An International Journal of Analytical Chemistry

ταλαντα

talanta

PERGAMON PRESS
OXFORD • LONDON • NEW YORK • PARIS

1969 VOLUME 16, NO. 10 OCTOBER

Birkhäuser Verlag, Basel and Stuttgart

electro*analytical* abstracts

International Journal dealing with the documentation of all aspects of electroanalytical chemistry, including fundamental electrochemistry.

Editor: *G. Milazzo*, Roma (Italy).

Annual subscription:
sFr. 290.–;
single numbers sFr. 55–.
Bimonthly.
In publication since 1963
(formerly 'Abstracts
Section', by Elsevier).
Size 17,2 × 24,5 cm.

An abstracting service on electrochemistry seems to be particularly needed *because papers on fundamental electrochemistry or on problems solved with the aid of electrochemical methods are scattered in nearly all other sections* into which the abovementioned classical abstracting periodicals are subdivided, from physical to analytical, from inorganic to general, from organic to pharmaceutical.
This is the reason why 'Electrochemical Abstracts' began its publication some three years ago. However, the title of this abstracting service must not be misinterpreted. Not only *analytical* electrochemistry is dealt with, but also all *fundamental electrochemistry*, and *any other topic* that is more or less related to electrochemistry or that utilizes electrochemical methods. About 500 periodicals and all available nonperiodical reports are abstracted, until now producing about 2500 abstracts yearly, and perhaps still more in the near future.
Furthermore, the rapidly-growing number of papers of interest to readers of this abstracting periodical will be closely followed, so that it is expected that vol. 4 will offer about 3500 abstracts, nearly double the number published in the first volume. For many of them the author's abstracts are utilized, by courtesy of the original periodicals, in order to speed up the publication of the abstracts.
The abstracts are classified into eleven sections, of which the first two, Fundamental Electrochemistry and Apparatus, are of general interest and collect the papers of fundamental and theoretical electrochemistry and those devoted to instrumentation. The following eight are classified according to the different electrochemical methods: Polarography, Amperometry, Potentiometry, Conductometry, Electrolysis, Coulometry, Electrophoresis, and other methods. The last section contains the abstracts of papers devoted to some other topics, which, though related to electrochemistry, are not easily classifiable into one of the preceding sections. A section devoted to Book Reviews and New Books is also included.
It is the aim of the Editor to offer a service which will fully cover all sections of electrochemistry, and which, after the unavoidable initial difficulties, will become progressively more useful to anyone directly or indirectly interested in this important branch of chemistry.
The Editor will be grateful to colleagues for any constructive criticism and suggestions which, in addition to his own experience, may be used to improve the service in every possible way.

Orders
through your bookseller
or newsagent

Please ask for a free copy
from the publishers:

Birkhäuser Verlag,
CH-4000 Basel 10
(Switzerland)

Birkhäuser

Chromatographia

An International Journal for Rapid Communication in Chromatography and Related Techniques

The august issue features:

A Procedure for the precise Evaluation of Gas Chromatograms by means of Process Computers

Comparison of some Adsorbents in Gas-Solid Chromatography

Quantitative Procedures in Thin-Layer Chromatography

Recent Advances in Thin-Layer Chromatography

Improved Amino Acid Analysis
(Automated Integration and Computer Processing of Data)

Chromatographia features original contributions, series and short communications covering the whole range of chromatographic techniques. The international scientific community is represented within the Board of Editors as well as by the regional editors in England, France, Germany and Hungary.
With CHROMATOGRAPHIA a continuous flow of information and exchange of views between scientists all over the world has been made possible.

CHROMATOGRAPHIA is a monthly with contributions in three languages (English, French, German)

Subscription rate for firms, public authorities, institutes and libraries:

$47.- p.a. (Private subscribers $15.-)

Pergamon Press Inc.
Maxwell House, Fairview Park,
Elmsford, New York 10523

Pergamon Press Ltd.
Headington Hill Hall, Oxford,
England

Friedr. Vieweg & Sohn GmbH
D-33 Braunschweig P.O.B. 185
W-Germany

17 V 86

NEW TITLES FOR ORGANIC CHEMISTS FROM THE BUTTERWORTH GROUP

Structure of Organic Solids

International Union of Pure and Applied Chemistry

1969 92 pages 94 illustrations 58s

21st International Congress of Pure and Applied Chemistry

International Union of Pure and Applied Chemistry

1969 278 pages 148 illustrations £5

Send for further information to:

BUTTERWORTHS · ILIFFES · NEWNES
88 Kingsway London WC2

THE PERGAMON TRANSLATION SERVICE

backed by the Pergamon Group's resources producing 200 learned and technical journals and over 600 books a year.

copies of articles on scientific, technical and educational subjects published in the open literature of any country can be obtained for TRANSLATION

TRANSLATION of articles appearing in Pergamon Publications into any required language can be provided.

Fees are moderate

Enquiries should be addressed to:
PERGAMON PRESS LIMITED—
Translation Service
Maxwell House, 348/350 Gray's Inn Road,
London WC1, telephone: 01-837 6484

a selection of new learned journal titles from Pergamon

Accident Analysis and Prevention

This new international journal is designed to provide a forum for research and discussion on all aspects of industrial and transport safety, including the prevention of injury due to accidents. Emphasis is placed on the systems approach, cost effectiveness studies and the development of statistical procedure for analysis of accident data. *Quarterly*

Automatica

Automatica is published as the official journal of IFAC—International Federation for Automatic Control.

The subjects of the papers cover a wide variety of topics to illustrate the activities of IFAC and the developments in the area of automatic control, systems science and cybernetics. These papers concern the theory and application of systems and components; the creation, fabrication and transportation of materials, both the inert and the living; the generation and transmission of power and information; and the realms of ecology, geology and biology including control of the weather, pollution and natural resources. The aim of the journal, is to select the most promising papers of those presented at the IFAC meetings, to evaluate them through reviews, to have them rewritten as necessary, and to publish them regularly. *Bi-monthly*

Metron

Sira measurement and control abstracts and reviews.

Metron is the new title and up-dating of the established journal formerly known as Sira Abstracts and Reviews. The aim of Metron is to assist scientists, technologists and managers searching for new techniques and developments in the field of measurement and control by providing an awareness and search tool for the technical literature. *Monthly*

Journal of The Franklin Institute

In January, this the oldest and most highly revered American journal which is devoted to Science and the Mechanic Arts, commenced publication with Pergamon Press and is now in its 143rd year of publication. Papers cover all the traditional branches of mathematics and the physical sciences, pure and applied, as well as in interdisciplinary fields or composite sciences that combine the philosophies of two or more disciplines. *Monthly*

International Journal for Radiation Physics and Chemistry

This journal provides a specialised medium of wide distribution for articles dealing with the physical and chemical effects of ionising radiation and closely related topics. The journal encourages the expression and discussion of different points of view and since publication is in English, French, German and Russian, the coverage and discussion is truly international. *Quarterly*

Soil Biology and Biochemistry

This new journal is intended to act as an organ of research on studies of soil organisms, their biochemical activities and their influence on the soil environment and plant growth. The scope of the journal is wide and embraces accounts of original research on the biology, ecology and biochemical activities of all forms of life that exist in the soil environment. *Quarterly*

Journal of Steroid Biochemistry

is international in scope and its articles on fundamental research make a notable contribution to experimental and theoretical knowledge. The papers cover a broad range of subjects in endocrinology ranging from mechanism of action of steroids at cellular and molecular levels to steroids in physiological and pathological conditions both in humans and animals. *Late 1969* *Quarterly*

Back Issues An extensive stock of back issues of all Pergamon Journals is available. For details please write for our back issues price list.

Discounts Available New Subscribers wishing to order *complete* runs of back issues can obtain these at a special 25% discount.

Up to Date Records The new 1970 price list and catalogue is available. If you have not received these please write to Dept. ED. Your request will be dealt with immediately.

Pergamon Press
Headington Hill Hall Oxford OX3 0BW England
Maxwell House Fairview Park Elmsford New York 10523 USA

Spectrochimica Acta

This international journal for the rapid communication of original work dealing with atomic and molecular spectroscopy is published in two parts.

PART A MOLECULAR SPECTROSCOPY

Editors Prof. Sir Harold Thompson St. John's College Oxford
Prof. M. Kent Wilson National Science Foundation Washington DC

This journal deals particularly with qualitative and quantitative analysis, the determination of molecular parameters and general theory. Also included are papers on nuclear magnetic resonance spectra, electron spin resonance spectra, optical rotary dispersion, and the design and performance of instruments and components.

Papers recently published include:
M. J. HITCH and S. D. ROSS The infra-red spectra of 1:3- and 1:4- dithian and pentamethylene sulphide
C. L. HONEYBOURNE and G. A. WEBB A spectroscopic study of some N:N′ disubstituted 1:3 di-imines
ULF BLINDHEIM and THOR GRAMSTAD Studies of hydrogen bonding-XX. Hydrogen bonding ability of phosphoryl compounds containing N-P and S-P bonds
R. T. BAILEY Infrared and laser Raman spectra of methyl-*cyclo*pentadienyl nickel nitrosyl
Published Monthly

PART B ATOMIC SPECTROSCOPY

Editors Dr. M. Margoshes Division of Block Eng. Maryland U.S.A.
Dr. K. Laqua Institut für Spektrochemie Dortmund Germany

Presents research papers on all regions of the electromagnetic spectrum, in so far as they have direct physicochemical interest. The main subjects include the determination of fundamental atomic data, new experimental procedures, and measurements or calculations of the properties of radiation sources or detectors.

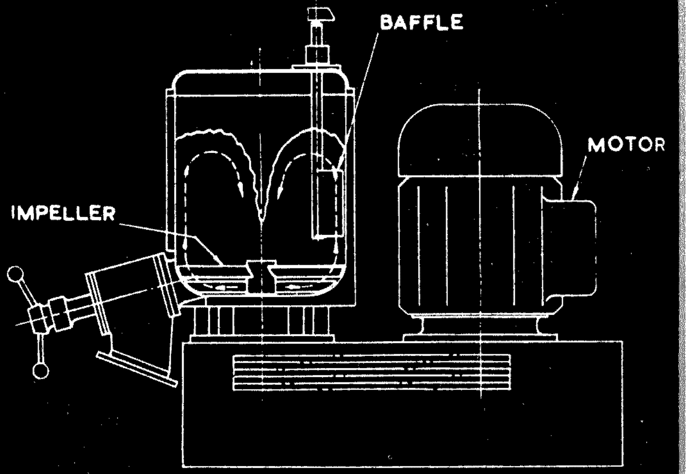
Papers recently published include:
H. JÄGER Temperaturmessungen an Mischplasmen im 30 Amp Gleichstrombogen
J. O. KARTTUNEN and W. R. HARMON Determination of uranium in ores and in solution using a portable non-dispersive X-ray spectrograph
A. CARNEVALE and A. J. LINCOLN A computer program to determine photographic emulsion calibration curves
E. E. PICKETT and S. R. KOIRTYOHANN The nitrous oxide-acetylene flame in emission analysis – III. Aluminum, gallium, indium, thallium, germanium, and tin

Write for full details and an inspection copy of either part of the journal.
Details of other journals in the field can also be sent to you.

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

1966

7/69


BAFFLE
MOTOR
IMPELLER

Talanta

An International Journal of Analytical Chemistry

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

Editor-in-Chief

Dr.R.A.Chalmers, Department of Chemistry, University of Aberdeen, Old Aberdeen, Scotland

Assistant Editors

Dr.D.Betteridge, University College, Swansea, Wales
Dr.J.R.Majer, University of Birmingham, England
Dr.I.L.Marr, University of Aberdeen, Scotland

Regional Editors

Professor I.P.Alimarin, Vernadsky Institute of Geochemistry and Analytical Chemistry, U.S.S.R. Academy of Sciences, Vorobievskoe Shosse 47a, Moscow V-334, U.S.S.R.
Professor E.Blasius, Institut für Analytische Chemie und Radiochemie der Universität des Saarlandes, 66 Saarbrücken 15, Bundesrepublik Deutschland
Mr.H.J.Francis, Jr., Pennsalt Chemicals Corporation, 900 First Avenue, King of Prussia, Pennsylvania 19406, U.S.A.
Professor J.S.Fritz, Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.
Dr.M.Pesez, Roussel-Uclaf, 102 et 111 route de Noisy, Romainville (Seine), France
Dr.R.Přibil, Laboratory of Analytical Chemistry, Polarographic Institute of J. Heyrovský, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia

Consulting Editors

Dr.M.Williams, Oxford, England
Professor C.L.Wilson, Belfast, N. Ireland

Editorial Board

Chairman: Mr.Robert Maxwell, *Chairman and Managing Director, Pergamon Press Ltd.*
Dr.R.A.Chalmers, *Editor-in-Chief*
Dr.M.Williams, *Consulting Editor*
Professor C.L.Wilson, *Consulting Editor*
Professor R.Belcher, *representing Advisory Board*
Dr.D.Betteridge, *Assistant Editor*
Dr.J.R.Majer, *Assistant Editor*
Mr.H.J.Francis, Jr., *representing Regional Editors*
Mr.G.F.Richards, *Director, Pergamon Press Ltd.*

Annual Subscription Rates (including postage)

Published monthly—1 volume per annum
\$10(£3.10)—For *bona fide* students, who place their orders with the publisher together with a note from their professor or tutor certifying their status
Private individuals whose departmental libraries subscribe, may obtain this Journal for their personal use at the reduced rate of \$15(£5.5) per annum
\$90(£36)—For libraries, government laboratories, research establishments, manufacturing houses and other multiple-reader institutions
Payments must be made in advance
Back numbers are available—write for Back Issues Price List

Publishing Offices

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

Copyright © 1969 Pergamon Press Ltd.

ห้องสมุด กรมวิทยาศาสตร์
11 2 พ.ค. 2513

Advisory Board

Aims and Scope

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

Allied Journals

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

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

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

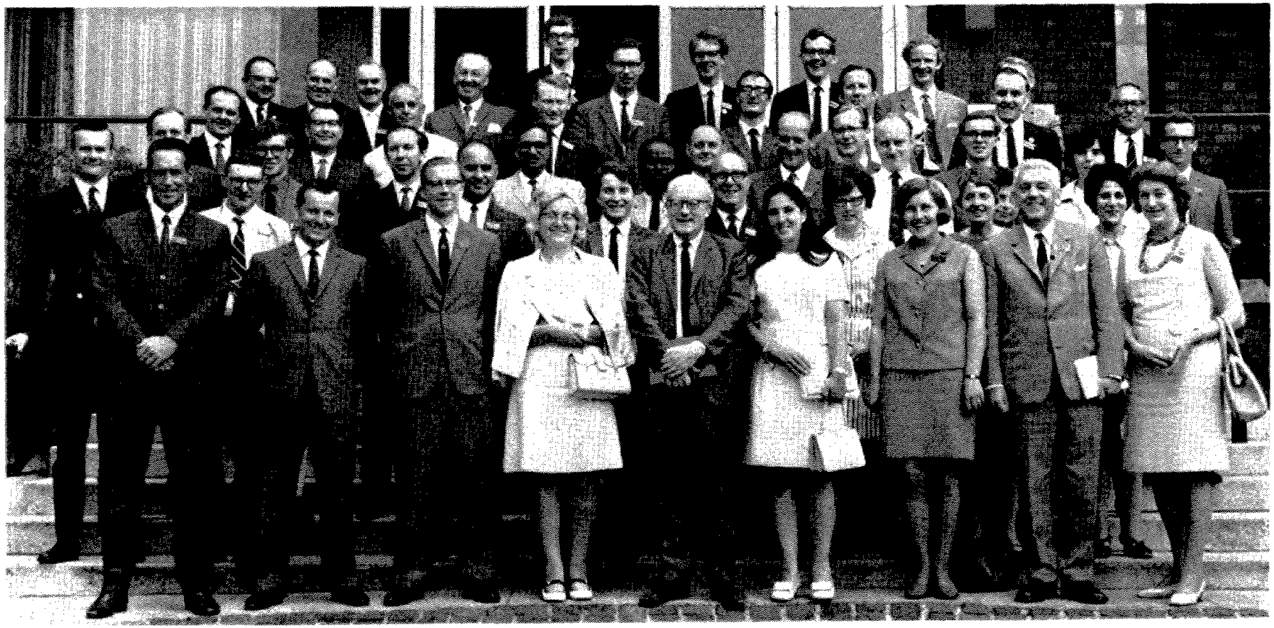
Presentation of

BELCHER HONOUR ISSUE
and
FIFTH TALANTA MEDAL

The presentations were made during the course of the International Symposium on Analytical Chemistry held at the University of Birmingham (UK) from 21st to 25th July 1969. Organized by the Midlands Section of the Society for Analytical Chemistry, under the patronage of the International Union of Pure and Applied Chemistry, the symposium coincided with the sixtieth birthday of Prof. R. Belcher. The scientific programme was planned to reflect his many interests in the analytical field.

◁ On behalf of the Editorial Board and Publisher of *Talanta*, Mr. G. F. RICHARDS (Pergamon Press) congratulates Prof. BELCHER (on right) after presenting him with a leather-bound copy of the Belcher Honour Issue (*Talanta*, 1969, **16,** July). All contributions to the Honour Issue were made by former and present members of the Birmingham School of Analytical Chemistry.

In his capacity as Chairman of the Advisory Board, Prof. BELCHER presents the Fifth Talanta Medal to Dr. A. WALSH (Australia). The Award was made for Dr. Walsh's contributions to the evolution of atomic absorption spectroscopy, which technique has revolutionized the scene in trace analysis. ▽



The Birmingham School of Analytical Chemistry
1948–1969

THE LOUIS GORDON MEMORIAL AWARD

The Editorial Board and the Publisher of TALANTA have great pleasure in announcing that the Louis Gordon Memorial Award for 1968, for the best-written paper published that year in TALANTA, has been made to Professor H. Flaschka and Dr. J. Garrett, for their two papers on 'Substoichiometric Masking', *Talanta*, 1968, **15**, 589, 595.

Talanta, 1969, Vol. 16, pp. 1341 to 1352. Pergamon Press. Printed in Northern Ireland

A MEMBRANE ELECTRODE FOR NITRATE AND OTHER UNIVALENT ANIONS

THOMAS N. DOBBELSTEIN and HARVEY DIEHL
Department of Chemistry, Iowa State University Ames, Iowa 50010, U.S.A.

(*Received* 24 *March* 1969. *Accepted* 22 *April* 1969)

Summary—A membrane electrode has been developed which is responsive to nitrate and other univalent anions but non-responsive to sulphate and other multivalent anions and to cations other than hydrogen. The membrane is prepared by polymerizing a mixture of phenol, formaldehyde, ammonia and nickel nitrate directly to a film for mounting in the usual cell-with-membrane assembly. Response to hydrogen ion is 0·30 mV per pH unit, to nitrate 0·60 mV per pNO_3 (activity) unit. Based on chemical composition and behaviour, physical properties, and electrical response, a structure and mechanism for exchange with hydrogen ion and nitrate ion and for internal electrical conduction has been postulated. Applications have been made to the determination of nitrate and to the detection of end-points.

THE recent reviews of Eisenmann[1] on glass electrodes, and of Rechnitz[2,3] on the general problem of membrane electrodes, make unnecessary at this time any detailed bibliographic treatment of a field which at the moment is burgeoning and gives promise of some of the most useful of all analytical tools developed in this quarter century. Mention must be made, however, of the work of the Minnesota biochemist Karl Sollner on collodion membranes, the Missouri soil chemist Marshall on clay membranes, and the Gulf Refining Corporation chemist Wyllie on polystyrene membranes impregnated with exchange resins, all of which appeared in the *Journal of Physical Chemistry* during the 1940's and 1950's. While it is true that none of their electrodes found adoption by working analysts, the papers of these men, together with a few other noteworthy individual contributions, represent a body of literature which present workers can ignore only unfairly, at the risk of missing ideas fundamental to the game and of reworking approaches already mined.

At this stage, the manufacture of an ion-specific electrode is still largely empirical but highly important because of the great boon it would be to have for each of the common ions an electrode as uniquely specific and as remarkably easy of operation as is the glass electrode for the hydrogen ion. Basically it appears that the problem of specificity is the old one of specificity of reagents in general plus the two new ones of providing exchange at the membrane surface and providing a pathway for the conduction of electricity through the body of the membrane. We record here our work with membranes impregnated with nickel dimethylglyoximate, to save others from wasting time on such a system, and on a nickel-bearing Bakelite membrane electrode which curiously does not respond to nickel but does to univalent anions.

Membranes impregnated with nickel dimethylglyoximate

Membranes of collodion, of epoxy polyester, and of phenol-formaldehyde, containing nickel dimethylglyoximate, proved unsatisfactory, either by giving no response or by having no selectivity toward nickel. The response to differences in the concentration of various cations in contact with the opposite sides of the collodion-nickel dimethylglyoximate membrane was the same as that of collodion alone. Epoxy membranes showed no response to a number of cations tested, but when impregnated with nickel dimethylglyoximate responded to nickel and to various other cations; further tests showed that almost any solid incorporated into the membrane produced the same effect and it was concluded that polymerization was probably incomplete and in some manner probably provided a pathway for the diffusion of ions through the membrane.

Phenol-formaldehyde (Bakelite) membranes, alone and when impregnated with nickel dimethylglyoximate, similarly proved inert to cations and anions. Because it was suspected that the nickel dimethylglyoximate was not uniformly dispersed through the resin, nickel 4,4′-dihydroxybenzildioximate was prepared and incorporated into the polymerizing mixture on the theory that the phenolic groups would participate in the polymer structure and provide a uniform matrix; the electrical resistance of this membrane was as high as that of the membrane prepared from resin alone (10^{11} ohm/mm^2) and also proved non-responsive. To give better dissolution of the nickel 4,4′-dihydroxybenzildioximate, the polymerizing mixture was made strongly alkaline with potassium hydroxide; the resulting membrane proved responsive to a number of cations and it was then shown that this was a consequence of the potassium added and that the nickel dioximate was immaterial. These experiments are not described in detail here and can be found in the M. S. thesis of T. N. Dobbelstein;[4] they led directly to a useful membrane, for experiments with a polymerizing mixture of phenol, formaldehyde, nickel nitrate and ammonia yielded a membrane non-responsive to nickel and other cations but responsive to univalent anions.

Membranes prepared by polymerizing phenol, formaldehyde, ammonia and nickel nitrate

The polymerization of phenol and formaldehyde takes place in three stages, forming successively: at 50–70° Bakelite A (a viscous liquid, soluble in ethanol and acetone); at 70–100° Bakelite B (an elastic solid, insoluble in water and ethanol); at 100–200° Bakelite C (a hard, brittle, very insoluble solid). The linkage between the aromatic rings of phenol-formaldehyde resins is generally considered to be methylene groups attached at the positions *ortho* and *para* to the hydroxyl group, the polymer chains being tied together by occasional cross-linkage. In addition, when ammonia is used to effect polymerization, some di(methylene)amine links are formed.

