>Errata</b> . . . . .	354
<b>Author Index</b> . . . . .	355
<b>Cumulative Indexes Volumes 101-110</b> . . . . .	359

## CONTENTS

Interfacial properties of precipitate-based ion-selective electrodes. Rotating disk impedance measurements of the $Ag_2S/Ag^+$ (aqueous) interface R. K. Rhodes and R. P. Buck (Chapel Hill, NC, U.S.A.) . . . . .	185
The mechanism of the potential response of bromide-selective electrodes based on mercury salts A. Hulanicki, R. Lewandowski and A. Lewenstam (Warsaw, Poland) . . . . .	197
Electrochemical enzymatic determinations of ethanol and L-lactic acid with a carbon paste electrode modified chemically with nicotinamide adenine dinucleotide T. Yao and S. Musha (Sakai, Japan) . . . . .	203
Détermination des constantes de dissociation ionique du chlorure de nitrosyle et de $N_2O_4$ dans le sulfolane M. Wartel, A. Boughriet et J.-C. Fischer (Villeneuve, France) . . . . .	211
Dosage électrochimique du cobalt. I. Etude des courbes intensité-potentiel du système cobalt(III)/cobalt(II) en milieu picolique G. Clement (Cluny, France) and M. R. Pâris (Dijon, France) . . . . .	219
Dosage électrochimique du cobalt. II. Application aux aciers à faible ou à moyenne teneurs G. Clement (Cluny, France) and M. R. Pâris (Dijon, France) . . . . .	227
Determination of the water content in muscovites containing large amounts of fluorine by Karl Fischer titration after fusion with silicon dioxide K. Yamaya (Tokyo, Japan) . . . . .	233
Characterization of polycyclic aromatic hydrocarbons in shale oil by chromatography and fluorescence densitometry R. J. Hurtubise and J. D. Phillip (Laramie, WY, U.S.A.) . . . . .	245
Rapid analysis for polynuclear aromatic hydrocarbons by linear-sweep differential pulse voltammetry K. C. Burrows and M. C. Hughes (Bethlehem, PA, U.S.A.) . . . . .	255
Fluorescence properties of domperidone and its determination in pharmaceutical preparations W. Baeyens and P. de Moerloose (Ghent, Belgium) . . . . .	261
Dosage du baryum dans l'eau et les liquides biologiques par spectrométrie d'émission avec source plasma haute fréquence Y. Mauras et P. Allain (Angers, France) . . . . .	271

*(continued on inside page of the cover)*

© Elsevier Scientific Publishing Company, 1979.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior written permission of the publisher, Elsevier Scientific Publishing Company, P.O. Box 330, 1000 AH Amsterdam, The Netherlands.

Submission of an article for publication implies the transfer of the copyright from the author to the publisher and is also understood to imply that the article is not being considered for publication elsewhere.

Submission to this journal of a paper entails the author's irrevocable and exclusive authorization of the publisher to collect any sums or considerations for copying or reproduction payable by third parties (as mentioned in article 17 paragraph 2 of the Dutch Copyright Act of 1912 and in the Royal Decree of June 20, 1974 (S. 351) pursuant to article 16 b of the Dutch Copyright Act of 1912) and/or to act in or out of court in connection therewith.

Printed in The Netherlands.