In this work, Bakelite A was first prepared under carefully controlled conditions; the Bakelite A was then dissolved in ethanol together with nickel nitrate and ethylene glycol and polymerized to Bakelite C so as to yield a film directly. The latter was then mounted so that solutions could be placed on opposite sides of it and the potential developed across the membrane measured. Surprisingly the phenol-formaldehyde resins incorporating ammonia and nickel nitrate did not respond to cations but did to univalent anions, particularly nitrate.

Preparation of Bakelite A. Temperature, ratio of phenol to formaldehyde, and time, each proved important in the preparation of a Bakelite A. At 60° the preliminary polymerization took too long, at 70° too much insoluble polymer formed; 65° proved best. In the procedure finally elaborated, a mixture of equal weights of phenol and 37% formaldehyde was held at 65° for 8 hr in a covered container and for 5 more hr with the cover removed; during these periods the mixture was stirred every 30 min. Additional formaldehyde, about 20% of that taken initially, was added, the vessel was covered and the mixture placed in an oven at 65° for 30 min with stirring every 10 min. The cover was then removed and the mixture heated at 65° with occasional stirring until a clear Bakelite A was obtained, about 3 hr.

Preparation of membrane. Bakelite A (approximately 1·7 g), nickel nitrate, ethylene glycol (serving as plasticizer), and some further formaldehyde were dissolved in 20 ml of ethanol. The mixture was stirred well and then poured as a thin layer into a Petri dish (100-mm diameter). The dish was placed in an oven at 65° and the solvent evaporated. The temperature of the oven was then raised 10°/hr to 130°, maintained at 130° for 12 hr (causing polymerization to Bakelite C), and then allowed to drop slowly to room temperature. The membrane was then soaked in water at 65° after which it was easily stripped from the dish.

Manner of testing membrane. A circular disc of the membrane was cut while still moist and mounted between two L-shaped flanged tubes held together by a spring clamp, Fig. 1. Reference solution (0·10M potassium nitrate) and test solution were placed in the arms of the cell, Beckman 39170 fibre-junction saturated calomel electrodes were inserted into the solutions, and the potential difference was measured with a Cary Model 31 vibrating reed electrometer. When the cells were not in use, the calomel electrodes were stored in water, the test solution was replaced by water, and the two arms of the cell were stoppered.

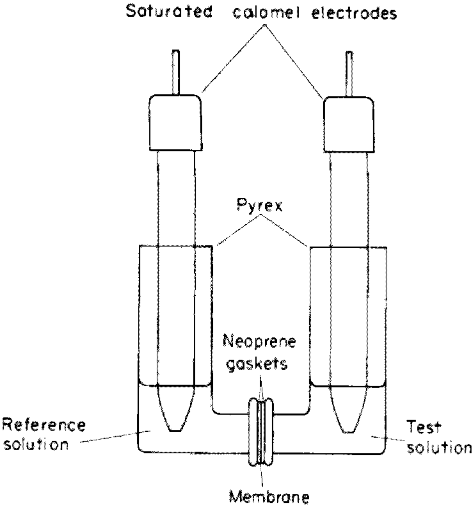


FIG. 1.—Cell for mounting membranes.

The physical character and the response of the membranes proved highly dependent on the nature and amount of base used to catalyse the polymerization, the nature of the phenol, the ratio of phenol to formaldehyde, the nature of the salt incorporated, the amount of salt (nickel nitrate was the best), the temperature of polymerization, and the time of polymerization.

Responsive membranes were not obtained from resins prepared by using strong acids or strong bases as catalysts but were obtained when ammonia was used. A minimum amount of ammonia was required but better resins were not obtained by using more than the minimum. The response of a membrane made by using methylamine in place of ammonia was good, but unsatisfactory membranes were obtained with ethylamine, isopropylamine, dimethylamine, trimethylamine, ethylenediamine and 2-aminoethanol.

Membranes were also prepared by using, in place of phenol, resorcinol, hydroquinone, *m*-cresol and 3,5-dimethylphenol. None of these membranes proved as satisfactory as that from phenol. The amount of nickel nitrate hexahydrate was varied over the range 10–25% by weight of the polymerization mixture; good response was obtained from the membranes containing from 16 to 22%, the response and physical characteristics above and below this being unsatisfactory. Incorporation of other ethanol-soluble metal nitrates, in amounts equivalent to the 16–22% of nickel nitrate replaced, gave varying results. The iron(III) and copper(II) nitrate membranes became opaque and black during the polymerization and the resulting membranes were extremely brittle and poor in response to nitrate. The aluminium, calcium, cobalt, hydrogen, and lithium nitrate membranes were also poor. With the exception of the cobalt nitrate membrane, the charge-to-size ratios of these cations are considerably different from that of the nickel ion. The cobalt nitrate membrane, after being conditioned by soaking for several days in 0·1*M* potassium nitrate, became approximately equivalent in response to the nickel nitrate membrane. The magnesium nitrate and zinc nitrate membranes were about equal to the nickel nitrate membrane in response but after several days no longer responded properly. The charge-to-size ratio here is again close to that of nickel but the long-range stability and the reproducibility in response made the nickel nitrate membrane superior.

The response of a membrane prepared with nickel perchlorate was as good as that with nickel nitrate. Precipitation occurred with nickel chloride and the response was poorer.

Properties of the phenol-formaldehyde-ammonia-nickel nitrate membrane. Membranes were prepared from the same Bakelite A, without nickel nitrate, and with 20% by weight of nickel nitrate hexahydrate, no ethylene glycol being added to either. After the usual conditioning by soaking in water, portions of the membranes were dried at 110° and analysed, Table 1.

The analyses indicate that about one amine group was present for every seven phenol groups in the parent resin. An internally consistent interpretation of the

TABLE I.—ELEMENTAL ANALYSIS OF PARENT AND NICKEL-BEARING MEMBRANES

Element	Found %	Atom ratio	Atom ratio	Atom ratio	Atom ratio
Phenol-formaldehyde-ammonia membrane					
			Per atom of nitrogen		
C	75·5$_8$	6·30	47·0		
H	5·9$_3$	5·88	43·8		
N	1·8$_7$	0·134	1·00		
O*	16·6$_2$	1·04	7·76		
Phenol-formaldehyde-ammonia-nickel nitrate membrane					
			Per atom of nickel	Per atom of nickel less $Ni(NO_3)_3$	Per atom of nickel (less $Ni(NO_3)_3$ per atom of nitrogen)
C	66·9$_0$	5·57	115	115	47·5
H	5·1$_4$	5·11	105	105	43·4
N	3·6$_9$	0·263	5·42	2·42	1·00
O*	21·4$_3$	1·34	27·6	18·6	7·69
Ni	2·8$_4$	0·0484	1·00	0·00	

* By difference.

data was obtained on the basis that the nickel atom was associated with three nitrate groups. Subtracting $Ni(NO_3)_3$ from the atom ratio leaves for the resin framework a ratio of C:H:N:O close to that of the parent resin (compare right-hand columns of the two parts of Table I). Apparently, the composition of the resin skeleton is not altered by the introduction of the nickel and there are about 2·4 amine groups per nickel atom. The phenol groups could be involved in the union with nickel as well as the amine groups, but apparently nitrato groups are co-ordinated to the nickel.

The amount of nickel and of nitrate removed from the membrane in the soaking operation was determined by measuring accurately the nickel nitrate hexahydrate added to the polymerization mixture, and the nickel and nitrate in the water used for the conditioning. The latter was recovered quantitatively and nickel and nitrate determined on aliquots. The nickel was determined by adding excess of standard EDTA, buffering at pH 7 with ammonium acetate and back-titrating with standard copper(II), using Calcein as indicator. Nitrate was determined by using the membrane which is the subject of this paper; aliquots were buffered at pH 2·1 with citric acid and the potential was measured and the concentration calculated from a calibration curve prepared from similar measurements made on serial dilution of a standard sodium nitrate solution. The results are given in Tables II and III.

TABLE II.—NICKEL REMOVED FROM PHENOL-FORMALDEHYDE-AMMONIA-NICKEL NITRATE MEMBRANE DURING CONDITIONING OPERATION

Nickel nitrate hexahydrate added, %*	*mmole*	Nickel removed, *mmole*	Nickel remaining, *mmole/*1·8 *g of membrane*
10	0·786	0·009	0·775
13	1·057	0·276	0·781
16	1·347	0·564	0·783
19	1·660	1·016	0·644
22	1·997	1·412	0·585
25	2·358	1·796	0·562

* Of polymerization mixture.

TABLE III.—NITRATE REMOVED FROM PHENOL-FORMALDEHYDE-AMMONIA-NICKEL NITRATE MEMBRANE DURING CONDITIONING OPERATION

Nickel nitrate hexahydrate added, %*	*mmole*	Nitrate removed, *mmole*	Nitrate remaining, *mmole*	Ratio of nitrate to nickel remaining
10	1·57	0·0692	1·50	1·94
13	2·11	0·158	1·96	2·51
16	2·70	1·00	1·70	2·18
19	3·32	2·04	1·28	1·99
22	4·00	2·82	1·18	2·02
25	4·72	3·55	1·17	2·08

* Of polymerization mixture.

In the best membranes, those prepared from starting mixtures containing 16–22% of nickel nitrate hexahydrate, it appears that two nitrate ions per nickel ion are left in the resin. This is not in agreement with the interpretation of the analytical data presented in Table I, which indicates that three nitrate ions per nickel ion remain.

The experiments were made on different batches of resin and this probably simply indicates the variation in composition from lot to lot, of water content and the effects of drying.

With 35 g of the membrane material ground to 60-mesh, column and batch experiments were conducted with 0·01*M* nickel nitrate; no detectable change was found in the concentration of nickel or of nitrate. Thus, the resin did not behave as a bulk ion-exchange material toward either nickel or nitrate.

The infrared spectra of the parent and nickel-bearing resins, obtained by using a Beckman IR8 instrument, indicated that secondary and tertiary amines were present and that in the nickel-bearing resin these groups are altered in some manner, presumably by co-ordination to nickel. A prominent band for nitrate was also present.

The resistance of the membranes was determined with a Keithley Model 601 electrometer; found: parent resin dried at 110°, $5{\cdot}7 \times 10^{11}$ ohm/mm^2; nickel-bearing resin dried at 110°, $1{\cdot}7 \times 10^{11}$ ohm/mm^2; parent resin membrane after soaking 12 hr in water at 65°, $3{\cdot}3 \times 10^{2}$ ohm/mm^2.

No bands were detected in the X-ray powder diffraction pattern of the parent resin. One band only was present in the pattern of the nickel-bearing resin, corresponding to a distance of 0·1887 nm. Examination under the polarizing microscope showed the nickel-free membrane to be non-birefringent. The membranes derived from polymerization mixtures containing 15–22% of nickel nitrate hexahydrate were uniformly birefringent over large areas; above and below these amounts, the material was amorphous with scattered areas of birefringence. Evidently the phenol-formaldehyde-ammonia-nickel nitrate resin is crystalline in character.

Response to hydrogen ion. Citric acid was titrated with 0·10*M* sodium hydroxide and both pH and the response of the phenol-formaldehyde-ammonia-nickel nitrate membrane were measured at each step in the titration, the pH being measured with a Beckman 40495 high alkalinity electrode. Solid potassium hydroxide was added to obtain pH above 12·5. The response of the membrane, Fig. 2, was linear over the pH range 4–11·5 with a response of 33 mV per pH unit. Above pH 12 the response was sharply reversed, Fig. 2.

Response to nitrate ion. The response to nitrate was determined on four serial dilutions of a standard sodium nitrate solution, each series buffered at a specific pH. The buffers were prepared from citric acid and disodium hydrogen phosphate, materials toward which it had been previously shown that the membrane showed no response.

The response of the membrane to nitrate was 60 mV per pNO$_3$ unit but in the opposite direction to the response to hydrogen ion, Fig. 3. The range of pNO$_3$ over which the membrane responded linearly was limited by the hydrogen ion concentration, being greater for higher hydrogen ion concentrations, Fig. 3.

Response to other anions. Serial dilutions of 1·00*M* solutions of sodium thiocyanate, sodium nitrate, sodium bromide, potassium chloride, sodium perchlorate, sodium dihydrogen phosphate, and potassium ferricyanide, and of 0·100*M* potassium sulphate were prepared and the response to each member of each series was determined, Fig. 4.

The membrane responded to the univalent anions but not to bivalent and tervalent anions, and with the exception of the hydrogen ion, the membrane did not respond to cations.

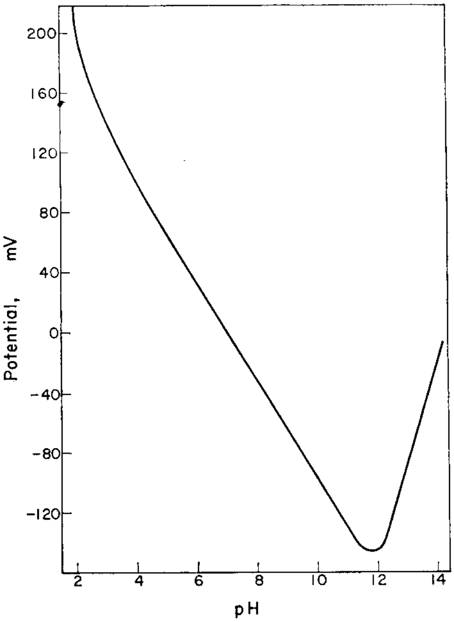


FIG. 2.—The potential of the phenol-formaldehyde-ammonia-nickel nitrate membrane as a function of pH.

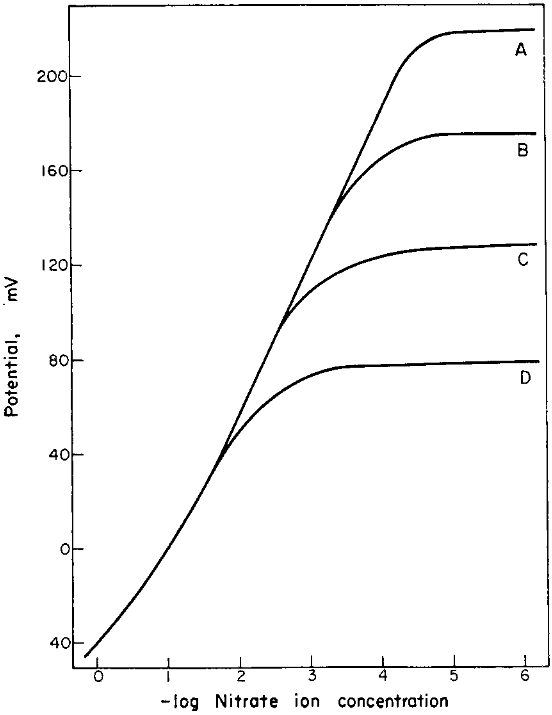


FIG. 3.—The effect of pH on the response of the phenolformaldehyde-ammonia-nickel nitrate membrane to nitrate.

A—pH 2·1	C—pH 4·0
B—pH 3·0	D—pH 5·1

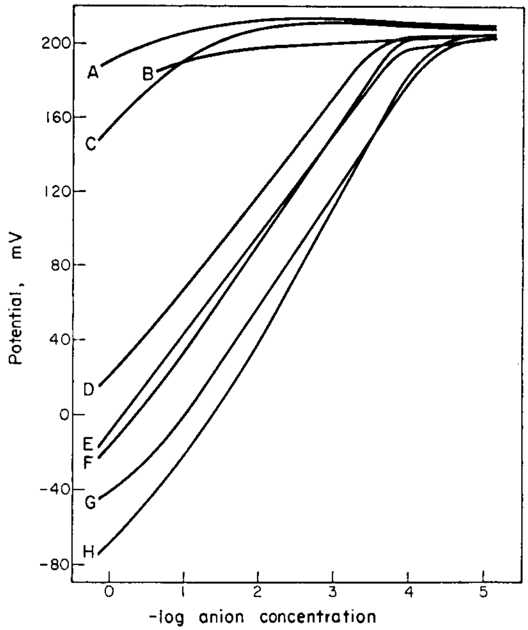


FIG. 4.—The response of the phenol-formaldehyde-ammonia-nickel nitrate membrane to various anions.

A—potassium ferricyanide, B—potassium sulphate,
C—sodium dihydrogen phosphate, D—sodium perchlorate,
E—potassium chloride, F—sodium bromide,
G—sodium nitrate, H—sodium thiocyanate

Stability of response. Various test solutions (10^0, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, $10^{-6}M$ potassium nitrate) were placed in one arm of the cell (Fig. 1) and the potential toward a reference solution of 0·100M potassium nitrate was measured, saturated potassium sulphate–mercury(I) sulphate reference electrodes being used. The measurements were made at intervals over a period of 10 hr; response was constant over this time and stirring of the solutions had no effect on the potential.

Response of membrane and activity. The potential developed across the membrane by solutions 1·00, 0·1000, 0·0100 . . . 1·00 × $10^{-5}M$ in sodium nitrate, each solution buffered at pH 2·1 with citric acid, was measured, Table IV. The activity of these solutions was calculated by using activity coefficients previously reported[5] and response *vs.* activity was plotted, Fig. 5.

Applications of the membrane. The first practical applications of the membrane were to problems which arose in the course of this very work, the determination of the nitrate removed from the first-formed membrane in the soaking operation, and again in showing that no appreciable nitrate was taken up by the resin by exchange with a surrounding solution of nickel nitrate, In application, the solution taken for analysis was buffered with citric acid to pH 2·1, diluted to a convenient volume, a portion placed in the cell, and the potential measured against a 0·0100M sodium nitrate reference solution. An appropriate calibration curve was prepared in like manner.

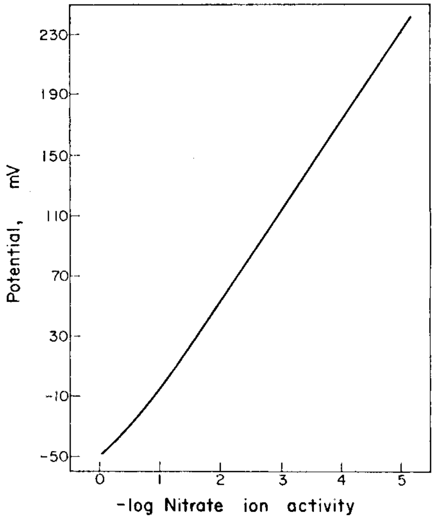


FIG. 5.—Potential response of the phenol-formaldehyde-ammonia-nickel nitrate membrane as a function of the activity of nitrate.

Use was made of the membrane to locate the end-point in the titrations of bromide, chloride, and thiocyanate with silver sulphate. A sharp and reproducible change in potential was obtained in each titration. The titration curve obtained in one titration of potassium chloride with silver sulphate is shown in Fig. 6. The change in potential at the end-point was about 120 mV, a very satisfactory value which provided great precision. During the titration, a film of silver chloride formed on the surface of the membrane and the membrane responded to the silver ion beyond the end-point in the same manner that a silver chloride-impregnated membrane responds to the anion or cation in common with the precipitate anion or cation;[6] the potential was greater than expected or experienced when no film of silver salt was formed.

A potentiometric titration of nitrate with nitron, a precipitating agent for nitrate, was attempted, but the nitron nitrate proved too soluble and a sharp change in potential at the end-point was not obtained.

TABLE IV.—COMPARISON OF RESPONSE OF THE PHENOL-FORMALDEHYDE-AMMONIA-NICKEL NITRATE MEMBRANE TO NITRATE ION WITH KNOWN ACTIVITY OF NITRATE ION

Concentration of test solution, $NaNO_3$, *M*	Potential response *mV*	Change in response per 10-fold change in concentration	Activity coefficient[4]	Activity of test solution	Change in response per 10-fold change in activity *mV*
1·00	−41·1		0·55	$5·5 \times 10^{-1}$	
$1·00 \times 10^{-1}$	−0·1	41·0	0·77	$7·7 \times 10^{-2}$	43·0
$1·00 \times 10^{-2}$	55·5	55·6	0·90	$9·0 \times 10^{-3}$	60·0
$1·00 \times 10^{-3}$	115	59·5	0·97	$9·7 \times 10^{-4}$	60·0
$1·00 \times 10^{-4}$	175	60·0	1·00	$1·0 \times 10^{-4}$	60·0
$1·00 \times 10^{-5}$	234	59·9	1·00	$1·0 \times 10^{-5}$	59·0

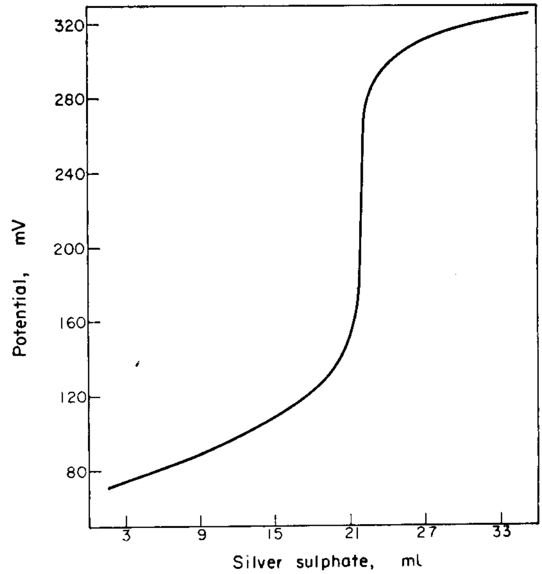


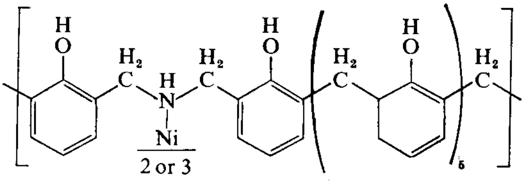
FIG. 6.—Potentiometric titration of chloride with silver, using the phenol-formaldehyde-ammonia-nickel nitrate membrane as an indicator electrode.

DISCUSSION

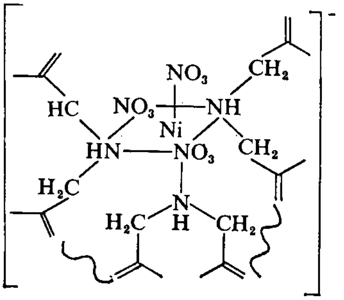
Currently, the behaviour of ion-specific electrodes is explained on the basis of ion-exchange between membrane and solution occurring at the surface, plus some mechanism for the conduction of electricity, however minute, through the bulk of the membrane. Utilizing this explanation, we attempt an interpretation of the observations recorded above on the phenol-formaldehyde-ammonia-nickel nitrate membrane.

Basic, of course, are the observations that the membrane responds to anions and not to cations other than hydrogen, and that it responds to nitrate and other univalent anions but not to bivalent or tervalent anions. Basic also are the observations that the response to hydrogen ion is in the opposite direction to that to nitrate and only half as great, *i.e.*, 30 mV per pH unit in contrast to 60 mV per pNO_3 unit.

The presence of nickel and of amino nitrogen are essential and nitrate groups are present. The ammonia nitrogen is present as secondary and tertiary amino groups and there is one such nitrogen atom for every seven or so aromatic rings. For each nickel atom between two and three amino groups are present and close to three nitrate groups. We conceive thus for the polymer skeleton with random cross-linking by attachment of methylene groups at the *para*-positions and to the amine nitrogen (making it tertiary) and with a six-covalent structure about the nickel



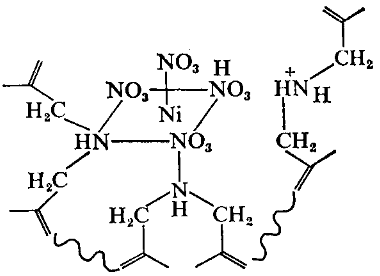
atom, with each nickel unit carrying a negative charge:



Because the response to hydrogen ion is in the opposite direction (and the hydrogen ion of opposite charge) to that to nitrate and only half as great, we postulate for the basic reaction

$$[R] + NO_3^- + 2H^+ = [R^{H}_{HNO_3}]$$

and picture the mechanism as the displacement of an amino group from the co-ordination sphere of the nickel atom by the formation of the ammonium ion and the addition of a molecule of nitric acid, the nitrato group entering the open position and the positive charge on the hydrogen ion offsetting the negative charge on the nickel site:



This hypothesis also provides an explanation for the change in response of the membrane to nitrate with pH, Fig. 3; the fraction of amino groups in the ammonium form will increase with decreasing pH, leaving open more positions about the nickel atoms for attachment of the nitric acid. Another way of looking at this is as a competition for the site on the nickel atom between nitrato group and amine. A unique aspect is that this is an exchange reaction with one participant in the exchange a permanent constituent of the exchanging body itself.

The structure postulated leaves a hydrogen ion in the matrix, essentially free to move from one negatively charged nickel site to another and thus provides an electrolytic process for the conduction of electricity through the body of the membrane.

That the nickel-free phenol-formaldehyde-ammonia-nickel nitrate membrane is crystalline, as judged by X-ray powder pattern and birefringence, must be of significance although no physical relation between crystallinity and potential response is immediately obvious. The crystallinity does ensure a uniform distribution of the nickel sites through the matrix and ensures that electrical conduction is not a mere accident. It can be hardly accidental, too, that only over the range of 15–22% of nickel nitrate hexahydrate in the polymerizing mixture is a uniformly crystalline material obtained and only over this range a responsive membrane prepared.

The response of the membrane to sodium nitrate was linear over the pNO_3 range 1–5 with a slight curvature upwards between pNO_3 0 and 1, Fig. 6. As an analytical tool, the membrane is, of course, used in conjunction with a calibration curve but it is apparent that it, like other membrane electrodes, measures activity rather than concentration.

The response of this membrane to the activity of the nitrate ion, is excellent with respect to rapidity, stability, reproducibility and theoretical response. That it does not differentiate nitrate from other univalent anions is perhaps unfortunate but that it does differentiate nitrate from sulphate, phosphate and other multivalent anions should prove useful.

Acknowledgement—The authors express their appreciation to the College of Science and Humanities of the Iowa State University for funds for the purchase of the apparatus used in this work. Dr. Dobbelstein expresses his appreciation to the University for the graduate teaching assistantship held while the work was in progress.

Zusammenfassung—Eine Membranelektrode wurde entwickelt, die auf Nitrat und andere einwertige Anionen anspricht, nicht jedoch auf Sulfat und andere mehrwetige Anionen und auf Kationen außer Wasserstoffionen. Die Elektrode wird folgendermaßen hergestellt: man polymerisiert ein Gemisch von Phenol, Formaldehyd, Ammoniak und Nickelnitrat direkt zu einem Film und bringt diesen in der üblichen Zelle an. Wasserstoffionen geben 0,30 mV pro pH-Einheit, Nitrat 0,60 mV pro pNO_3-Einheit (Aktivität). Auf Grund der chemischen Zusammensetzung und des Verhaltens, der physikalischen Eigenschaften und des elektrischen Ansprechens wird eine Struktur aufgestellt und ein Mechanismus für den Austausch mit Wasserstoff und Nitrationen sowie für den Elektrizitätstransport im Innern postuliert. Angewandt wurde die Elektrode zur Bestimmung von Nitrat und zu Endpunktsanzeigen.

Résumé—On a élaboré une électrode à membrane qui est sensible au nitrate et autres anions monovalents mais ne répond pas au sulfate et autres anions plurivalents et aux cations autres que l'hydrogène. On prépare la membrane en polymérisant un mélange de phénol, formaldéhyde, ammoniaque et nitrate de nickel directement en un film pour montage dans l'assemblage usuel cellule avec membrane. La réponse à l'ion hydrogène est de 0,30 mV par unité pH, au nitrate 0,60 mV par unité pNO_3 (activité). En se basant sur la composition et le comportement chimiques, les propriétés physiques et la réponse électrique, on a admis une structure et un méchanisme pour l'échange avec l'ion hydrogène et l'ion nitrate et pour la conduction électrique interne. Des applications ont été faites à la détermination du nitrate et à la détection de points de fin de dosage.

REFERENCES

1. G. Eisenmann, *Biophysic. J.*, 1962, **2**, 259.
2. G. A. Rechnitz, *Chem. Eng. News*, 1967, **45**, No. 25, 146.
3. *Idem*, *Anal. Chem.*, 1965, **37**, No. 1, 29A.
4. T. N. Dobbelstein, *M.S. Thesis*, Iowa State University, 1966.
5. W. M. Latimer, *The Oxidation States of the Elements*, 2nd Ed., Prentice-Hall, New York, 1952.
6. E. Pungor, J. Havas and K. Tóth, *Acta Chim. Acad. Sci. Hung.*, 1964, **41**, 239.

Talanta, 1969, Vol. 16, pp. 1353 to 1360. Pergamon Press. Printed in Northern Ireland

UNTERSUCHUNGEN ZUR OPTIMIERUNG DER REAKTIONSBEDINGUNGEN FÜR DIE KATALYTISCHE JODWIRKUNG AUF DAS SYSTEM CE(IV)-ARSENIGE SÄURE (EINE MODIFIZIERTE SANDELL-KOLTHOFF-REAKTION)*

GÜNTER KNAPP und HANS SPITZY
Institut für Allgemeine Chemie, Mikro- und Radiochemie
Technische Hochschule Graz, Österreich

(*Eingegangen am* 6. *März* 1969. *Angenommen am* 24. *April* 1969)

Zusammenfassung—Auf Grund neuerer Anschauungen (Deman 1964) über den Reaktionsmechanismus der Sandell-Kolthoff-Reaktion wird der Einfluß verschiedener Säuren variierender Konzentration auf die durch Jod katalysierte Redoxreaktion 2Ce(IV) + As(III) → 2Ce(III) + As(V) untersucht. Danach steigt die katalytische Aktivität des Jods in salpetersauren Reaktionsgemischen auf das 20-fache gegenüber jener in den herkömmlichen schwefelsauren Medien. Als Vorteil ergeben sich wesentlich kürzere Reaktionszeiten. Weiters erweist sich die katalytische Reaktion in Salpetersäure gegenüber Fremdionen als weitgehend unempfindlich, wodurch ihre besondere Eignung zur Bestimmung von Jodspuren gegeben ist.

DIE katalytische Wirkung von Jod auf das Redoxsystem $2Ce^{4+} + As^{3+} \rightarrow 2Ce^{3+} + As^{5+}$ wurde erstmals von Sandell und Kolthoff[1] zur quantitativen Bestimmung von Jodspuren herangezogen. Diese Reaktion steht heute in der Jodspurenanalytik an erster Stelle. Trotz der großen Zahl von Veröffentlichungen auf diesem Gebiet waren bisher nur wenige Autoren um die Aufklärung des Reaktionsmechanismus bemüht. Feigl[2] beschrieb einen Reaktionsablauf, der später von Kontaxis und Pickering[3] näher untersucht wurde:

$$Ce^{4+} + J^- \rightarrow Ce^{3+} + \tfrac{1}{2}J_2 \qquad (1)$$

$$J_2 + As^{3+} \rightarrow 2J^- + As^{5+} \qquad (2)$$

Deman[4] vertritt eine ganz andere Anschauung über den Ablauf der Katalysereaktion:

$$J_2 + 2Ce^{4+} \rightarrow 2J^+ + 2Ce^{3+} \quad \text{geschwindigkeitsbest.} \qquad (3)$$

$$2J^+ + As^{3+} \rightarrow J_2 + As^{5+} \quad \text{schnell} \qquad (4)$$

Das sehr instabile J^+ reagiert unter anderem mit H_2O

$$J^+ + H_2O \rightleftharpoons HJO + H^+ \qquad (5)$$

Nach Gleichung (5) ist das Gleichgewicht mit steigender Acidität des Reaktionsgemisches weitgehend auf die Seite des katalytisch aktiven J^+ verschoben. Folglich kann für den Reaktionsablauf der pH-Wert des Reaktionsgemisches nicht ohne Bedeutung sein.

---

* Diese Arbeit wurde in Verbindung mit dem Forschungskontrakt Nr. 384/RB der International Atomic Energy Agency, Wien, ausgeführt.

Seit Sandell und Kolthoff[1] wird die katalytische Jodbestimmung durchwegs in schwefelsaurem Reaktionsmedium ausgeführt. Strickland und Maloney[5] sowie Štolc[6] untersuchten den Einfluß der Schwefelsäurekonzentration des Reaktionsgemisches auf die Empfindlichkeit der Katalysereaktion. Danach nimmt die Empfindlichkeit bei Steigerung der Schwefelsäurekonzentration von 0,5m auf 2,5m ungefähr um den Faktor 1,5 zu, sinkt jedoch bei noch höheren Schwefelsäurekonzentrationen wieder ab. Dieses Verhalten dürfte auf zwei Faktoren mit entgegengesetzter Wirkung zurückzuführen sein. Einerseits ist die steigende Protonenaktivität im Sinne der Gleichung (5) empfindlichkeitssteigernd, andererseits macht sich aber durch die erhöhte Sulfatkonzentration eine störende Komplexbildung mit dem Cer(IV) bemerkbar.[7] Daher wurden in der vorliegenden Arbeit zum Ansäuern des Reaktionsgemisches nur Säuren verwendet, deren Anionen weniger zur Komplexbildung mit Cer(IV) neigen. Untersuchungen in dieser Richtung sind nicht bekannt. Lediglich eine Arbeit von Hoch, Sinnett und McGavack[8] beschäftigt sich mit dem Einfluß von Perchlorsäure auf die Katalysereaktion in schwefelsaurer Lösung.

Für die nachstehenden Untersuchungen wurden Salpetersäure und Perchlorsäure ausgewählt; Salzsäure schied wegen der katalytischen Wirkung größerer Chloridmengen aus. Um den Einfluß der zu untersuchenden Säuren nicht durch die Wirkung der Schwefelsäure zu überdecken betrug der Schwefelsäuregehalt der Reaktionsgemische nur etwa 0,03 m. Diese geringe Schwefelsäuremenge wird zur Bereitung der verwendeten Ce(IV)-Lösung benötigt, um das Cer in Lösung zu halten. Salpetersaure bzw. perchlorsaure Cer(IV)-Lösungen wurden wegen ihrer geringen Stabilität nicht verwendet.

EXPERIMENTELLER TEIL

Geräte

Reaktionsgefäße: Eprouvetten 17 × 70 mm mit Schliffstopfen.

Reagenzien

Cer(IV)-Lösung. $Ce(SO_4)_2.4H_2O$ (6g) wird in 100 ml bidest. Wasser und 10 ml konzentrierter Schwefelsäure gelöst. Anschließend wird mit bidest. Wasser auf 500 ml aufgefüllt.

As(III)-Lösung. As_2O_3 (4g) wird in 50 ml 1m KOH gelöst, 2 ml konzentrierte Schwefelsäure sowie 2g NaCl zugegben und mit bidest. Wasser auf 500 ml aufgefüllt.

Jodid-Stammlösung. Natriumjodid, bei 120° getrocknet, (118·1 mg) wird mit bidest. Wasser in 1000 ml gelöst. Diese Lösung enthält 100 μg J/ml und wird nach Bedarf weiter verdünnt. Kühl und in dunkler Flasche aufbewahren.

Jodid-Gebrauchslösung. Stammlösung (1 ml) wird mit bidest. Wasser auf 1000 ml aufgefüllt.

Bidestilliertes Wasser. Destilliertes Wasser wird in einer Quarzapparatur über Kaliumkarbonat destilliert.

Untersuchungen zum Einfluß verschiedener Säuren variierender Konzentration

In das Reaktionskölbchen werden 0–1 ml Jodidlösung (0–100 ng J^-), 0,4 ml As(III)-Lösung und 0–2 ml HNO_3 (65%) bzw. $HClO_4$ (60%) pipettiert und mit bidest. Wasser jeweils auf 6 ml aufgefüllt. Das Kölbchen wird verschlossen in ein auf 35° thermostatisiertes Wasserbad gestellt. Nach 15 Min Temperaturangleich wird das Kölbchen dem Wasserbad entnommen, 0,5 ml Cer(IV)-Lösung zugegeben und nach Umschütteln ns Wasserbad zurückgestellt. Nach 15 Min erfolgt die photometrische Messung der verbliebenen Cer(IV)-Konzentration in einer 20-mm Küvette bei 420 nm. Der Logarithmus der Extinktion wird gegen die Jodkonzentration aufgetragen.

Untersuchung des Fremdioneneinflusses

In das Reaktionskölbchen werden 0,2 ml Jodidlösung (20 ng J^-), 0,4 ml As(III)-Lösung, 1,3 ml HNO_3 (65%) und Lösungen der entsprechenden Fremdionen pipettiert. Anschließend wird mit bidest. Wasser auf 6 ml aufgefüllt und in der vorhin beschriebenen Weise ausgemessen.

ERGEBNISSE UND DISKUSSION

Einfluß verschiedener Säuren auf die Jodkatalyse

Untersucht wurde der Einfluß von Salpetersäure bzw. Perchlorsäure auf die Jodkatalysewirkung in einem an Schwefelsäure 0,03m Reaktionsmedium.

Bei Zugabe steigender Jodmengen wird nach festgesetzter Reaktionszeit die Cer(IV)-ionenkonzentration photometrisch gemessen; der Logarithmus der Extinktion wird gegen die Jodkonzentration aufgetragen, wodurch Geraden resultieren. Danach nimmt die der Eichgeradensteigung proportionale Empfindlichkeit der Reaktion d.h. die katalytische Wirkung des Jods auf die Redoxreaktion mit steigender Salpetersäurekonzentration zu.

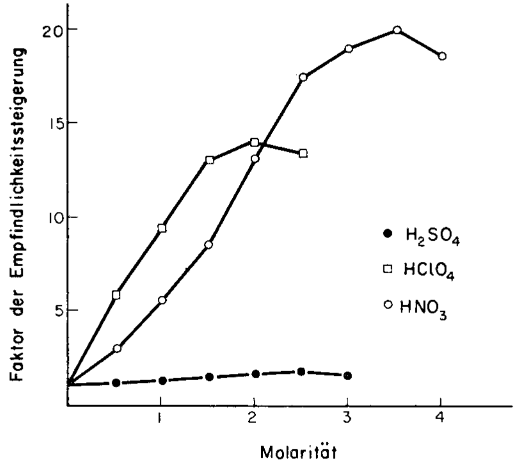


ABB. 1.—Abhängigkeit der Empfindlichkeit der Jodkatalyse von der Acidität des Reaktionsgemisches bei Verwendung verschiedener Säuren.

Die Empfindlichkeit der Jodbestimmung nach dieser katalytischen Methode läßt sich mathematisch erfassen. Da die Reaktion formal erster Ordnung abläuft, gilt nachstehende Beziehung:

$$-\frac{d[Ce^{4+}]_t}{dt} = k[Ce^{4+}]_t \, . \, [J] \tag{6}$$

Daraus erhält man

$$\ln\,[Ce^{4+}]_t = \ln\,[Ce^{4+}]_{t=0} - k\,.\,t\,.\,[J] \tag{7}$$

$$[J] = \frac{\ln\,[Ce^{4+}]_{t=0} - \ln\,[Ce^{4+}]_t}{k\,.\,t} = \frac{\Delta\ln\,[Ce^{4+}]}{k\,.\,t} \tag{8}$$

Aus Gleichung (8) sind jene Parameter zu entnehmen, die es gestatten, die Nachweisgrenze für Jod herabzusetzen bzw. die Empfindlichkeit zu steigern. Diese wächst mit steigendem Wert der Reaktionskonstanten (k) und zunehmender Reaktionszeit (t). Wie gezeigt bewirkt die Verwendung von Salpetersäure eine Steigerung des Wertes der Reaktionskonstanten (k). Die Steigung der Eichgeraden (ln $[Ce^{4+}]$ gegen [J]) ist daher ein Maß für die Empfindlichkeit, da sie der Reaktionskonstanten (k) bzw. der Reaktionszeit (t) proportional ist [Gleichung (7)].

Der Einfluß steigender Säurekonzentrationen auf die Zunahme der katalytischen Aktivität des Jods ist in Abb. 1 für Schwefelsäure, Perchlorsäure und Salpetersäure vergleichend dargestellt. Das Empfindlichkeitsmaximum liegt für alle drei Säuren im Bereich zwischen 2 und 3,5 m. In perchlorsaurer Lösung wird eine Empfindlichkeitssteigerung auf das 15-fache erreicht, in salpetersaurer Lösung sogar auf das 20-fache. In schwefelsaurer Lösung hingegen ist nur eine sehr geringe Abhängigkeit der Empfindlichkeit von der Schwefelsäurekonzentration festzustellen.[5,6]

Die wesentlich höhere Empfindlichkeit der Katalysereaktion in salpetersaurer Lösung läßt sich in zweierlei Hinsicht nützen. Man kann unter Beibehalten der Reaktionszeit von 15 Min Jodkonzentrationen im Zehntel-Nanogrammbereich, also um 1 Zehnerpotenz unter der bisher erfaßbaren Menge bestimmen (Abb. 2).

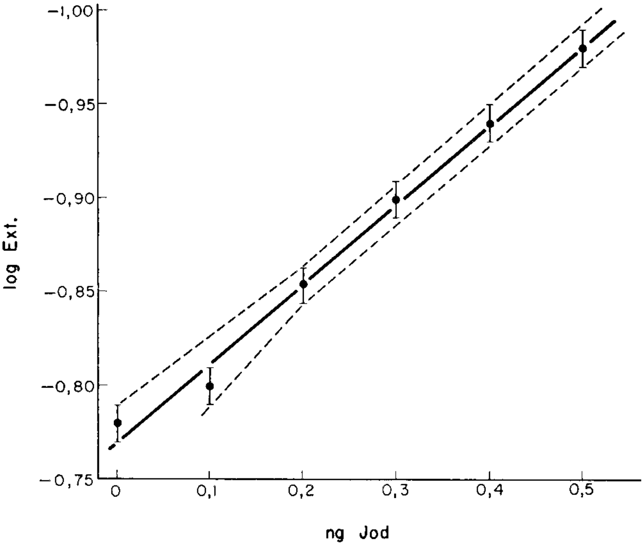


ABB. 2.—Eichgerade zur Bestimmung von Jodspuren im Zehntel-ng-Bereich (max. Fehlerbreite eingetragen).
Reaktionstemp.: 37°C
Reaktionszeit: 15 Min

Weiters sind für Jodbestimmungen im Nanogrammbereich wesentlich kürzere Reaktionszeiten möglich als in schwefelsaurer Lösung.

Einfluß von Fremdionen auf die Jodkatalyse in salpetersaurer Lösung

Um die Brauchbarkeit dieser modifizierten Sandell-Kolthoff Reaktion für die Praxis zu prüfen, wurde der Einfluß von Fremdionen untersucht. In folgender Tabelle I sind die zugesetzten Ionen und ihr Einfluß auf das Reaktionsgeschehen angeführt.

Unterscheidet man die Fremdionen nach Art ihres Einflusses auf die Reaktion so ist eine Einteilung in drei Gruppen möglich. Abbildung 3 zeigt die Änderung der Lage einer Eichgeraden, wenn störende Ionen einer dieser drei Gruppen vorhanden sind.

Zur ersten Gruppe gehören Elemente, die selbst katalytisch wirken (Cl, Br, Os, Ir). Durch ihren Einfluß wird die Eichgerade parallel zu höheren Werten verschoben.

Ionen der zweiten Gruppe sind z.B. Ag^+, Hg^+ und CN^-, die mit dem Katalysator Jod undissoziierte Verbindungen bilden. Die gestörte Eichgerade, die unter Einfluß dieser Ionen meist nicht mehr linear verläuft, geht zwar durch den O-Punkt der ursprünglichen Eichgeraden, weist aber eine geringere Steigung auf.

Tabelle I.—Einfluß von Fremdionen

Untersuchte Ionen	Maximaler Fremdionenzusatz, *µg* bzw. *mg/ml* Reaktionsgemisch	Wirkung auf die Jodkatalysereaktion, ab
Na^+	20 mg	keine
K^+	20 mg	keine
Ca^{2+}	10 mg	keine
Mg^{2+}	10 mg	keine
Zn^{2+}	1 mg	keine
Cu^{2+}	1 mg	keine
Fe^{3+}	1 mg	Hemmung ab 40 µg
Ag^+	1 µg	Hemmung ab 0,04 µg
Hg^+	0,02 µg	Hemmung ab 0,1 ng
F^-	10 µg	Hemmung ab 1 µg
Cl^-	6 mg	kat. Wirk. ab 100 µg
Br^-	0,6 mg	kat. Wirk. ab 10 µg
SO_4^{2-}	4 mg	Hemmung ab 0,4 mg
PO_4^{3-}	3,5 mg	Hemmung ab 0,3 mg
CH_3COO^-	200 mg	Hemmung ab 20 mg
CN^-	1 mg	Hemmung ab 20 µg

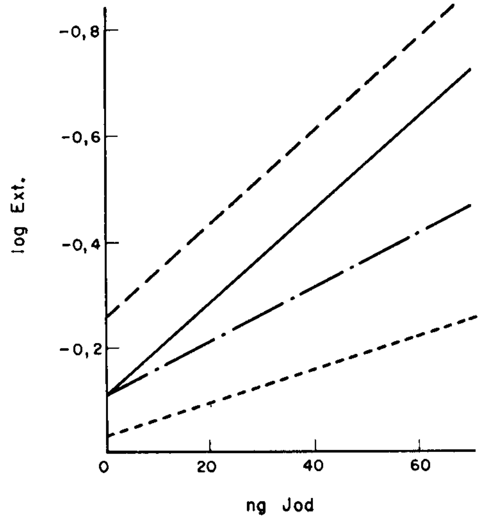


Abb. 3.—Eichgeraden für Jod bei Einfluß störender Fremdionen.

——— Eichgerade ohne störenden Einfluß

– – – – Einfluß katalytisch wirkender Fremdionen (z.B.: Cl^-, Br^-).

– · – · Einfluß von Fredionen, die mit Jod wenig dissoziierte Verbindungen bilden (z.B.: CN^-, Ag^+, Hg^+).

· · · · · Einfluß von Fremdionen, die mit einer Komponente des Redoxsystems Cer(IV)-arsenige Säure in Wechselwirkung treten (z.B. F^-, SO_4^{2-}, PO_4^{3-}).

Zur dritten Gruppe gehören schließlich Ionen wie F^-, SO_4^{2-} oder PO_4^{3-}. Sie hemmen die Reaktion, indem sie nicht mit dem Katalysator sondern mit einer anderen Komponente des Redoxsystems in Wechselwirkung treten. Sulfat z.B. bildet mit Cer(IV) recht beständige Komplexe.[7] Die gehemmte Eichgerade hat eine geringere Steigung als die ungehemmte und geht durch einen O-Punkt, der auf der Ordinate tiefer liegt als der ursprüngliche, da auch die Reaktion ohne Jodzusatz gehemmt wird.

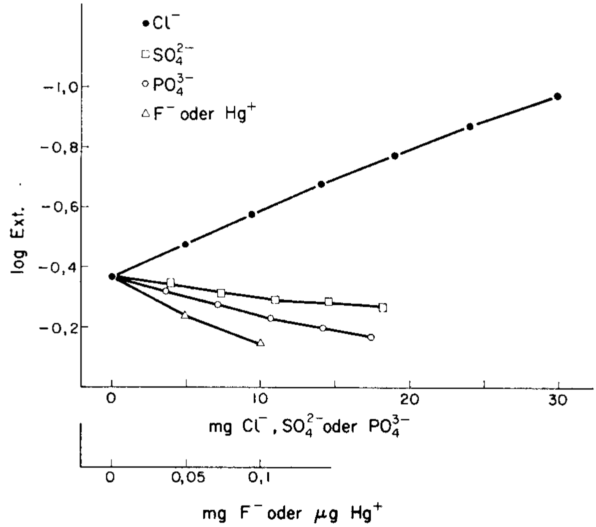


ABB. 4.—Einfluß von Chlorid, Sulfat, Phosphat, Fluorid oder Quecksilber auf Jodkatalysereaktionen (vorgelegte Jodmenge 20 ng).

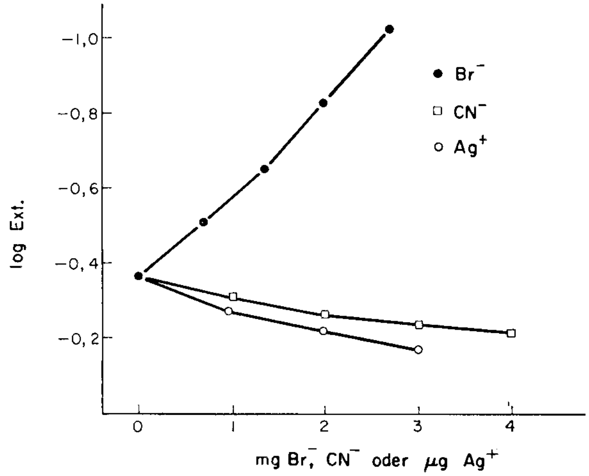


ABB. 5.—Einfluß von Bromid, Cyanid oder Silber auf Jodkatalysereaktionen (vorgelegte Jodmenge 20 ng).

In den Abb. 4 und 5 ist der Einfluß einiger Ionen auf die katalytische Wirkung des Jods in salpetersaurer Lösung in Abhängigkeit von der zugesetzten Menge wiedergegeben.

Die Redoxreaktion Cer(IV)-arsenige Säure wird nicht nur von Jod, sondern unter anderem auch von Osmium katalysiert. Die Jodbestimmung mit der herkömmlichen Sandell-Kolthoff-Reaktion in schwefelsaurem Medium liefert unter dem Einfluß geringster Osmiumspuren völlig falsche Ergebnisse, da die katalytische Aktivität des Osmiums die des Jods um etwa den Faktor 6 übertrifft. Die Verhältnisse in salpetersaurer Lösung liegen gerade umgekehrt. Die katalytische Aktivität des Osmiums nimmt nur geringfügig zu, während die des Jods auf das 20-fache steigt. Abbildung 6 zeigt Eichgeraden von Jod bzw. Osmium in schwefelsaurem bzw. salpetersaurem Reaktionsgemisch. Temperatur und Reaktionszeit sind identisch, so daß direkte Vergleiche angestellt werden können.

Zusammenfassend kann über den Fremdioneneinfluß auf die modifizierte Sandell-Kolthoff-Reaktion gesagt werden: Vergleicht man die hier angestellten Untersuchungen mit ähnlichen Arbeiten über Fremdioneneinflüsse auf die klassische Katalysereaktion, wie sie z.B. von Sandell und Kolthoff[1] oder Štolc[6] durchgeführt wurden, so ergeben sich einige wesentliche Unterschiede. Der Einfluß von Kationen auf die Jodkatalysewirkung in salpetersaurer Lösung ist im allgemeinen wesentlich schwächer. Selbst Kationen wie Ag^+ und Hg^+ hemmen das modifizierte System bei weitem weniger als die klassische Ausführungsform. Andererseits werden aber die Halogene Chlor und Brom ähnlich dem Jod in ihrer katalytischen Aktivität durch Salpetersäure stark erhöht und beeinflussen daher diese Reaktion wesentlich stärker als dies in schwefelsaurer Lösung der Fall ist.

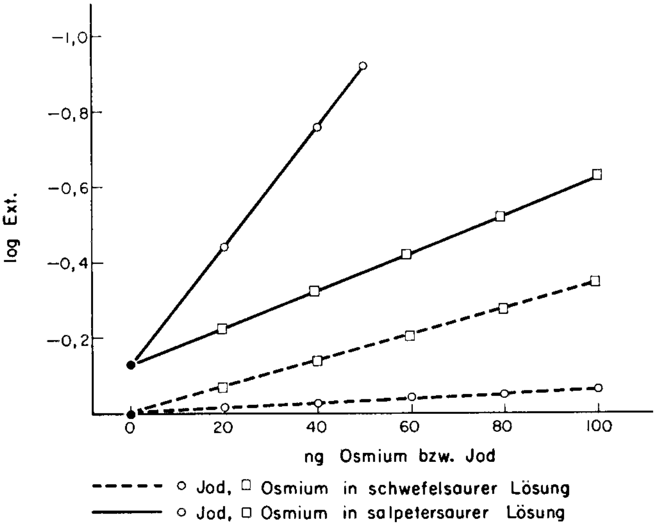


Abb. 6.—Katalytische Wirkung von Jod bzw. Osmium auf das schwefelsaure bzw. salpetersaure Katalysesystem.
Reaktionstemp.: 35°C
Reaktionszeit: 2 Min.

Betrachtet man die Ursachen der Empfindlichkeitssteigerung im salpetersauren System, so dürften 2 Faktoren maßgeblich daran beteiligt sein. Erstens bewirkt eine hier vermiedene hohe Sulfationenkonzentration Hemmung der Jodkatalysewirkung (Abb. 4), die wahrscheinlich auf der Bildung von Cer(IV)-sulfat-Komplexen[7] beruht. Zweitens ist nach dem Reaktionsschema von Deman[4] die Oxydation des J zum J^+ der geschwindigkeitsbestimmende Schritt (Gleichung 3). Das höhere Oxydationspotential des Cer(IV) in salpetersaurer Lösung dürfte eine Beschleunigung dieser Teilreaktion bewirken.

Auf Grund der vorliegenden Ergebnisse erweist sich die Ausführung der Katalysereaktion in salpetersaurer Lösung zur quantitativen Bestimmung geringster Jodspuren in Wässern bzw. biologischem Material nach Veraschung als sehr gut geeignet. Die kurzen Reaktionszeiten ermöglichten die Entwicklung einer automatischen Schnellmethode zur Bestimmung von Jodspuren, worüber gesondert berichtet wird.[9]

Summary—The influence of different acids on the rate of the iodine-catalysed redox reaction between Ce(IV) and As(III) has been investigated. The catalytic activity of iodine in nitric acid solutions is 20 times that in the sulphuric acid solutions which have been used so far. The catalytic reaction in nitric acid is also far less sensitive towards accompanying ions, making the system more useful for the determination of traces of iodine.

Résumé—On a étudié l'influence de différents acides sur la vitesse de la réaction redox catalysée par l'iode entre Ce(IV) et As(III). L'activité catalytique de l'iode dans des solutions d'acide nitrique est 20 fois celle notée dans les solutions d'acide sulfurique que l'on a utilisées jusqu'ici. La réaction catalytique en acide nitrique est aussi beaucoup moins sensible vis-à-vis des autres ions simultanément présents, rendant le système plus utile pour la détermination de traces d'iode.

LITERATUR

1. E. B. Sandell und I. M. Kolthoff, *J. Am. Chem. Soc.*, 1934 **56,** 1426.
2. F. Feigl, *Analyse mit Hilfe von Tüpfelreaktionen;* Akadem. Verlag. Leipzig, 1935.
3. N. E. Kontaxis und D. E. Pickering, *J. Clin. Endocr.*, 1958, **18,** 774.
4. J. Deman, *Mikrochim. Acta*, 1964, 67.
5. R. D. Strickland und C. M. Maloney, *Anal. Chem.*, 1957, **29,** 1870.
6. V. Štolc, *Estimation of Iodocompounds in Biological Material*, Slovak Academy of Sciences, Bratislava, 1966.
7. R. L. Moore und R. D. Anderson, *J. Am. Chem. Soc.*, 1945, **67,** 167; 1949, **71,** 2577.
8. H. Hoch, S. L. Sinnett und T. H. McGavack, *Clin. Chem.*, 1964, 799.
9. G. Knapp und H. Spitzy, *Talanta*, 1969, **16,** 1361.

Talanta, 1969, Vol. 16, pp. 1361 to 1368. Pergamon Press. Printed in Northern Ireland

EINE APPARATUR ZUR AUTOMATISCHEN JODBESTIMMUNG IM NANOGRAMMBEREICH*

GÜNTER KNAPP und HANS SPITZY
Institut für Allgemeine Chemie, Mikro- und Radiochemie
Technische Hochschule in Graz, Österreich

(*Eingegangen am* 6. *März* 1969. *Angenommen am* 24. *April* 1969)

Zusammenfassung—Auf Grund der von Knapp und Spitzy[1] modifizierten Sandell-Kolthoff-Reaktion wurde eine Apparatur zur automatischen Jodbestimmung entwickelt. Dieses nach einem neuen Meßprinzip arbeitende Gerät gestattet die Analyse von 40 Proben pro Stunde. Die Nachweisgrenze liegt bei 0,5 ng Jod. Da pro Bestimmung bis zu 4 ml Probelösung eingesetzt werden können, entspricht dies einer Grenzkonzentration von 0,12 ng/ml.

AUTOMATISIERTE Jodbestimmungen im Spurenbereich haben heute im klinischen Forschungs- und Routinebetrieb große Bedeutung erlangt. Die Ursachen hiefür liegen im Anfall einer großen Anzahl von Proben und im Bestreben, subjektive Fehler möglichst auszuschalten. Das Hauptproblem bei der Entwicklung eines solchen automatischen Verfahrens ist die Erfordernis, aus dem Ablauf der katalytischen Reaktion automationsgerechte Daten zu entnehmen, die der jeweiligen Konzentration des Katalysators Jod entsprechen. Es gibt verschiedene Möglichkeiten die durch Jodspuren katalysierte Reaktion Cer(IV)–arsenige Säure quantitativ auszuwerten.

1. Bei einer definierten Cer(IV)-Ausgangskonzentration wird nach einer bestimmten Zeit der Cer(IV)-Restgehalt photometrisch bestimmt. Die erhaltenen Extinktions- bzw. Transmissionswerte stehen in direktem Zusammenhang mit der Jodkonzentration. Die meisten manuellen Verfahren sowie das derzeit bedeutendste automatische System† werten nach diesem Prinzip aus. Da bei dieser Meßtechnik pro Analyse nur eine kurze photometrische Messung am Ende der Reaktionszeit nötig ist, kann auch bei langsam ablaufenden katalytischen Reaktionen, wie dies bei der herkömmlichen Jodkatalyse in schwefelsaurem Medium nach Sandell und Kolthoff[2] der Fall ist, ein großer Probendurchsatz erreicht werden. Nachteilig ist, daß die Cer(IV)-Ausgangskonzentration sehr genau eingehalten werden muß, da sich jede Abweichung davon direkt im Ergebnis ausdrückt. Ferner ist es bei diesem Verfahren nicht möglich den Verlauf der Katalysereaktion zu verfolgen, um daraus Schlüsse auf etwaige Fehler und damit falsche Resultate ziehen zu können.

2. Ein bei katalytischen Reaktionen allgemein anwendbares Verfahren besteht in der Messung der Reaktionszeit, die benötigt wird um einen bestimmten Bereich der Reaktion zu durchlaufen. Der reziproke Wert dieser Reaktionszeit ist der Katalysatormenge direkt proportional. Dieses Verfahren wurde u.a. auch auf die

---

* Diese Arbeit wurde in Verbindung mit dem Forschungskontrakt Nr. 384/RB der International Atomic Energy Agency, Wien, ausgeführt.

† AutoAnalyzer, Technicon Instruments Corporation.

Reaktion Cer(IV)-arsenige Säure angewandt und automatisch arbeitende Analysengeräte beschrieben.[3,4] Da hier praktisch die Reaktionsgeschwindigkeit auf dem Umweg über die reziproke Reaktionszeit gemessen wird, ist ein exaktes Einhalten der Cer(IV)-Konzentration nicht nötig. Störende Änderungen der Reaktionsgeschwindigkeit treten erst bei Schwankungen der Cer(IV)-Ausgangskonzentration über 5% auf. Dieses Verfahren hat den Nachteil, daß es nur schwer an eine automatische Probenvorbereitung angeschlossen werden kann, da ein zeitlich konstanter Meßablauf fehlt. Proben niederen Katalysatorgehaltes benötigen eine lange Meßzeit, solche hoher Gehalte hingegen eine kurze.

Um einerseits ein konstantes Meßintervall zu erhalten und andererseits auf die zuverlässigere direkte Messung der Reaktionsgeschwindigkeit nicht verzichten zu müssen, wurde in dieser Arbeit ein neuer Weg beschritten:

3. Jede Reaktion läßt sich einer bestimmten Reaktionsordnung zuordnen. Die durch Jod katalysierte Reaktion Cer(IV)-arsenige Säure läuft formal I. Ordnung ab. Daher läßt sie sich mathematisch beschreiben:

$$-\frac{\mathrm{d}[\mathrm{Ce}^{4+}]_t}{\mathrm{d}t} = k \, . \, [\mathrm{Ce}^{4+}]_t \, . \, [\mathrm{J}] \tag{1}$$

In Abweichung von dem sonst für Reaktionen erster Ordnung üblichen Ansatz geht noch die Jodkonzentration als geschwindigkeitsbestimmender Faktor in die Gleichung (1) ein. Durch Lösung dieser Gleichung erhält man

$$\ln [\mathrm{Ce}^{4+}]_t = \ln [\mathrm{Ce}^{4+}]_{t=0} - k \, . \, [\mathrm{J}] \, . \, t \tag{2}$$

Verfolgt man die Cer(IV)-konzentration photometrisch und wählt die Reaktionsbedingungen so, daß das Beer'sche Gesetz Gültigkeit besitzt, so läßt sich Gleichung (2) umwandeln:

$$\ln E_t = \ln E_O - k_{\mathrm{E}} \, . \, [\mathrm{J}] \, . \, t \tag{3}$$

E_t = Extinktion zur Zeit t
E_O = Extinktion zur Zeit $t = 0$
k_{E} = Konstante

Wird die Extinktion während einer Katalysereaktion fortlaufend gemessen und deren Logarithmus gegen die Zeit aufgetragen, so resultiert die sogenannte Reaktionsgerade. Nach Gleichung (3) ist die Steigung (tg α) dieser Reaktionsgeraden proportional der gesuchten Jodkonzentration. Beobachtet man die Katalysereaktion bei verschiedener Jodkonzentration über einen konstanten Zeitraum t_1, so sind die Ordinatenabschnitte der Reaktionsgeschwindigkeit und damit der Jodkonzentration direkt proportional.

Das im Zuge dieser Arbeit entwickelte Analysengerät transformiert die der Transmission proportionale Spannung des Photometerausganges in eine dem Logarithmus der Extinktion proportionale Spannung. Diese Transformation geht nach der mathematischen Beziehung in Gleichung (5) vor sich

$$E = \log \frac{1}{T} \, . \, 100 = 2 - \log T \tag{4}$$

$$\log E = \log (2 - \log T) \tag{5}$$

Die daraus resultierende Reaktionsgerade wird über einen Zeitraum von einer Minute aufgezeichnet. Der zugehörige Ordinatenabschnitt gegen die Jodkonzentration aufgetragen ergibt die Eichgerade.

Ein großer Vorteil dieser Methode besteht darin, daß die Messung in jedem Stadium des Reaktionsablaufes durchgeführt werden kann, soferne noch innerhalb des Photometermeßbereiches gearbeitet wird. Ferner ist es möglich, manche Fehler, die durch bestimmte Fremdionen, organische Substanzen oder alte Reagenzien hervorgerufen werden, zu erkennen. Die Reaktion läuft unter solchen Umständen oft nicht mehr I. Ordnung ab, so daß statt Reaktionsgeraden gekrümmte Linien resultieren.

Diese Meßtechnik hat mit der unter *2.* beschriebenen Methode gemeinsam, daß Schwankungen der Cer(IV)-Ausgangskonzentration keine so gravierenden Fehler hervorrufen wie dies bei der unter *1.* angeführten Methode gegeben ist. Allerdings kann bei dem Verfahren der Zeitmessung wie auch bei der hier ausgearbeiteten Meßtechnik in der nachstehend beschriebenen Apparatur jeweils nur eine Analyse durchgeführt werden. Ein hoher Probendurchsatz ist daher nur bei rasch ablaufenden katalytischen Reaktionen zu erzielen. Dies ist bei der hier angewandten und an anderer Stelle beschriebenen Modifizierung[1] der Sandell-Kolthoff-Reaktion gegeben, da durch Verwendung von salpetersauren Reaktionsgemischen anstelle der bisher üblichen schwefelsauren wesentlich kürzere Reaktionszeiten resultieren.

PRINZIP UND AUFBAU DER MESSEINRICHTUNG

Die Meßanordnung besteht aus einem Photometer und dem Auswertegerät. Für die vorliegende Jodbestimmungsapparatur muß ein Photometer eingesetzt werden, das Messungen entweder über einen Monochromator oder mittels Quecksilberlampe und Interferenzfiltern bei 365 nm zuläßt. Exakte Reaktionsgeraden sind nur dann zu erhalten, wenn die Cer(IV)-Lösung dem Beer'schen Gesetz gehorcht; dies ist jedoch in schwefelsauren Reaktionsgemischen nur in den niederen Konzentrationsbereichen der Fall.

Im salpetersauren Reaktionsgemisch konnte eine befriedigende Übereinstimmung der Cer(IV)-ionenkonzentration mit der Extinktion bis zu einer Konzentration von 10^{-3}m beobachtet werden. Da das Absorptionsmaximum von Cer(IV) bei 315 nm liegt, muß man trachten, möglichst nahe an diesen Bereich heranzukommen um mit geringen Cer(IV)-konzentrationen arbeiten zu können. Unter 360 nm macht sich jedoch eine störende Absorption durch Salpetersäure bemerkbar (Abb. 1), so daß die benachbarte Quecksilberlinie von 365 nm für die vorliegenden Messungen herangezogen wurde. Gewöhnliche Filterphotometer sind nicht geeignet, da dann das Beer'sche Gesetz wegen zu großer Bandbreite keine Gültigkeit besitzt.

Abbildung 2 zeigt ein Fließbild der vollständigen Apparatur zur Jodbestimmung. In das Reagenzglas 1 werden der Reihe nach die Probelösung und die Reagenzien gefüllt. Anschließend wird dieses Reaktionsgemisch mittels einer Pumpe 7 über die Rohrleitung 2 durch eine Durchflußthermostatisiereinrichtung 3 gesaugt. Dabei erhält das Reaktionsgemisch innerhalb weniger Sekunden die gewünschte Reaktionstemperatur. Im Anschluß an die Durchflußthermostatisiereinrichtung 3 gelangt das Reaktionsgemisch in die ebenfalls thermostatisierte Durchflußküvette 6 (10-mm Schichtdicke). Sobald sich die Küvette zur Gänze mit dem Reaktionsgemisch gefüllt hat, wird die Pumpe 7 abgeschaltet und der Meßvorgang gestartet. Das Photometer 5 liefert eine der Transmission proportionale Spannung. Diese Photometerspannung wird nun im Auswertegerät 10 wie schon vorhin erläutert einer doppellogarithmischen Transformation unterworfen und die daraus resultierende Reaktionsgerade registriert. Die Meßdauer beträgt eine Minute. Der Ordinatenabschnitt der Reaktionsgeraden ist der Jodkonzentration proportional. Nach beendeter Messung wird das System automatisch mit destilliertem Wasser gespült.

Photometereinheit

Abbildung 3 zeigt den schematischen Aufbau dieser Einheit bestehend aus dem eigentlichen Photometer, der Probeneinsaugeinheit mit Vorwärmspirale sowie die automatisch arbeitende Spülvorrichtung.

Prinzipiell wurde der Vorgang der Probenbeschickung bereits in Abb. 2 erklärt. Hier soll auf

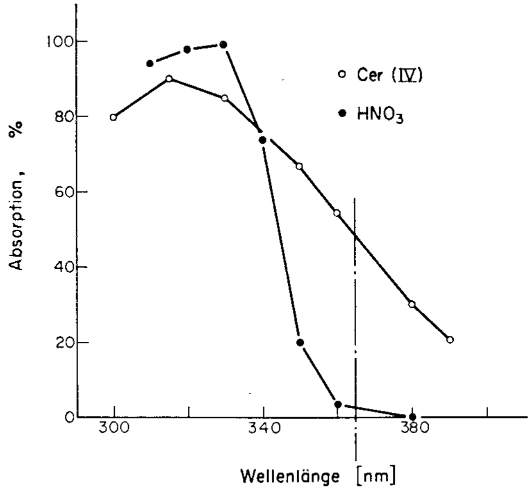


ABB. 1.—Absorptionskurven von Cer(IV) und HNO_3.

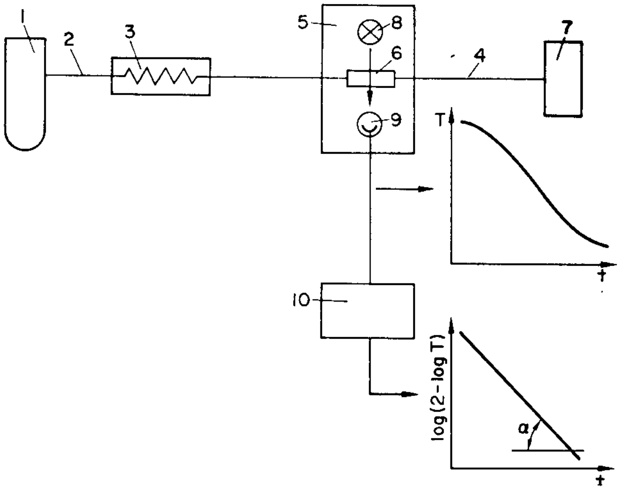


ABB. 2.—Fließbild der neuen Jodbestimmung.
1 Reaktionsgefäß, 2 Zuleitung, 3 Vorwärmspirale, 4 Saugleitung, 5 Photometer, 6 thermostatisierte Durchflußküvette, 7 Pumpe, 8 Lampe, 9 Photozelle, 10 Auswertegerät mit Funktionswandler.

technische Einzelheiten eingegangen werden. Der Saugrüssel 1 ist schwenkbar angeordnet und wird durch den Motor 2 betätigt. Die Proben werden mit einer Wasserstrahlpumpe eingesaugt, die am Ende des Leitungssystems, bestehend aus Saugrüssel 1, Vorwärmspirale 3, Durchflußküvette 4 und Elektroventil 5, angeschlossen ist. Um das Vakuum und damit die Einsauggeschwindigkeit regülieren zu können, ist ein Feinregulierventil 6 für Zuluft an der Vakuumleitung angeschlossen. Die Einsauggeschwindigkeit wird auf 0,6 bis 0,8 ml pro Sekunde eingestellt. Da das Reaktiongemisch *ca.* 6 ml beträgt, ergibt sich eine Einsaugzeit von 8 bis 10 Sekunden. Nach Ablauf der Messung wird der Spülvorgang durch einen Impuls vom Auswertegerät ausgelöst. Der Motor 2 senkt den Rüssel 1 in ein Niveaugefäß 7, in das destilliertes Wasser aus der Vorratsflasche 8 nachfließt. Gleichzeitig wird das Elektroventil 5 geöffnet.

Nach 20 Sekunden Spülen wird das Ventil 5 geschlossen und der Rüssel 1 in die Ausgangsposition geschwenkt. Somit ist nach jeder Messung eine ausreichende Spülung des gesamten Systems gewährleistet.

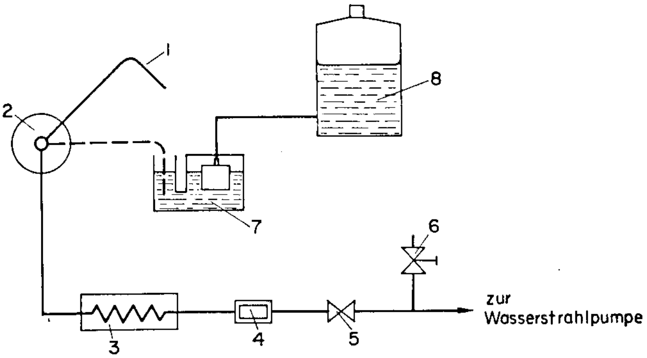


Abb. 3.—Schema der Probenbeschickung mit automatischer Spüleinrichtung. 1 schwenkbarer Saugrüssel, 2 Antriebsmotor für Saugrüssel, 3 Vorwärmspirale, 4 thermostatisierte Durchflußküvette, 5 Magnetventil, 6 Feinregulierventil, 7 Niveaugefäß, 8 Vorratsflasche für destilliertes Wasser.

Auswertegerät

Das Auswertegerät hat die Aufgabe, die doppellogarithmische Transformation der Transmission in den Logarithmus der Extinktion durchzuführen, und die daraus resultierende Reaktionsgerade in der Weise zu schreiben, daß der Ordinatenabschnitt direkt zur Jodbestimmung herangezogen werden kann. Weiters hat das Auswertegerät den Steuerimpuls für die automatische Spülung zu liefern.

Unter den vielen Möglichkeiten, eine doppellogarithmische Transformation durchzuführen, wurde nach vielen Versuchen eine elektromechanische Version ausgewählt. Das Kernstück des Auswertegerätes besteht aus einem Kompensationsschreiber der Fa. Görz, der so umgebaut wurde, daß das Abgleichpotentiometer 1 vom Schreibermotor 2 über eine Kurvenscheibe 3 angetrieben wird (Abb. 4). Diese Kurvenscheibe erlaubt die Transformation der im Photometer gemessenen Transmission in log (2 − log T) nach Gleichung (5). Wird die Katalysereaktion mit dem so modifizierten Schreiber aufgezeichnet, so erhält man die gewünschte Reaktionsgerade.

Weitere Elemente des Auswertegerätes sind die Magnetkupplung 4 und der Rückstellmotor 5 für die Schreiberfeder 6, sowie die elektrische Steuereinheit einschließlich Zeitwerk. Die Schreiberfeder steht im Ruhezustand am O-Punkt. Startet man eine Messung durch Knopfdruck, so wird die Schreiberfeder 6 über die Magnetkupplung 4 an den Schreibermotor 2 gekuppelt und zeichnet die Reaktionsgerade von der O-Linie beginnend auf. Gleichzeitig wird das Minutenzeitwerk in Tätigkeit gesetzt. Nach einer Minute wird die Kupplung 4 ausgeschaltet und die Feder 6 vom Rückstellmotor

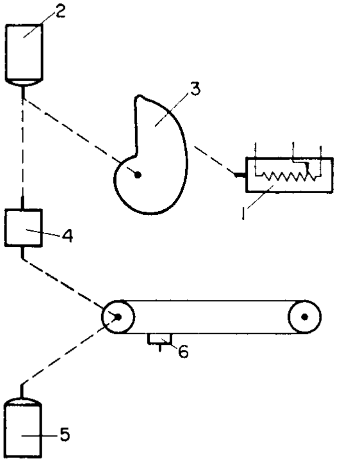


Abb. 4.—Schematischer Aufbau des Funktionswandlers im Auswertegerät. 1 Abgleichpotentiometer, 2 Schreibermotor, 3 Kurvenscheibe, 4 Magnetkupplung, 5 Rückstellmotor für Schreiberfeder, 6 Schreiberfeder.

5 auf die O-Linie zurückbefördert. Dadurch entsteht am Schreiberpapier für jede Messung eine Zacke. Die Zackenhöhe ist direkt proportional der Jodkonzentration. Abbildung 5 zeigt mit diesem Gerät erhaltene Werte von Jodbestimmungen im Nanogrammbereich, aus denen die Eichgerade erstellt wird. Dieses Auswertegerät hat als weitere Besonderheit noch den Vorteil der automatischen Umschaltung auf einen erweiterten Meßbereich bei hohen Jodkonzentrationen. Ist nämlich die Jodkonzentration der zu untersuchenden Probe so hoch, daß die Schreiberfeder in einer Minute über die zur Verfügung stehende Schreiberbreite hinausschreiben würde, so schaltet sich das Gerät bereits nach einer halben Minute ab (30, 40 bzw. 50 ng in Abb. 5). Die so resultierende Zackenhöhe ist nur mit 2 zu multiplizieren und kann mit Hilfe der Eichgeraden ausgewertet werden. Damit steht der doppelte Meßbereich zur Verfügung.

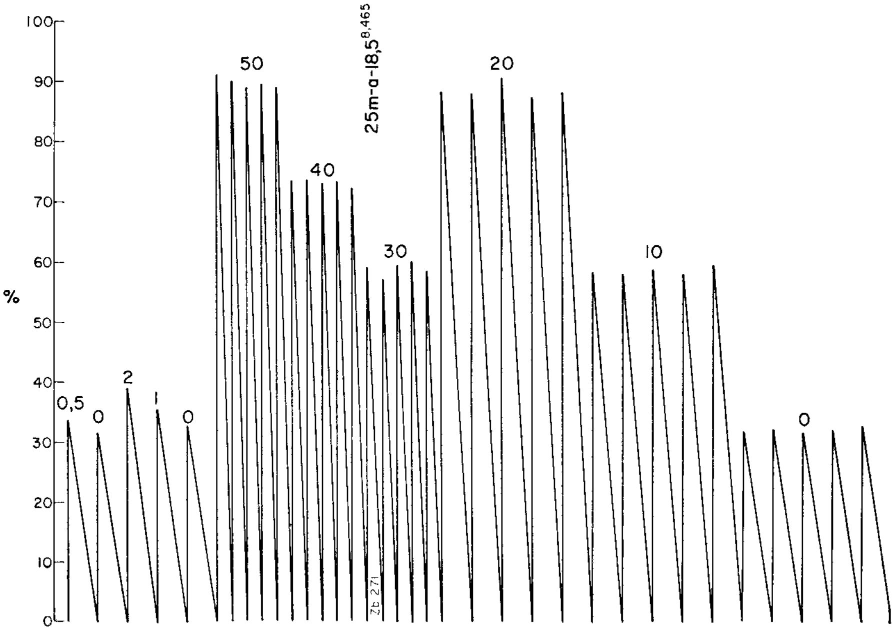


ABB. 5.—Vom Auswertegerät aufgezeichnete Analysenergebnisse in ng.

ARBEITSMETHODE

Reagenzien

Cer(IV)-*Lösung*. $Ce(SO_4)_2 . 4H_2O$ (3 g) wird in 100 ml bidest. Wasser und 10 ml konzentrierter Schwefelsäure gelöst. Anschließend wird mit bidestilliertem Wasser auf 500 ml aufgefüllt.

As(III)-*Lösung*. As_2O_3 (4 g) wird in 50 ml 1m KOH gelöst, 2 ml konzentrierte schwefelsäure und 2 g Na Cl zugegeben und mit bidest. Wasser auf 500 ml aufgefüllt.

Jodat-Stammlösung. Kaliumjodat (Merck *p.a.*, 168,64 mg), bei 120°C getrocknet, wird mit bidest. Wasser in 1000 ml gelöst. Diese Lösung enthält 100 μg J/ml und wird nach Bedarf weiter verdünnt.

Bidestilliertes Wasser. Destilliertes Wasser wird in einer Quarzapparatur über Kaliumkarbonat destilliert.

Durchführung von Jodbestimmungen mit dem Analysengerät

In ein graduiertes Reaktionsgefäß werden die jodid-, jod- oder jodathältige Probelösung, 0,5 ml As(III)-Lösung und 1,3 ml HNO_3(65%) pipettiert. Nach Auffüllen mit bidest. Wasser auf 5,5 ml werden 0,25 ml Cer(IV)-Lösung zugegeben. Kurzes Schütteln nach jeder Reagenzzugabe bewirkt eine gute Durchmischung der Reaktionslösung. Nun saugt man durch Betätigen des Elektroventils das Gemisch in die auf 38° thermostatisierte Meßanordnung. Anschließend wird der Startknopf gedrückt. Die Messung sowie die nachfolgende Spülung des Systems laufen automatisch ab. Etwa alle 1,5 Min kann eine Probe eingesaugt werden.

ERGEBNISSE UND DISKUSSION

Bei der Analyse jodathältiger Proben zeigte sich, daß die Reduktion des katalytisch inaktiven Jodat zum katalytisch wirksamen Jod durch dreiwertiges Arsen in stark salpetersaurer Lösung praktisch momentan erfolgt. Im herkömmlichen schwefelsauren Milieu beanspruchte der Reduktionsschritt hingegen einige Minuten. Daher kann der im Vergleich zu Jodideichlösung stabilere Jodatstandard Verwendung finden. Bei Verwendung von Dosierautomaten zur Zugabe der einzelnen Reagenzien ist die Bereitung der Reaktionsgemische ohne Schwierigkeit in wenigen Sekunden zu bewerkstelligen.

Der Tabelle I sind Analysenergebnisse jodhältiger Probelösungen einschließlich der auftretenden Fehlerabweichungen zu entnehmen. Die Reproduzierbarkeit der Meßanordnung beträgt etwa ±0,2 ng. Damit ist die Nachweisgrenze mit 0,5 ng Jod gegeben. Da bei der vorliegenden Zusammensetzung des Reaktionsgemisches etwa 4 ml Probelösung eingesetzt werden, beträgt die Grenzkonzentration 0,12 ng/ml.

TABELLE I

Jod vorgelegt, *ng*	Jod gemessen, *ng*	Mittelwert und mittlere Fehlerabweichung, *ng*	rel. Fehler, %
0,5	0,4 0,5 0,3 0,6 0,4	0,44 ± 0,21	±47,7
10,0	9,9 10,2 9,9 9,9 10,6	10,1 ± 0,14	±1,4
20,0	20,2 20,5 19,7 19,8 20,5	20,14 ± 0,17	±0,85

Die Jodbestimmung mit diesem weitgehend automatisch arbeitenden Analysengerät auf Basis der modifizierten Sandell-Kolthoff-Reaktion[1] ist auf Grund des hohen Probendurchsatzes und der einfachen Handhabung sowohl für den Routinebetrieb als auch für Einzelanalysen gut geeignet. Dieses System kann ebensogut zur quantitativen Auswertung anderer Bestimmungen herangezogen werden. Sollte die entsprechende Reaktion nicht I. Ordnung ablaufen, muß eine dem Reaktionsablauf angepaßte Kurvenscheibe eingesetzt werden. Es ist dies ein weiterer Weg zur Automation auf dem großen Gebiet der katalytischen Reaktionen in der Spurenanalytik.

Summary—On the basis of the Sandell-Kolthoff reaction as modified by Knapp and Spitzy an apparatus for automatic iodine determinations has been developed. This instrument works according to a new principle of measurement and allows the analysis of 40 samples per hour. The detection limit is 0·5 ng of iodine. The sample volume per determination can be up to 4 ml, which corresponds to a concentration limit of 0·12 ng/ml.

Résumé—Sur la base de la réaction de Sandell-Kolthoff modifiée par Knapp et Spitzy, on a élaboré un appareil pour dosages automatiques de l'iode. Cet instrument travaille selon un nouveau principe de mesure et permet l'analyse de 40 échantillons par heure. La limite de détection est de 0,5 ng d'iode. Le volume d'échantillon par détermination peut atteindre 4 ml, ce qui correspond à une limite de concentration de 0,12 ng/ml.

LITERATUR

1. G. Knapp und H. Spitzy, *Talanta*, 1969, **16**, 1353.
2. E. B. Sandell und I. M. Kolthoff, *J. Am. Chem. Soc.*, 1934, **56**, 1462.
3. H. L. Pardue und R. L. Habig, *Anal. Chim. Acta*, 1966, **35**, 383.
4. G. E. James und H. L. Pardue, *Anal. Chem.*, 1968, **40**, 796.

Talanta, 1969, Vol. 16, pp. 1369 to 1382. Pergamon Press. Printed in Northern Ireland

METAL COMPLEXES WITH TROPOLONES

YAG DUTT and R. P. SINGH
Department of Chemistry, University of Delhi, India

and

MOHAN KATYAL
Chemistry Department, Dalhousie University, Halifax, Canada

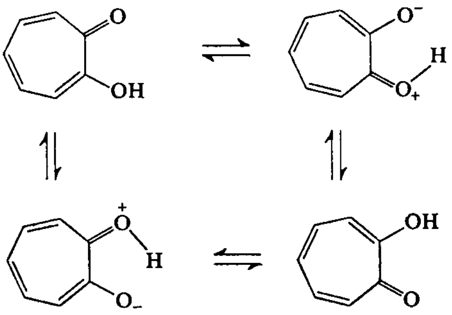
(*Received* 7 *June* 1968. *Revised* 9 *December* 1968. *Accepted* 26 *March* 1969)

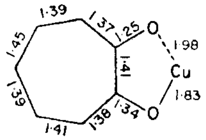
Summary—A review of the analytical applications of tropolone and its derivatives.

SINCE the characterization of the tropolone molecule in 1945 by Dewar[1] several reviews of tropolone chemistry have appeared,[2–6] but none on the analytical applications, a field which has also received some attention. It is the purpose of this review to fill this need.

The non-benzenoid aromatic molecule tropolone(I) is stabilized by resonance and tautomerism, so that the ketonic group is masked, and the behaviour is that of the enol form. It is weakly acidic,[7–9] with $pK_a = 6{\cdot}71$, and forms complexes with many metals. The complexes with copper(II) and with iron(III) are readily crystallized, and have been used for the purification and separation of tropolones.[7]

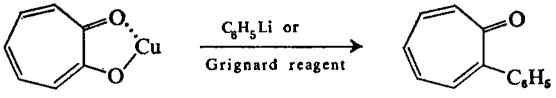
I





II

The structure of the copper complex, **II**, has been determined, thus throwing some light on the nature of the bonding in the molecule.[10–12] This complex has also been used as the starting point for synthetic routes using Grignard reagents or organolithium compounds, leading to 2-alkyl and 2-aryltropones.[13–16]

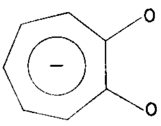


Tropolone complexes with metal ions have been widely studied. Even before the elucidation of the structure of the parent compound, complexes of hinokitiol (β-isopropyltropolone, or β-thujaplicin) with Cu(II), Ni, Mn(II), Zn, Mg, Co(II), Co(III), Cr(III), and Fe(III) had been prepared.[17,18] The stability constants of tropolone complexes with a number of bivalent metal ions have been reported, and the order of the stabilities is Cu(II) > Be > Pb > (Zn, Ni) > Co(II) > Mg > Ca[19-21] which is in accordance with the usual Irving-Williams order.[22]

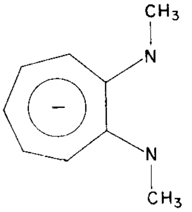
With bivalent metal ions, 1:3 complexes with hinokitiol have been obtained from alcoholic solution as salts of univalent metals.[23,24] Hseu has reported the existence of several complex ions of Cu, Zn, Cd, Ni, Mn and Co with varying degrees of co-ordination.[25] Potentiometric and spectrophotometric methods have been used to determine stability constants for various complexes of α-carboxy-β-methyltropolone.[26] The existence of 1:1, 1:2, and 1:3 complexes of this reagent with lanthanide elements has also been reported.[27] The stability of these complexes increases with atomic number (and hence with decreasing ionic radius).[28] The wavelength of maximum absorbance of these complexes decreases with increasing atomic number (and hence with stability), indicating an increased covalency with atomic number.[29] Similar work has been done on the lanthanide complexes with β-methyltropolone and β-isopropyltropolone.[30] Lead and cadmium form complexes with these reagents, which give irreversible polarographic waves.[31]

Studies in high-co-ordination chemistry, particularly of group III, IV and V elements, have lead to the synthesis of chelates of many of these elements with tropolone and with its derivatives.[32-38] The chelates of silicon, germanium, tin, and phosphorus with *N,N′*-dimethylaminotroponimine are all subject to acid-catalysed hydrolysis, but the boron chelate is stable.[32]

The hydrolysis of these chelates has been followed by using ^{18}O tracer techniques.[33] In the case of four- and six-co-ordinate cationic chelates such as $T_2B^+I^-$, $T_3Si^+I^-$, $T_3Ge^+I^-$ and $T_3P^{2+}\ 2I^-$ (where T = the tropolone ion) the attack is mainly by the ligand hydroxyl group. A similar mechanism seems likely for hydrolysis of $T_4Nb^+Cl^-$, but the talantum chelate $T_4Ta^+Cl^-$ suffers attack mainly at the metal atom.



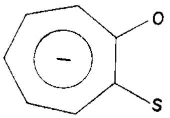
(T)



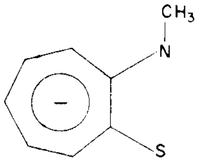
III

Spectroscopic studies by the same authors[34] have led to the postulation of seven- and eight-co-ordinate structures for a number of metal chelates with the tropolone ion. The colours of the chelates are ascribed to electron-transfer from the ligand to the metal. A tetratropolone complex of thorium has been prepared, and shown by molecular weight determination to be a monomer in organic solvents. A solid salt with the composition $NaThT_5$ has also been prepared, but this appears to be highly associated in solution, so a co-ordination number of ten can only be tentatively suggested.[35] Lanthanide complexes corresponding to LT_3 may be prepared in the solid state[36] but these too are associated in solution. Claims are made for higher co-ordination numbers for some of these ions. Erbium and lutetium complexes seem to form trimers in solution.

Transition metal chelates with *N*,*N*′-dimethylaminotroponimine(**III**), with 2-thiotropone (**IV**), and with *N*-methylaminothiotropone (**V**) have been studied,[38] and the chemistry of these compounds found to be similar to that of those derived from tropolone itself. The ions of these compounds are most conveniently represented as shown here without specific double bonds being drawn.



(**IV**)



(**V**)

Stability constants of some bivalent metal complexes with α-carboxy-β-methyltropolone have been determined by potentiometric and spectrophotometric methods.[39] The order of stability observed in this case is $UO_2 > Cu > Ni > Zn > Co(II) > Cd > Mn > Mg > Ca > Sr > Ba$. Stability constants of the rare-earths with this reagent have been determined potentiometrically[40] and spectrophotometrically.[41] In this series the stability increases with atomic number, as has also been observed with complexes with β-methyltropolone and β-isopropyltropolone.[42] Polarography has been applied to the study of the lead and copper complexes.[43]

Dyrssen has carried out extensive investigations on the solvent extraction of metal complexes with tropolone[44] and its β-isopropyl derivative,[45] and has determined the composition of various extracted species. The same author[44] and Rydberg[46] have measured the stability constants of thorium complexes with tropolone, and of β-isopropyltropolone complexes with Ag, Cu(II), Ni, Co(II), Zn, Cd, Ca, Sr, Ba, and Fe(III).[47] Dyrssen has also discussed the effect of the structure of tropolone and other ligands on the stability and distribution constants of thorium complexes.[48]

Oka and coworkers have determined spectrophotometrically the composition and stability of iron(III) complexes with tropolone,[49] and have carried out similar studies on metal complexes of 5-sulphotropolone, reporting the stabilities of uranium,[50] thorium, [51] and iron(III)[52] complexes. A linear relationship was found between the pK_a values of various 5-substituted tropolones and the stabilities of the corresponding iron(III) complexes.[53,54]

Spectrophotometric studies on uranium[55] and iron(III)[56] complexes with β-methyltropolone, β-isopropyltropolone and α-carboxy-β-methyltropolone, and germanium complexes with tropolone[57] have yielded stability constants and information on composition. Infrared spectra of tropolone, its derivatives and complexes have also been recorded.[58]

Many of the metal complexes with tropolones are coloured. These are mostly those with metal ions in their highest oxidation states, *e.g.*, Fe(III), Ti(IV), Pb(IV), Ce(IV), Nb(V), though not with Th(IV) and Zr(IV) *etc*, which have comparatively stable oxidation states. The most probable explanation of the colours is the existence of charge transfer from ligand to metal. The coloured tropolone complexes have been made use of for the spectrophotometric determinations of these metal ions. Some of the more highly conjugated tropolones, such as the hydroxybenzotropolones, are themselves coloured. When these compounds form complexes, the absorption bands shift to longer wavelengths, a fact that can be made use of for spectrophotometric determinations, *e.g.*, of Th(IV) and of Zr(IV). Derivatives like purpurogallin contain, besides the tropolone group, other possible sites for co-ordination and can therefore form polynuclear insoluble complexes which lend themselves to gravimetric methods of determination and separation. Details of the various types of complexes are summarized in Table I.

TABLE I.—METAL COMPLEXES WITH TROPOLONES

	Type of complex formed	Co-ordination number	References
Bivalent elements			
Cu, Be, Hg, Pd	ML_2	4	36, 37
Mg, Ca, Sr, Ba, Mn, Co, Ni, Pb, Fe, Zn, Cd	ML_2 (polymeric)	6	36, 19
Ca, Sr, Ba, Cd, UO_2	ML_2, LH	6	45
Mg, Mn, Co, Ni, Zn	ML_3^-	6	23, 24, 45
Tervalent elements			
B	ML_2^+	4	32, 37
Bi, Sb	ML_2Cl	6	32
Fe, Ga, Rh, Cr, Ti, Al, Sc	ML_3	6	34, 19
Sb, Bi	ML_3	6 or 7(?)	36
Rare earths, Y, In	ML_3((polymeric)	7 or 8	32, 34, 36
Eu, Ho, Yb, Lu	ML_3, LH	8	45
Rare earths, Y, In, Sc, Bi	ML_4^-	8	34, 36
Quadrivalent elements			
Ge, Si	ML_3^+	6	32, 57, 76
Ge, Si	ML_4	6	32
Sn, Ti	ML_2Cl_2	6	32, 34, 36 86, 83
Sn, Ti	ML_3Cl	7	32, 34, 36, 86, 85
Sn, Pb, Zr, Hf, Ce	ML_4	8	32, 83
Th, U	ML_4	8 or more	45, 83, 44, 46
Th, U	ML_5^-	10	45, 44, 46, 98
Quinquevalent elements			
P	ML_3^{2+}	6	32, 33
V, Mo	MOL_2Cl	6 or 7	34
V, Mo	MOL_3	7	34, 36
Sb, Nb, Ta	ML_4^+	8	33, 34, 37
As	$M(OH)_2L_2^+$		32
Sexivalent elements			
Mo	MO_2L_2	6	84

PREPARATION OF TROPOLONES

Tropolone—I

This has been synthesized by several routes, such as oxidation of cycloheptanone followed by dehydrogenation,[59,60] or ring-expansion of benzene with diazomethane.[7,61] Other routes involve prior reduction of benzene[62,63] or starting with tropolone derivatives.[64–66] Tetrafluorocycloheptadiene, obtained by interaction of cyclopentadiene and tetrafluoroethylene, gives tropolone on treatment with potassium acetate and acetic acid.[67]

Tropolone-5-sulphonic acid—VI

Heat tropolone (6·7 g) and sulphamic acid (4·13 g) together for 5 hr at 150–160°, dissolve the product in water and extract with benzene. Concentration of the aqueous layer and repeated crystallization gives the ammonium salt[68] in good yield; m.p. 280°.

α-Carboxy-β-carboxymethyltropolone—VII

Add hydrogen peroxide (25 ml of 100-vol) dropwise to purpurogallin (10 g) in 23% potassium hydroxide solution (650 g) heated to 90–95°. Cool the mixture, add sodium bisulphite (5 g) and acidify the clear red solution with 40% sulphuric acid (270 ml). Filter off the precipitated potassium sulphate and extract the filtrate continuously for 40 hr with ether. From the dark red extract, after drying, a dark brown oil is obtained, which yields yellow crystals. Recrystallization from glacial acetic acid gives a colourless product; m.p. 183–184° with decomposition.[69]

α-Carboxy-β-methyltropolone—VIII

Heat the β-carboxymethyl compound (10 g) in nitrobenzene (50 ml) at 170° till evolution of gas ceases. Dilute the cooled solution with ether, filter, extract with sodium bicarbonate solution, and acidify the extract. The product may be recrystallized from hot water after purification with charcoal;[70] m.p. 190–192° with decomposition.

β-Methyltropolone—IX

Heat α-carboxy-β-carboxymethyltropolone to its melting point, and purify the product by sublimation and crystallization from light petroleum; m.p. 76–77°.[69]

β-Isopropyltropolone—X

Available commercially, and may be used without further purification.

Purpurogallin—XI

Add slowly a solution of sodium iodate (8 g) in water (100 ml) to pyrogallol (10 g) dissolved in a little cold water. The precipitated purpurogallin may be recrystallized from anisole;[71] m.p. 276°.

Dibromopurpurogallin—XII

Add bromine (1 g) to purpurogallin (1 g) suspended in acetic acid. Leave to stand for 24 hr, drain on a porous tile, and recrystallize from glacial acetic acid;[72] m.p. 204°.

Purpurogallin carboxylic acid—XIII

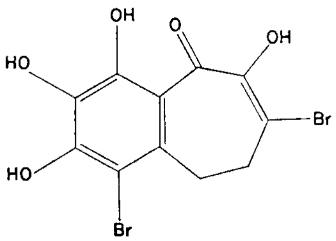
Add simultaneously solutions of pyrogallol (31 g in 250 ml of water) and potassium iodate (53 g in 500 ml of water) with stirring to an ice-cold slurry of sodium gallate [obtained by adding gallic acid (47 g) to sodium bicarbonate (21 g) dissolved in water (300 ml)]. The addition should take about 45 min. Stir for a further 15 min, acidify with 25 ml of 10*M* hydrochloric acid, leave to stand overnight and then filter. Extract the filtrate three times with a total of 1 l. of ether, and extract the air-dried precipitate several times with hot methanol. Concentrate the extracts, collecting the orange crystals in batches as they form, and drying them in air;[73] m.p. 320°.

3′,4′-Dihydroxybenzotropolone—XIV

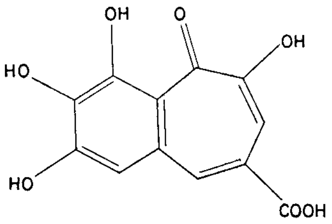
Add simultaneously pyrogallol (1 g in 10 ml of water), and a 4% aqueous solution of potassium iodate to a solution of catechol (2·5 g in 20 ml of water) and 15 ml of 4% potassium iodate solution. Extract the precipitate with hot benzene, and purify by recrystallization from ethanol.[74] The dark red needles melt at 189–190°.

Dimethylpurpurogallin—XV

Add an ethereal solution of diazomethane to purpurogallin (5 g in 200 ml of dioxan). After 12 hr evaporate the mixture, and recrystallize the product from ethanol;[75] m.p. 156°.



XII



XIII

ANALYTICAL APPLICATIONS

Of the elements which have been studied, only seven will be discussed in detail, and relevant data for the others are included in Tables II and III. Stability constants are summarized in Table IV.

TABLE II.—GRAVIMETRIC DETERMINATION OF ELEMENTS

Element	Reagent	pH range	Weighing form	Ignition temp., °C	Separations	Ref.
Al	XI	4·0–6·5	Al_2O_3	900		81
Bi	XI	1·5–6·5	Bi_2O_3	1000		81
Ce(IV)	XI	4·5–6·0	CeO_2	900		81
	XII	3·0–6·0				
	XIII	4·0–6·0				
	XIV	2·5–6·0				
Cu(II)	XI	4·0–6·0	CuO	900		81
Pb	XI	4·0–6·5	complex	130–140		81
Mo(VI)	XI	0·0–4·0	MoO_3	500–550°	Th, U(VI), lanthanides at pH 0	81,99
	XII	0·5–6·0			Ti, Zr	81
	XIII	0·0–3·5				
	XIV	1·0–3·5				81
Th	XI–XIV	2·5–6·0	ThO_2	900	lanthanides at pH 2·5	81
Ti(IV)	XI–XIII	1·0–6·5	TiO_2	900		81
	XIV	1·0–5·5				
U(VI)	XI	4·0–6·5	U_3O_8	900		81
	XII	3·0–6·5				
	XIII	3·5–6·5				
	XIV	3·5–5·5				
Zr	XI–XIII	0·0–6·5	ZrO_2	900	Th, U(VI) lanthanides at pH 0	81
	XIV	0·0–5·5				

Iron

Tropolone gives a green 1:1 complex in the presence of excess of iron(III) and a brownish red 1:3 precipitate with excess of reagent.[49] The 1:1 complex, formed in the pH range 0–1, has absorption maxima at 435 and 582 nm, and a formation constant of $1·0 \times 10^{11}$. The higher complex is formed in the pH range 1·3–8·5, and has maxima at 425, 550, and 595 nm. Beer's law is valid for both complexes, and either iron (up to 0·07 μg/ml) or tropolone (up to $10^{-5}M$) may be determined. The 1:3 complex is also extractable into chloroform, and may be used for the spectrophotometric determination of iron.[101]

Complexes of iron(III) with tropolone-5-sulphonic acid[52] have been studied, and also those of several substituted tropolones.[56] The stepwise formation constants for these are given in Table III.

α-Carboxy-β-methyltropolone is most suitable for the spectrophotometric determination of iron, as the complexes are soluble in water.[56] Beer's law is obeyed at pH 5–7 for the range 0–3 ppm of iron, at 420 nm. Few other metals give coloured complexes, so the selectivity is good. The β-methyltropolone complex may be efficiently extracted into chloroform, and there is no interference from the ions SCN^-, F^-, $C_2O_4^{2-}$, PO_4^{3-}, tartrate and citrate.

Table III.—Spectrophotometric studies and determinations

Element	Reagent	Nature of complex, conditions	Ref.
Fe(III)	I	ML(pH 0·05–1·0), ML_3(pH 1·3–8·5)	49*
		ML, ML_2, ML_3 as pH increases	101*
	VI	ML, ML_2, ML_3(pH 3·5–7·0)	52*
	VIII–X	ML, ML_2, ML_3 as pH increases	56*
	XV	ML_2(pH 3·0), ML_3(pH 8·0)	82
	others	ML	53, 54
Ge	I	ML_2, ML_3	57
	XI	ML_2, 3*N* HCl or H_2SO_4, aqueous ethanol	77*, 78*, 100
	XVI	ML_3	76*
Mo(VI)	VIII	ML, ML_2 at pH 2·0	84
	XI	ML(pH 1·0 and 6·0), M_2L(pH 4·0)	82*
	XIV, XV	ML	82
Nb(V)	I	Probably ML_4, soluble in $CHCl_3$	101*
Sn(IV)	XI, XIV	ML, precipitation at pH $>$ 2·0	82
Th	I	ML, ML_2, ML_3, ML_4, ML_5, ML_6	44, 46
	VI	ML(2*M* $HClO_4$), ML_2(pH 3·0)	51*
	X	ML_4(pH 5·3–6·1)	83*
	XIV, XV	ML, ML_2	82*
Ti(IV)	I	ML_2(pH 2·4–2·6), ML_3(pH 3·70)	83*, 85*
	VIII–X	ML_2, ML_3	86*
	XV	ML_2	82
U(VI)	VI	ML, ML_2	50*
	VIII–X	ML, ML_2 with increasing pH	55
	X	ML_2 in pyridine medium	93*
	XIV, XV	ML	82*
V(V)	XV	ML_2, pH 3·5	82
Zr	I	ML_4, pH 4·8–5·0	83*
	VIII	ML, ML_2	84
	XI		94*
	XI, XV	ML, ML_2	82, 95*

* Denotes determination.

Germanium

Germanium is reported to form two complexes in aqueous solution—$Ge(OH)_2L_2$ and GeL_3^+—the stability constants for which are given.[57] The sensitive colour reaction between germanium and 3-hydroxytropolone, in which a 1:3 complex is formed, has been used in a spectrophotometric method for the determination of the element.[76]

A 1:2 complex with purpurogallin, stabilized in solution by the addition of gelatin, has been utilized for the determination of germanium in flue-dust. As the complex is formed in 3*N* acid, most of the common ions do not interfere.[77,78]

Molybdenum

Molybdenum forms 1:1 and 1:2 complexes with α-carboxy-β-methyltropolone at low pH, which dissociate as the pH is raised.[84] Both dimethylpurpurogallin and 3′,4′-dihydroxybenzotropolone form 1:1 complexes with molybdenum(VI) which are stable in the pH range 2·5–3·5.

Purpurogallin and its derivatives precipitate molybdenum(VI) quantitatively from 1*M* hydrochloric acid containing ammonium nitrate, thus effecting a separation from thorium, uranium, rare-earths *etc.* In the presence of fluoride, separation from titanium and zirconium is possible at pH 3·5.[99] In aqueous ethanolic medium, the precipitate is soluble, and the purple colour may be made the basis of a spectrophotometric method for the element.[82]

TABLE IV.—STABILITY CONSTANTS*

Metal	Method	Temp.	Medium	Log of equilibrium constant, remarks	Ref.
$C_7H_6O_2$	**Tropolone**				
H^+	gl	30	50% dioxan	K_1 8·12	19, 20
	dis	25	0·1($NaClO_4$)	K_1 6·71	9
	sp	—	0·5Na(H)Cl	K_1 6·67, K_2 −0·53	57
	sp	—	—	K_1 6·42	53
Be^{2+}	gl	30	50% dioxan	K_1 8·4, K_2 7·0	19, 20
Ca^{2+}	gl	30	50% dioxan	K_1 4·8, K_2 3·2	19
Co^{2+}	gl	30	50% dioxan	K_1 7·0, K_2 5·9, K_3 3·8	19
Cu^{2+}	gl	30	50% dioxan	K_2 7·9	19
Fe^{3+}	sp	—	—	K_1 11·0	49
	sp	—	—	K_1 10·51	53
Ge^{4+}	sp	—	0·5Na(H)Cl	$K(Ge(OH)_4 + 2HL \rightleftharpoons Ge(OH)_2L_2)$8·03	57
				$K(Ge(OH)_4 + 3HL + H^+ \rightleftharpoons GeL_3^+)$13·3	57
Mg^{2+}	gl	30	50% dioxan	K_1 5·5, K_2 4·4	19
Ni^{2+}	gl	30	50% dioxan	K_1 7·7, K_2 6·1, K_3 4·0	19, 20
Pb^{2+}	gl	30	50% dioxan	K_1 8·0, K_2 6·00	19
Th^{4+}	dis	25	0·1($NaClO_4$)	K_1 9·61, K_2 8·63, K_3 7·65, K_4 6·67, K_5 2·29, K_6 1·87	44
	dis	25	0·1($NaClO_4$)	K_2 7·43, K_3K_4 13·96, K_5K_6 4·34	46
Zn^{2+}	gl	30	50% dioxan	K_1 7·5, K_2 6·5, K_3 3·5	19
$C_8H_8O_2$	**β-Methyltropolone**				
H^+	sp	—	0·2($NaClO_4$)	K_1 7·07	42
	gl	—	0·5(KNO_3) 50% C_2H_5OH	K_1 7·46	55
	gl		0·1($NaClO_4$)	K_1 7·55	56
			40% dioxan		20
	gl	30	50% dioxan	K_1 8·69	20
Be^{2+}	gl	30	50% dioxan	K_1 9·4, K_2 7·7	20
Ca^{2+}	gl	30	50% dioxan	K_1 5·3, K_2 3·6	20
Ce^{3+}	sp	—	0·2($NaClO_4$)	K_1 6·12	42
Co^{2+}	gl	30	50% dioxan	K_1 7·9, K_2 6·2	20
Dy^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·36	42
Er^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·57	42
Fe^{3+}	sp	—	0·1($NaClO_4$) 40% dioxan	K_1 11·88, K_2 10·94, K_3 9·60	56
Gd^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·10	42
Ho^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·42	42
La^{3+}	sp	—	0·2($NaClO_4$)	K_1 6·12	42
Lu^{3+}	sp	—	0·2($NaClO_4$)	K_1 8·01	42
Mg^{2+}	gl	30	50% dioxan	K_1 6·0, K_2 4·6, K_3 3·1	20
Nd^{3+}	sp	—	0·2($NaClO_4$)	K_1 6·78	42
Ni^{2+}	gl	30	50% dioxan	K_1 8·4, K_2 6·6, K_3 4·1	20
Pb^{2+}	gl	30	50% dioxan	K_1 9·6, K_2 6·6	20
Pr^{3+}	sp	—	0·2($NaClO_4$)	K_1 6·71	42
Sm^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·07	42
UO_2^{2+}	sp	—	0·5(KNO_3) 50% C_2H_5OH	K_1 9·62, K_2 6·98	55
	gl	—	0·5(KNO_3) 50% C_2H_5OH	K_2 6·93	55
Y^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·38	42
Yb^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·74	42
Zn^{2+}	gl	30	50% dioxan	K_1 8·4, K_2 6·8, K_3 3·6	20

---

* The style of *Stability Constants*, eds. L. G. Sillén and A. E. Martell, Spec. Publn. No. 17, Chem. Soc. London, 1964, is used for convenience in collation. Some constants are taken from that publication by permission.

TABLE IV (*Contd.*)

Metal	Method	Temp.	Medium	Log of equilibrium constant, remarks	Ref.
$C_7H_6O_5S$	**5-Sulphotropolone**				
H^+	sp	—	—	K_1 4·66	50
	sp	25	—	K_1 5·07	53
Fe^{3+}	sp	—	—	K_1 8·72, K_2 7·43, K_3 5·72	52, 53
Th^{4+}	sp	—	—	K_1 7·95, K_2 6·15	51
UO_2^{2+}	sp	25	—	K_1 6·86, K_2 4·66	50
$C_8H_5O_2N$	**5-Cyanotropolone**				
H^+	sp	25	2·0*M*	K_1 3·72	54
Fe^{3+}	sp	25	2·0*M*	K_1 7·56	54
$C_7H_5O_2Cl$	**5-Chlorotropolone**				
H^+	sp	—	—	K_1 5·62	53
Fe^{3+}	sp	—	—	K_1 9·92	53
$C_7H_5O_2Br$	**5-Bromotropolone**				
H^+	sp	—	—	K_1 5·54	53
Fe^{3+}	sp	—	—	K_1 9·74	53
$C_7H_5O_4N$	**5-Nitrotropolone**				
H^+	sp	—	—	K_1 2·64	53
Fe^{3+}	sp	—	—	K_1 6·56	53
$C_{10}H_{12}O_2$	**β-Isopropyltropolone**				
H^+	dis	25	0·1($NaClO_4$)	K_1 7·04	45
	sp	—	0·2($NaClO_4$)	K_1 7·01	42
	sp	—	0·1($NaClO_4$) 40% dioxan	K_1 7·55	56
	gl	—	0·5(KNO_3) 50% C_2H_5OH	K_1 7·42	55
	gl	25	50% C_2H_5OH	K_1 7·66	21
	gl	30	50% dioxan	K_1 8·70	20
Ba^{2+}	dis	25	0·1($NaClO_4$)	K_1 1·87, K_2 0·87	45
Be^{2+}	gl	30	50% dioxan	K_1 9·1, K_2 7·5	20
Ca^{2+}	gl	30	50% dioxan	K_1 5·4, K_2 3·6	20
	dis	25	0·1($NaClO_4$)	K_1 2·77, K_2 1·77	45
Cd^{2+}	dis	25	0·1($NaClO_4$)	K_1 5·27, K_2 4·67, K_3 3·78	45
Ce^{3+}	sp	—	0·2($NaClO_4$)	K_1 6·53	42
Co^{2+}	gl	30	50% dioxan	K_1 7·9, K_2 6·3, K_3 3·8	20
	dis	25	0·1($NaClO_4$)	K_1 5·8, K_2 5·0	45
Cu^{2+}	dis	25	0·1($NaClO_4$)	K_1 9·55, K_2 8·75	45
	pol	30	50% C_2H_5OH	β_3 9·4	43
	gl	25	50% C_2H_5OH	K_1 6·71, K_2 4·0	21
Dy^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·33	42
Er^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·49	42
Fe^{3+}	sp	—	0·1($NaClO_4$), 40% dioxan	K_1 11·80, K_2 10·96, K_3 9·54	56
	sp	—	1·0(Na, H)ClO_4	K_1K_a 4·04, K_2K_a 4·11, K_3K_a 2·36	45
Gd^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·15	42
Ho^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·40	42
La^{3+}	sp	—	0·2($NaClO_4$)	K_1 6·29	42
Lu^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·95	42
Mg^{2+}	gl	30	50% dioxan	K_1 6·2, K_2 4·8, K_3 3·0	20
Nd^{3+}	sp	—	0·2($NaClO_4$)	K_1 6·70	42
Ni^{2+}	gl	30	50% dioxan	K_1 8·5, K_2 6·5, K_3 4·0	20
	gl	25	50% C_2H_5OH	K_1 6·08, K_2 5·30, K_3 3·60	21
	dis	25	0·1($NaClO_4$)	K_1 5·90, K_2 5·20	45

TABLE IV (*Contd.*)

Metal	Method	Temp.	Medium	Log of equilibrium constant, remarks	Ref.
$C_{10}H_{12}O_2$	**β-Isopropyltropolone**				
Pb^{2+}	gl	30	50% dioxan	K_1 9·7, K_2 6·7	20
	gl	25	50% C_2H_5OH	K_1 5·81, K_2 4·45	21
Pr^{3+}	sp	—	0·2($NaClO_4$)	K_1 6·74	42
Sm^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·04	42
Sr^{2+}	dis	25	0·1($NaClO_4$)	K_1 2·70, K_2 1·70	45
Th^{4+}	sp	25	0·01, 50% C_2H_5OH	β_4 31·17	83
Ti^{4+}	sp	25	0·01, 50% C_2H_5OH	β_2 21·17, β_3 28·95	83, 85
UO_2^{2+}	dis	25	0·1($NaClO_4$)	K_1 9·5, K_2 8·5	45
	sp	—	0·5(KNO_3) 50% C_2H_5OH	K_1 9·62, K_2 6·92	55
	gl	—	0·5(KNO_3) 50% C_2H_5OH	K_2 6·88	55
Y^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·28	42
Yb^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·62	42
Zn^{2+}	dis	25	0·1($NaClO_4$)	K_1 6·18, K_2 5·38, K_3 3·44	45
	gl	25	50% C_2H_5OH	K_1 5·14, K_2 2·90	21
	gl	30	50% dioxan	K_1 8·7, K_2 7·0, K_3 3·6	20
Zr^{4+}	sp	25	0·01, 50% C_2H_5OH	β_4 20·46	83
$C_9H_8O_4$	**α-Carboxy-β-methyltropolone**				
H^+	gl	—	0·1($NaClO_4$)	K_1 7·40, K_2 2·50	56
	gl	—	0·5(KNO_3)	K_1 7·31, K_2 2·68	55
	sp	—	0·2($NaClO_4$)	K_1 7·45	39
	gl	—	0·2($NaClO_4$)	K_1 7·45, K_2 2·48	40, 41
Ba^{2+}	sp	—	0·2($NaClO_4$)	K_1 2·43	39
Ca^{2+}	sp	—	0·2($NaClO_4$)	K_1 3·05	39
Cd^{2+}	sp	—	0·2($NaClO_4$)	K_1 5·23	39
	gl	—	0·2($NaClO_4$)	K_1 5·28, K_2 3·83	39
Ce^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·20, $K(Ce^{3+} + L^{2-} + H^+ \rightleftharpoons CeHL^{2+})$9·85	41
	gl	—	0·2($NaClO_4$)	K_1 7·42, K_2 5·72, K_3 3·34	40
Co^{2+}	sp	—	0·2($NaClO_4$)	K_1 6·07	39
	gl	—	0·2($NaClO_4$)	K_1 6·30, K_2 4·82, K_3 2·82	39
Cu^{2+}	sp	—	0·2($NaClO_4$)	K_1 9·32	39
Dy^{3+}	gl	—	0·2($NaClO_4$)	K_1 8·28, K_2 6·78, K_3 4·00	40
Er^{3+}	sp	—	0·2($NaClO_4$)	K_1 8·65, $K(Er^{3+} + L^{2-} + H^+ \rightleftharpoons ErHL^{2+})$10·78	41
	gl	—	0·2($NaClO_4$)	K_1 8·35, K_2 6·85, K_3 4·18	40
Fe^{3+}	sp	—	0·1($NaClO_4$)	K_1 11·65, K_2 10·25, K_3 6·9	56
Gd^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·91, $K(Gd^{3+} + L^{2-} + H^+ \rightleftharpoons GdHL^{2+})$10·56	41
	gl	—	0·2($NaClO_4$)	K_1 8·02, K_2 6·38, K_3 3·82	40
Ho^{3+}	sp	—	0·2($NaClO_4$)	K_1 8·58, $K(Ho^{3+} + L^{2-} + H^+ \rightleftharpoons HoHL^{2})$10·62	41
	gl	—	0·2($NaClO_4$)	K_1 8·24, K_2 6·76, K_3 3·98	40
La^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·07, $K(La^{3+} + L^{2-} + H^+ \rightleftharpoons LaHL^{2+})$9·48	41
	gl	—	0·2($NaClO_4$)	K_1 7·20, K_2 5·56, K_3 3·40	40
Lu^{3+}	sp	—	0·2($NaClO_4$)	K_1 8·85, $K(Lu^{3+} + L^{2-} + H^+ \rightleftharpoons LuHL^{2+})$10·97	41
	gl	—	0·2($NaClO_4$)	K_1 8·64, K_2 7·06, K_3 4·60	40
Mg^{2+}	sp	—	0·2($NaClO_4$)	K_1 4·14	39
Mn^{2+}	sp	—	0·2($NaClO_4$)	K_1 4·96	39
Nd^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·69, $K(Nd^{3+} + L^{2-} + H^+ \rightleftharpoons NdHL^{2+})$10·14	41
	gl	—	0·2($NaClO_4$)	K_1 7·76, K_2 6·04, K_3 3·70	40

TABLE IV (*Contd.*)

Metal	Method	Temp.	Medium	Log of equilibrium constant, remarks	Ref.
$C_9H_8O_5$	**α-Carboxy-β-methyltropolone**				
Ni^{2+}	sp	—	0·2($NaClO_4$)	K_1 6·73	39
	gl	—	0·2($NaClO_4$)	K_1 6·83, K_2 5·22, K_3 3·11	39
Pr^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·45($Pr^{3+} + L^{2-} + H^+ \rightleftharpoons PrHL^{2+}$)10·07	41
	gl	—	0·2($NaClO_4$)	K_1 7·74, K_2 5·96, K_3 3·56	40
Sm^{3+}	sp	—	0·2($NaClO_4$)	K_1 7·99, K($Sm^{3+} + L^{2-} + H^+ \rightleftharpoons SmHL^{2+}$)10·36	41
	gl	—	0·2($NaClO_4$)	K_1 7·98, K_2 6·42, K_3 3·78	40
Sr^{2+}	sp	—	0·2($NaClO_4$)	K_1 2·61	39
UO_2^{2+}	sp	—	0·5(KNO_3)	K_1 9·22, K_2 6·75	55
	gl	—	0·5(KNO_3)	K_2 6·80	55
	sp	—	0·2($NaClO_4$)	K_1 9·60	39
	gl	—	0·2($NaClO_4$)	K_1 9·72, K_2 6·78	39
Y^{3+}	sp	—	0·2($NaClO_4$)	K_1 8·47, K($Y^{3+} + L^{2-} + H^+ \rightleftharpoons YHL^{2+}$)10·61	41
	gl	—	0·2($NaClO_4$)	K_1 8·26, K_2 6·62, K_3 3·96	40
Yb^{3+}	sp	—	0·2($NaClO_4$)	K_1 8·85, K($Yb^{3+} + L^{2-} + H^+ \rightleftharpoons YbHL^{2+}$)10·97	41
	gl	—	0·2($NaClO_4$)	K_1 8·60, K_2 7·00, K_3 4·42	40
Zn^{2+}	sp	—	0·2($NaClO_4$)	K_1 6·52	39
	gl	—	0·2($NaClO_4$)	K_1 6·68, K_2 5·44, K_3 3·24	39

Thorium

Dyrssen and Rydberg[44,46] used the distribution technique to investigate the complexes of thorium with tropolone, and from their data calculated the stepwise formation constants for the complexes 1:1–1:6. Thorium may be separated from tervalent ions—in particular from the lanthanides—by extraction as the β-isopropyltropolone complex from solutions of low pH.[45] Absorption by the 1:4 complex in the ultraviolet has been used for a spectrophotometric determination.[83] Thorium has also been determined spectrophotometrically as the 1:2 complex with tropolone-5-sulphonic acid at pH 2·9.[51] Complexes have been reported of thorium with α-carboxy-β-methyltropolone[84] (1:1, 1:2, and 1:3) and with 3′,4′-dihydroxybenzotropolone and dimethylpurpurogallin (1:1 and 1:2).[82] Purpurogallin and its derivatives precipitate thorium in the pH range 2·5–6·0, enabling the element to be separated from the rare-earths.

Titanium

In dilute hydrochloric acid, an intensely yellow complex is formed between titanium and β-isopropyltropolone. The existence of 1:2 and 1:3 complexes has been suggested[83,85] and studies using Job's method also suggest the existence of a 1:4 complex,[86] though as Watkins and Jones have pointed out[87] the maximum absorbance may not correspond to the M:L ratio for a given complex when a series of complexes is formed, and the existence of a 1:4 complex therefore seems rather doubtful.

The 1:3 complex of titanium with tropolone is soluble in chloroform, so it must have zero charge. Dyrssen[45] has reported the extraction of β-isopropyltropolone complexes of a number of metals, which contain a molecule of the tropolone in the acid form as an adduct. The titanium compound should be formulated $TiOL_2 . LH$.

In ethanol and other oxygenated solvents, this molecule may be replaced by a solvent molecule which would account for the formation only of a 1:2 complex in solutions of high ethanol content. An alternative suggestion is that of a dimer which Muetterties and Wright found to be soluble in chlorinated hydrocarbons, and formulated as $L_3TiO{\cdot}TiL_3$.[34]

The position of the absorption band of the complex shifts to higher wavelengths with increase in ligand concentration, which is characteristic of charge-transfer bands.[88,89] The position of the band is also solvent-dependent, again typical of charge-transfer complexes.[90]

Uranium

A series of complexes are formed with tropolone, and the 1:3 complex, which is extractable into chloroform, has the composition $UO_2L_2{\cdot}LH$.[45] The 1:2 complex with tropolone sulphonic acid, formed in the pH range 3·4–4·2, has been used for a spectrophotometric determination of uranium.[50] Complexes with other derivatives have also been reported.[55] A very sensitive colour reaction is given by dimethylpurpurogallin and uranium in the formation of a 1:1 complex[82] in the pH range 6–8. A spectrophotometric determination is possible, but many other ions interfere.

The absorption band is attributed to charge-transfer from the oxygen atoms in the uranyl group.[91,92] A solvent effect in the presence of pyridine has been made use of in a spectrophotometric determination.[93]

Zirconium

A 1:4 complex has been reported as being formed with β-isopropyltopolone in the pH range 4·8–5·0, and has been used for the spectrophotometric determination of the element.[83] Purpurogallin and its derivatives precipitate zirconium from 1*M* hydrochloric acid solution, allowing a separation from thorium, uranium and rare-earths to be made.[81] The parent compound can precipitate the metal from solutions as dilute as $10^{-5}M$ at an acid concentration of 0·1*N*.[82] A spectrophotometric determination with this reagent is also possible[94] and suffers from very few interferences. Coloured complexes are also formed with 3′,4′-dihydroxybenzotropolone[95] which may be used as a spectrophotometric reagent. The most stable complexes of the tropolones are those with zirconium.

CONCLUSION

The most recent work in the chemistry of the chelates of the tropolones is in the field of mixed complexes with various β-diketones and other donor molecules, particularly in connection with solvent extraction techniques.[96,97]

Of the many possible analytical applications of the tropolones, a few may be mentioned as being potentially useful. The spectrophotometric determinations of iron(III), niobium(V), and germanium with tropolone, and of zirconium and germanium with purpurogallin, and the gravimetric determinations of zirconium and molybdenum with purpurogallin all have very few interferences and at the same time offer good sensitivity.

Separations of thorium and uranium from the rare-earths by solvent-extraction of the tropolone complexes could be useful in the reprocessing of nuclear fuels.

The increasing stabilities of the rare-earth complexes with tropolones with atomic number could be used in conjunction with ion-exchange chromatography as a means of separating these elements.

Zusammenfassung—Eine Übersicht über die analytischen Anwendungen von Tropolon und seinen Derivaten.

Résumé—Une revue des applications analytiques de la tropolone et de ses dérivés.

REFERENCES

1. M. J. S. Dewar, *Nature*, 1945, **155**, 50.
2. P. L. Pauson, *Chem. Rev.*, 1955, **55**, 9.
3. J. W. Cook and J. D. Loudon, *Quart. Rev. London*, 1951, **5**, 99.
4. T. Nozoe, *Non-Benzenoid Aromatic Compounds*, ed. Ginsburg, p. 339. Interscience, New York, 1959.
5. *Idem*, *Progr. Chem. Org. Natural Products*, 1956, **13**, 232.
6. D. Lloyd, *Carbocyclic Non-Benzenoid Aromatic Compounds*, p. 117. Elsevier, Amsterdam, 1966.
7. W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, 1951, **73**, 828.
8. N. Yui, *Sci. Rep. Tohoku Univ. First Ser.*, 1956, **40**, 102.
9. D. Dyrssen, *Acta Chem. Scand.*, 1954, **8**, 1394.
10. J. M. Robertson, *J. Chem. Soc.*, 1951, 1222.
11. W. M. Macintyre, J. M. Robertson and R. F. Zahrobsky, *Proc. Roy. Soc. London, A*, 1965, **289**, 161.
12. G. J. WERKEMA, *Dissert. Abstr.*, 1966, **26**, 6398.
13. T. Nozoe, T. Mukai and J. Minigishi, *Proc. Japan Acad.*, 1952, **28**, 287.
14. W. von E. Doering and C. F. Hiskey, *J. Am. Chem. Soc.*, 1952, **74**, 5688.
15. W. von E. Doering and J. R. Mayer, *ibid.*, 1953, **75**, 2387.
16. R. D. Haworth and P. B. Tinker, *J. Chem. Soc.*, 1955, 911.
17. T. Nozoe, *Bull. Chem. Soc. Japan*, 1936, **11**, 295.
18. H. Iinuma, *Nippon Kagaku Zasshi*, 1943, **64**, 742.
19. B. E. Bryant, W. C. Fernelius and B. E. Douglas, *J. Am. Chem. Soc.*, 1953, **75**, 3784.
20. B. E. Bryant and W. C. Fernelius, *ibid.*, 1954, **76**, 1696, 3783, 4864.
21. K. Pan and T. M. Hseu, *J. Chinese Chem. Soc. Taiwan*, 1955, **2**, 23.
22. H. Irving and R. J. P. Williams, *Nature*, 1948, **162**, 746.
23. H. Iinuma, *Nippon Kagaku Zasshi*, 1943, **64**, 91.
24. *Idem*, *Gifu Daigaku Kogakubu Kenkyu Hokoku*, 1951, **1**, 41.
25. T. M. Hseu, *Formosan Sci.*, 1954, **8**, 57.
26. B. P. Gupta, Y. Dutt and R. P. Singh, *Indian J. Chem.*, 1967, **5**, 322.
27. *Idem*, *J. Indian Chem. Soc.*, 1966, **43**, 610.
28. *Idem*, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1806.
29. S. Chaberek and A. E. Martell, *Organic Sequestering Agents*, p. 47. Wiley, New York, 1959.
30. B. P. Gupta, Y. Dutt and R. P. Singh, *Indian J. Chem.*, 1967, **5**, 214.
31. B. C. Nair, Y. Dutt, B. P. Gupta and R. P. Singh, unpublished work.
32. E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, 1964, **86**, 5132.
33. *Idem*, *ibid.*, 1965, **87**, 21.
34. *Idem*, *ibid.*, 1965, **87**, 4706.
35. E. L. Muetterties, *ibid.*, 1966, **88**, 305.
36. E. L. Muetterties, H. Roesky and C. M. Wright, *ibid.*, 1966, **88**, 4856.
37. E. L. Muetterties, *Pure Appl. Chem.*, 1965, **10**, 53.
38. D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, 1963, **39**, 3513.
39. B. P. Gupta, Y. Dutt and R. P. Singh, *Indian J. Chem.*, 1967, **5**, 322.
40. *Idem*, *J. Indian Chem. Soc.*, 1966, **43**, 610.
41. *Idem*, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1806.
42. *Idem*, *Indian J. Chem.*, 1967, **5**, 214.
43. Z. F. Lin, *Formosan Sci.*, 1954, **8**, 63.
44. D. Dyrssen, *Acta Chem. Scand.*, 1955, **9**, 1567.
45. *Idem*, *Trans. Roy. Inst. Technol. Stockholm.* No. 188, 1962.
46. J. Rydberg, *Acta Chem. Scand.*, 1960, **14**, 157.
47. D. Dyrssen, *J. Inorg. Nucl. Chem.*, 1958, **8**, 291.
48. *Idem*, *Rec. Trav. Chim.*, 1956, **75**, 753.

49. Y. Oka and S. Matsuo, *Sci. Rep. Res. Inst. Tohoku Univ., A*, 1958, **10**, 299.
50. Y. Oka, K. Yamamoto and M. Katagiri, *Nippon Kagaku Zasshi*, 1963, **84**, 259.
51. Y. Oka, and M. Umehara, *ibid.*, 1963, **84**, 928.
52. Y. Oka, M. Umehara and T. Nozoe, *ibid.*, 1962, **83**, 703.
53. *Idem*, *ibid.*, 1962, **83**, 1197.
54. Y. Oka and K. Yamamoto, *ibid.*, 1964, **85**, 779.
55. Y. Dutt and R. P. Singh, *J. Indian Chem. Soc.*, 1965, **42**, 767.
56. *Idem*, *Indian J. Chem.*, 1966, **4**, 214.
57. A. Beauchamp and R. L. Benoit, *Can. J. Chem.*, 1966, **44**, 1615.
58. B. E. Bryant, J. C. Pariand and W. C. Fernelius, *J. Org. Chem.*, 1954, **19**, 1889.
59. J. W. Cook, A. R. Gibb, R. A. Raphael and A. R. Somerville, *Chem. Ind. London*, 1950, 427.
60. *Idem*, *J. Chem. Soc.*, 1951, 503.
61. W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, 1950, **72**, 2305.
62. E. E. van Tamelen and G. T. Hildahl, *ibid.*, 1956, **78**, 4405.
63. O. L. Chapman and P. Fitton, *ibid.*, 1963, **85**, 41.
64. A. P. ter Borg, R. van Helden and A. F. Bickel, *Rec. Trav. Chim.*, 1962, **81**, 17; 1962, **81**, 177.
65. T. Nozoe, T. Mukai and K. Takase, *ibid.*, 1955, **39**, 164.
66. T. Nozoe, T. Mukai, J. Minigishi and J. Fujisawa, *Sci. Rep. Tohoku Univ. First Ser.*, 1953, **37**, 388.
66. T. Nozoe, T. Mukai and K. Takase, *ibid.*, 1955, **39**, 164.
67. J. J. Drysdale, W. W. Gilbert, H. K. Sinclair and W. H. Sharkey, *J. Am. Chem. Soc.*, 1958, **80**, 245 and 3672.
68. T. Nozoe, S. Seto, T. Ikemi and T. Arai, *Proc. Japan Acad.*, 1951, **27**, 24.
69. R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, 1951, 561.
70. W. D. Crow, R. D. Haworth and P. R. Jefferies, *ibid.*, 1952, 3705.
71. T. W. Evans and W. M. Dehn, *J. Am. Chem. Soc.*, 1930, **52**, 3647.
72. A. G. Perkin and A. B. Steven, *J. Chem. Soc.*, 1903, **83**, 192.
73. W. D. Crow and R. D. Haworth, *ibid.*, 1951, 1325.
74. M. Murakami, K. Suzuki and E. Mishima, *Nippon Kagaku Zasshi*, 1954, **75**, 620.
75. R. D. Haworth, B. P. Moore and P. L. Pauson, *J. Chem. Soc.*, 1948, 1045.
76. Y. Oka and S. Matsuo, *Sci. Rep. Res. Inst. Tohoku Univ. A*, 1956, **8**, 532.
77. V. A. Nazarenko and E. N. Poluektova, *Zh. Analit. Khim.*, 1964, **19**, 1459.
78. H. H. Shih, C. C. Li and C. C. Chang, *Hua Hsueh Hsueh Pao*, 1961, **27**, 10.
79. R. Püschel and E. Lassner, *Chelates in Analytical Chemistry*, ed. H. Flaschka and A. J. Barnard, Dekker, New York, 1967.
80. A. K. Babko and B. I. Nabivanets, *Zh. Neorgan. Khim.*, 1957, **2**, 2096.
81. Y. Dutt and R. P. Singh, *Indian J. Appl. Chem.*, 1963, **26**, 77.
82. Y. Dutt, *Ph.D. Thesis*, Delhi University, 1965.
83. T. M. Hsu, *J. Chinese Chem. Soc. Taiwan*, 1961, **8**, 33.
84. Y. Dutt and R. P. Singh, *J. Indian Chem. Soc.*, 1966, **43**, 107.
85. T. M. Hsu, *J. Chinese Chem. Soc. Taiwan*, 1960 **7**, 124.
86. Y. Dutt and R. P. Singh, *Indian J. Chem.*, 1966, **4**, 424.
87. K. O. WATKINS and M. M. Jones, *J. Inorg. Nucl. Chem.*, 1962, **24**, 1607.
88. H. Fromherz and K. H. Lih, *Z. Phys. Chem. Leipzig, A*, 1931, **153**, 321.
89. L. E. Orgel, *Quart. Rev. London*, 1954, **8**, 422.
90. J. Bjerrum, A. W. Adamson and O. Bostrup, *Acta Chem. Scand.*, 1956, **10**, 329.
91. C. K. Jørgensen, *ibid.*, 1957, **11**, 175.
92. Z. Libus, *J. Inorg. Nucl. Chem.*, 1962, **24**, 619.
93. D. Dyrssen and S. Ekberg, *Acta Chem. Scand.*, 1962, **16**, 785.
94. I. P. Alimarin, I. V. Puzdrenova and S. Y. Dolnikova, *Zh. Analit. Khim.*, 1962, **17**, 700.
95. Y. Dutt and R. P. Singh, *Indian J. Chem.*, 1963, **1**, 471.
96. T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, 1964, **26**, 1727 and 2013.
97. *Idem*, *ibid.*, 1967, **29**, 1457, 1475 and 1489.
98. J. Selbin and J. D. Ortego, *J. Inorg. Nucl. Chem.*, 1968, **30**, 313.
99. Y. Dutt and R. P. Singh, *Current Sci. India*, 1966, **35**, 122.
100. A. Tchakirian and P. Barillard, *Compt. Rend.*, 1951, **233**, 256.
101. B. P. Gupta, Yag Dutt and R. P. Singh, unpublished work.

Talanta, 1969, Vol. 16, pp. 1383 to 1391. Pergamon Press. Printed in Northern Ireland

MICRODETERMINATION OF NITRATES AND NITRAMINES—I

TITRIMETRIC METHODS BASED ON THE REDUCTION WITH IRON(II), TITANIUM(III), AND A MIXTURE OF BOTH

WILLIAM IBRAHIM AWAD and SAAD S. M. HASSAN
Research Microanalytical Laboratories, Chemistry Department,
Faculty of Science, Ain Shams University, Cairo, U.A.R.

(*Received* 13 *September* 1968. *Revised* 24 *March* 1969. *Accepted* 23 *April* 1969)

Summary—Organic and inorganic nitrates are satisfactorily determined on the microscale by reduction with Fe(II). Titanium(III) reduces the nitrates in strongly acidic, citrate-buffered, and acetate-buffered media with the comsumption of 3, 6 and 8 equivalents respectively of Ti(III) per nitrate group. Nitramines are determined by reduction with a mixture of Ti(III) and Fe(II). Determination of nitrates and nitramines by *trans*-nitration with salicylic acid is suitable on the microscale. A new electrolytic reduction automatic microburette was devised for the reduction, storage and use of the titanium(III) solution.

DETERMINATION of the nitrate group in both organic and inorganic substances by the commonly used methods can lead to many difficulties, and little information is available about the microdetermination of this group. The titrimetric methods that have been proposed are based on reduction with Devarda's alloy,[1,2] iron(II),[3,4] vanadium(II),[5] chromium(II),[6,7] tin(II),[8,9] and titanium(III).[10,11] Acid-base titration in non-aqueous media has been also described.[12] However, most of these methods are either applied on the macro scale or to inorganic nitrates only.

In the present work, micro-methods involving iron(II), titanium(III), and a mixture of both are examined.

EXPERIMENTAL

Apparatus

A new electrolytic reduction automatic microburette has been devised (Fig. 1). The new burette is used as follows. Titanium(IV) sulphate solution[13] (0·1*M*, 500 ml), is introduced into the burette reservoir and the electrodes are inserted and connected to a 6-V battery as shown, with cathode immersed. After 3–4 hr reduction the electrodes are removed and the solution is diluted to about 0·05*M* with freshly twice distilled water. About 150 g of amalgamated zinc, 10 ml of concentrated sulphuric acid and 30 g of ammonium sulphate are added and carbon dioxide is bubbled through slowly overnight. A stream of carbon dioxide from a cylinder is passed for 5 min *via* tap T_1 and B with taps T_2 and T_3 open, in order to displace the air from D, B and the burette. The two free necks of the reservoir are then closed with stoppers and tap T_1 is connected *via* C so that the carbon dioxide forces the titanium solution in the flask into the burette through E. The burette is washed out several times in this way. This procedure is applied after every reduction. For titrations the burette is filled and the pressures inside and outside the reservoir are equalized by switching tap T_1 several times between B and C, and then the tap is left connected *via* B throughout the titration.

Reagents

All the reagents were of analytical grade unless otherwise specified. The *trans*-nitration mixture consisted of 50 g of salicylic acid, 450 ml of concentrated sulphuric acid and 50 ml of glacial acetic acid.

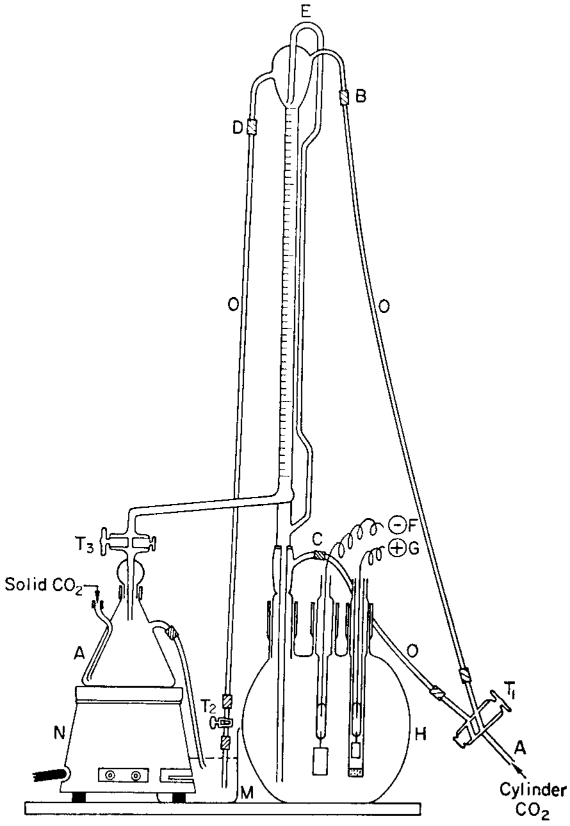


FIG. 1.—Electrolytic reduction automatic microburette.
(A) Reaction vessel; (F) and (G) platinum electrodes; (T_1) three-way tap; (H) 2-l flask; (N) magnetic stirrer; (O) polythene tubing; (M) water trap.

The nitrate and nitramine samples were MAR potassium nitrate, and nitroguanidine, nitrobiuret, urea nitrate, guanidine nitrate and nitron nitrate prepared in this department as very pure samples for analysis (confirmed by Dumas method). Pentaerythritol tetranitrate (PETN), cellulose trinitrate and hexahydro-1,3,5-trinitro-*s*-triazine (RDX) were standard samples of purity not less than 99% (confirmed by the nitrometer method).

Procedure

Iron(II) reduction method. Weigh accurately 2–5 mg of dry sample into a 100-ml flask provided with an inlet tube for carbon dioxide (*A* in Fig. 1). Dissolve the sample in acetone, add 5 ml of concentrated hydrochloric acid and sweep out the air with carbon dioxide for 5 min. Add 10 ml of 0·04*M* iron(II) ammonium sulphate for inorganic nitrates, or 10 ml of 0·15*M* for organic ones, and then 2 drops of 10% ammonium molybdate solution. Boil for 5 min, cool, add 30 ml of 1*M* hydrochloric acid, 3 ml of 75% phosphoric acid and 3 drops of diphenylbenzidine indicator (1% in conc. sulphuric acid). Titrate with 0·05*N* potassium dichromate to the first appearance of a permanent violet colour. Carry out a blank. Calculate the nitrate content on the basis that 3 moles of iron(II) are used per mole of nitrate group.

Titanium(III) reduction method. Dissolve 2–5 mg of sample in acetone. Add 5 ml of concentrated hydrochloric acid and then 10 ml of 0·04*M* titanium(III) sulphate after displacing the air with carbon dioxide for 5 min. Boil the solution for 2 min, cool, and titrate the excess of titanium(III) with 0·04*M* iron(III) ammonium sulphate. Add 0·5 ml of 10% ammonium thiocyanate solution near the end-point. Carry out a blank. Calculate the nitrate content on the basis that 3 moles of titanium(III) are required per mole of nitrate group.

Iron(II) and titanium(III) reduction method. Dissolve the nitramine sample (3–5 mg) in 1 ml of acetic acid, stirring and heating if necessary. Add 5 ml of concentrated hydrochloric acid, displace the air with carbon dioxide for 5 min and add 10 ml of 0·05*M* titanium(III) sulphate and about 0·5 g of iron(II) ammonium sulphate. Boil for 3 min, cool and titrate the excess of titanium(III) as described above. Four moles of titanium(III) are required per mole of nitramine group.

Trans-*nitration method.* Dissolve the nitrate or nitramine (3–5 mg) in 2–4 ml of the *trans*-nitration mixture, add about 5 mg of anhydrous aluminium chloride and warm gently till dissolution is complete. Add 10 ml of 75% sodium citrate solution and 10 ml of 0·04*M* titanium(III) sulphate. Boil for 3 min, cool, add 10 ml of 6*M* sulphuric acid and titrate the remaining titanium(III) as above. Six moles of titanium(III) are used per nitrate or nitramine group.

RESULTS AND DISCUSSION

Iron(II) *reduction*

When a nitrate and a known amount of iron(II) solution were boiled with hydrochloric acid of different strengths and the remaining iron(II) was determined after intervals of time, it was found that quantitative reduction took place in 15 min if 12*M* acid was used. The extent of reduction decreased with decreasing acid concentration (Fig. 2).

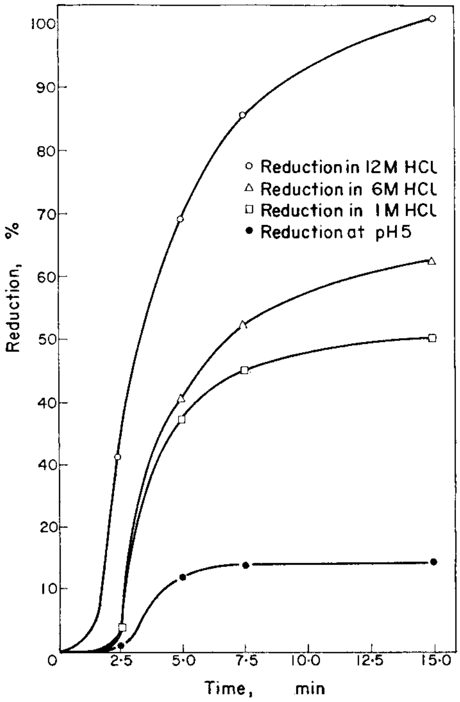


FIG. 2.—Reduction of potassium nitrate with iron(II) ammonium sulphate in different concentrations of hydrochloric acid.

When ammonium molybdate was used as catalyst, reduction was quantitative after about 2 min boiling when 12*M* hydrochloric acid was used and after 5 min boiling with the 6*M* acid (Fig. 3). Ammonium vanadate and tungstate had very low catalytic effect. The chloride ions may also have some effect on the rate of reaction, as shown by the results obtained with sulphuric acid (Fig. 4); addition of a small amount of sodium chloride increased the rate of reduction.

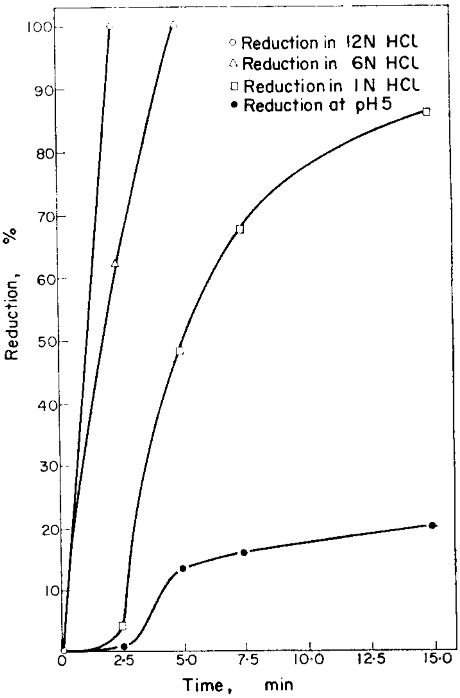


FIG. 3.—The catalytic effect of ammonium molybdate on the reduction of potassium nitrate with iron(II) ammonium sulphate.

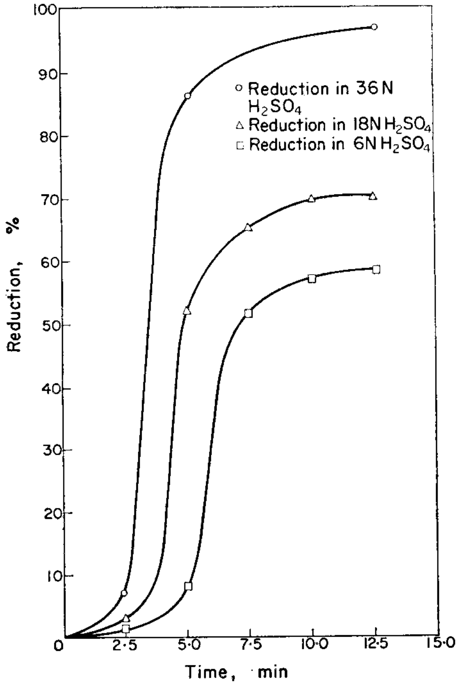


FIG. 4.—The use of sulphuric acid in the reduction of potassium nitrate with iron(II) ammonium sulphate in presence of ammonium molybdate as a catalyst.

Wirguin and Friedman[14] attributed the action of the chloride ions to their effect on the potential of the iron(II)/iron(III) couple and not to reaction with nitrate.

We, however, feel that NOCl is formed and is the effective oxidant, because if platinum is boiled with 4*M* hydrochloric acid and a few mg of potassium nitrate, enough is dissolved to yield a positive test for platinum ions in solution, indicating that the operative component of *aqua regia*, NOCl, is present.

Some organic and inorganic nitrates were satisfactorily analysed (Table I). The average absolute error was ±0·1% and the mean recovery 99·3%. Nitrate esters gave results consistently low by about 4% even with longer boiling and 0·08*M* iron(II). However, reduction with 0·15*M* iron(II) gave good results, the average absolute error being ±0·1% and the average recovery 100·1%. (Table I). Nitramines were recovered completely unreduced.

TABLE I.—REDUCTION WITH IRON(II) IN STRONG ACID MEDIUM

Sample	Nitrate-nitrogen, %	
	Calculated	Found
Potassium nitrate	13·85	13·9 13·9 13·7
Urea nitrate	11·38	11·4 11·4 11·5
Guanidine nitrate	11·47	11·4 11·5 11·6
Nitron nitrate	3·73	3·7 3·6 3·6
Pentaerythritol tetranitrate*	17·72	17·7 17·8 17·7

* The sample was reduced with 0·15*M* iron(II) solution.

Titanium(III) reduction

This reduction depends not only on the reaction medium but also on the nature of the nitrate sample. Citrate and acetate buffers and ammoniacal and acidic solutions were tested as reaction media. Acetate and citrate are known to lower the redox potential for the titanium couple, as shown by Kolthoff[15] and others[16] in the reduction of some nitro-compounds.

Reduction in citrate buffer. Nitrate ions were reduced by boiling for 2 min with titanium(III) in 50% sodium citrate solution. The results obtained when at least a 250% excess of 0·05*M* titanium(III) was present, showed a consumption of 6 moles of titanium per mole of nitrate group. The average recovery was 99·8% and the mean absolute error ±0·1%. Reduction with a smaller excess of titanium solution (*e.g.*, 100%) invariably gave low recoveries of 60–80%. Nitrate esters (*e.g.*, PETN) behaved similarly and the maximum absolute error obtained was ±0·3% (Table II). Reduction at room temperature for 10 min gave 50% recovery.

TABLE II.—REDUCTION WITH TITANIUM(III) IN CITRATE BUFFER MEDIUM

Sample	Nitrate-nitrogen, %	
	Calculated	Found
Potassium nitrate	13·85	13·8 13·9 13·8
Guanidine nitrate	11·47	11·4 11·4 11·5
Pentaerythritol tetranitrate	17·72	17·7 18·0 17·4

Reduction in acetate buffer. Titanium(III) solution (0·05*M*) reduces nitrate on boiling for 2 min in 50% sodium acetate solution. The reduction requires 8 moles of titanium(III) per mole of nitrate group when a 200% excess of titanium solution is used. The average absolute error for nitrate salts of inorganic and organic bases is ±0·1% (Table III), but reduction of nitrate esters is only 60–70% complete.

TABLE III.—REDUCTION WITH TITANIUM(III) IN ACETATE BUFFER MEDIUM

Sample	Nitrate-nitrogen, %	
	Calculated	Found
Potassium nitrate	13·85	14·0 13·9 14·1
Urea nitrate	11·38	11·4 11·3 11·3
Pentaerythritol tetranitrate	17·72	11·6 11·8 11·9

Reduction in ammoniacal medium. Potassium nitrate (~3 mg) was reduced by boiling for 2 min with 100% excess of titanium(III) solution in the presence of 10 ml of ammonia solution (sp. gr. 0·9). Acidification and titration of the excess of reductant showed a higher degree of reduction than the theoretical maximum. This was attributed to the loss of some titanium(III) through the formation of $Ti(OH)_4$ by reduction of water in this basic medium.[17] The mean absolute error was +3%.

Reduction in acid medium. Reduction of nitrate with 0·05*M* titanium(III) in ~4*M* hydrochloric acid medium was found to yield nitric oxide as with iron(II), but because of the stronger reducing properties of titanium(III) further reduction may take place. The average absolute error (20 determinations) for potassium nitrate was always positive (+0·2%), and volumetric measurement of the nitric oxide gas produced from this reaction gave a negative mean error (−0·2%).[18]

Nitrate esters, in general, behaved similarly (Table IV). Primary nitramines (*e.g.*, nitroguanidine) were only 80–90% reduced.

TABLE IV.—REDUCTION WITH TITANIUM(III) IN STRONG ACID MEDIUM

Sample	Nitrate-nitrogen, %	
	Calculated	Found
Potassium nitrate	13·85	14·0 14·1 14·1
Guanidine nitrate	11·47	11·6 11·5 11·5
Urea nitrate	11·38	11·6 11·6 11·4
Nitron nitrate	3·73	4·0 4·0 3·7
Pentaerythritol tetranitrate	17·72	17·7 17·6 17·5

Reduction with a mixture of titanium(III) and iron(II)

Neither iron(II) nor titanium(III), alone, was found to give a stoichiometric reduction of the nitramines (*e.g.*, nitroguanidine) on the microscale. Examination of the literature shows that such compounds are reduced with titanium(III) on the macro-scale in presence of excess of iron(II).[19]

The use of this mixture in hydrochloric acid medium for the micro-determination of nitroguanidine showed a reproducible consumption of 4 equivalents/mole. Reduction of nitrate esters with a mixture of titanium(III) and iron(II) in an acetate buffer gives concordant results corresponding to consumption of 6 moles of titanium(III) per mole of nitrate. In general, the mixture of titanium(III) and iron(II) is a suitable reducing agent for both the nitrates and nitramines. The average recovery is 99·3% and the mean absolute error ±0·2 (Table V).

TABLE V.—REDUCTION WITH TITANIUM(III) AND IRON(II) MIXTURE

Sample	Nitrate-nitrogen, %	
	Calculated	Found
Nitroguanidine*	13·46	13·4 13·2 13·4
Pentaerythritol tetranitrate†	17·72	17·4 17·0 17·6

* Reduction in hydrochloric acid.
† Reduction in acetate buffer.

Indirect method of reduction with titanium(III)

The use of nitrates or nitramines as nitrating agents for some reactive aromatic substances (*e.g.*, salicylic acid) in concentrated sulphuric acid can serve for their indirect determination—the *trans*-nitration method.[20]

The amount of salicylic–sulphuric acid mixture used in the nitration process and the time of contact between this mixture and the nitrate sample are important. A period of 5 min contact yielded only about 95% of the theoretical amount of the nitro-product. Quantitative recovery was obtained after contact for 10 min. Addition of anhydrous aluminium chloride reduced the time required for quantitative nitration to 2–3 min. A 4–5 ml portion of sulphuric–salicylic acid mixture is sufficient on the micro-scale for sample dissolution and nitration with either organic or inorganic nitrates.

The nitrosalicylic acid so produced from the nitration step is quantitatively reduced to the amino-derivative with 6 equivalents of titanium(III). Sodium citrate must be added before the reduction step in order to lower the acidity.

Satisfactory results were obtained in the analysis of some inorganic and organic salts of nitric acid. The average absolute error was ±0·1% with a mean recovery of 99·9%. Primary nitramines were similarly analysed with a mean absolute error of ±0·1%. A nitrate ester analysed by the same procedure gave results with a mean absolute error of −0·4% (Table VI).

TABLE VI.—*Trans*-NITRATION WITH SALICYLIC ACID FOLLOWED BY REDUCTION IN CITRATE BUFFER WITH TITANIUM(III)

Sample	Nitrate-nitrogen, %	
	Calculated	Found
Potassium nitrate	13·85	14·0 13·9 13·8
Urea nitrate	11·38	11·5 11·3 11·3
Guanidine nitrate	11·47	11·3 11·5 11·3
Nitron nitrate	3·73	3·7 3·9 3·7
Pentaerythritol tetranitrate	17·72	17·4 17·3 17·2
Nitroguanidine	13·46	13·5 13·4 13·2

Interferences

In general, organic compounds containing nitro (*e.g.*, dinitrobenzene), nitroso (*e.g.*, nitrosonaphthol), azo (*e.g.*, azobenzene) or hydrazo (*e.g.*, hydrazobenzene) groups show no interferences with the iron(II) method of reduction, but interfere when present with nitrate or nitramine samples if the titanium(III), titanium(III)–iron(II) and *trans*-nitration procedures are used.

Zusammenfassung—Organische und anorganische Nitrate lassen sich im Mikromaßstab zufriedenstellend durch Reduktion mit Eisen(II) bestimmen. Titan(III) reduziert Nitrate in stark sauren, citrat- und acetatgepufferten Medien unter Verbrauch von 3, 6 bzw. 8 Äquivalenten Ti(III) pro Nitratgruppe. Nitramine bestimmt man durch Reduktion mit einem Gemisch aus Ti(III) und Fe(II). Auch die Bestimmung von Nitraten und Nitraminen durch Umnitrierung mit Salicylsäure ist im Mikromaßstab angebracht. Zu Reduktion, Aufbewahrung und Gebrauch der Titan(III)-Lösung wurde eine neue automatische Mikrobürette mit elektrolytischer Reduktion entworfen.

Résumé—Les nitrates organiques et inorganiques sont déterminés de manière satisfaisante à l'échelle micro par réduction avec Fe(II). Le titane(III) réduit les nitrates en milieux fortement acide, tamponné au citrate et tamponné à l'acétate avec la consommation de 3, 6 et 8 équivalents de Ti(III) par groupe nitrate, respectivement. On dose les nitramines par réduction avec un mélange de Ti(III) et Fe(II). La détermination de nitrates et nitramines par *trans*-nitration avec l'acide salicylique est convenable à l'échelle micro. On a imaginé une nouvelle microburette automatique de réduction électrolytique pour la réduction, la conservation et l'emploi de la solution de titane(III).

REFERENCES

1. A. Devarda, *Chem. Ztg.*, **16**, 1892, 1952.
2. P. Howard, *Chem. Ind.*, 1963, **25**, 1031.
3. I. Kolthoff, E. Sandell and B. Moskovitz, *J. Am. Chem. Soc.*, 1933, **55**, 1454.
4. J. Grodzinski, *Anal. Chem.*, 1957, **29**, 150.
5. P. Banerjee, *J. Indian Chem. Soc.*, 1936, **13**, 301.
6. J. Lingane and R. Pecsok, *Anal. Chem.*, 1949, **21**, 622.
7. W. Selig, *U.S. At. Energy Comm.*, 1961, UCRL-6639, 30.
8. P. Szeberényi, *Z. Anal. Chem.*, 1932, **87**, 357.
9. T. Murakami, *Bunseki Kagaku*, 1958, **7**, 766; *Chem. Abstr.*, 1959, **53**, 19682.
10. A. Wellings, *Trans. Faraday Soc.*, 1932, **28**, 665.
11. H. Shankstar and T. Wilde, *J. Soc. Chem. Ind.*, 1938, **57**, 91.
12. R. Sarson, *Anal. Chem.*, 1958, **30**, 932.
13. R. Roseman and W. Thornton, *J. Am. Chem. Soc.*, 1935, **57**, 328.
14. C. Wirguin and D. Friedman, *Talanta*, 1960, **7**, 121.
15. I. Kolthoff, *Rec. Trav. Chim.*, 1924, **43**, 768; I. Kolthoff and C. Robinson, *ibid.*, 1926, **46**, 169.
16. P. Butts, W. Meikle, J. Shovers, D. Couba and W. Becker, *Anal. Chem.*, 1948, **20**, 947.
17. J. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. VII, p. 77. Longman, London, 1947.
18. W. I. Awad and S. S. M. Hassan, *Talanta*, 1969, **16**, 1393.
19. W. Brandt, J. Devries and E. Cantz, *Anal. Chem.*, 1955, **27**, 392.
20. H. Stalcup and R. Williams, *ibid.*, 1955, **27**, 543.

Talanta, 1969, Vol. 16, pp. 1393 to 1401. Pergamon Press. Printed in Northern Ireland

MICRODETERMINATION OF NITRATES AND NITRAMINES—II

GASOMETRIC METHODS BASED ON REDUCTION WITH MERCURY, IRON(II), TITANIUM(III) AND HYDROQUINONE

WILLIAM IBRAHIM AWAD and SAAD S. M. HASSAN
Research Microanalytical Laboratories, Chemistry Department,
Faculty of Science, Ain Shams University, Cairo, U.A.R.

(*Received* 13 *September* 1968. *Revised* 24 *March* 1969. *Accepted* 23 *April* 1969)

Summary—Four gasometric micro-methods based on the reduction of nitrates or nitramines to nitric oxide with mercury, iron(II), titanium(III) and hydroquinone in acid media are described. The mercury method is recommended for nitrate esters and secondary nitramines in the absence of aromatic compounds. The iron(II) method is advocated for primary nitramines and nitrate salts in the presence of aromatic compounds. Reductions with titanium(III) and hydroquinone are also successful with the nitrate salts in the presence of an aromatic moiety but the former gives less accurate results. The reduction conditions, mechanism, applications and limitations are described.

Two direct reactions are commonly used for the gasometric determination of the nitrates on the macro-scale: the mercury–sulphuric acid reduction (the nitrometer method),[1] and the iron(II)–acid reduction (Schultze-Tiemann).[2] Nitric oxide is produced and measured volumetrically,[1,2] manometrically,[3] or by reduction to elemental nitrogen.[4] The volume of the gas is a measure of the quantity of nitrogen present as nitrate.

In the nitrometer method the sample is dissolved in sulphuric acid and then introduced into a nitrometer filled with mercury, and vigorously shaken. The volume of gas is then measured, but the method suffers from many disadvantages.[5] Planchon[3] claims that manometric measurement is more precise. Gootz and Tunger[4] combined the nitrometer reaction and the Dumas method. In general, the nitrometer method is inapplicable to samples that liberate gases other than nitric oxide and is applied to the macro-analysis of only a few nitrates. In the Schultze-Tiemann method[2] the nitrate is boiled with iron(II)–acid solution and the liberated gas is driven off by steam into a measuring tube filled with concentrated alkali solution.

The convenience and accuracy of the gasometric finish attracted our attention and methods based on the reduction with mercury, iron(II) and titanium(III) were studied on the micro-scale. A new redox reaction with hydroquinone was found and applied to microdetermination of nitrates.

EXPERIMENTAL

Apparatus

A specially designed apparatus (Fig. 1) was constructed so that very small amounts of reductant are used, fresh reagent being used for each determination.

Reagents

All the reagents were of analytical grade unless otherwise specified. Standard nitrate and nitramine samples[6] were used.

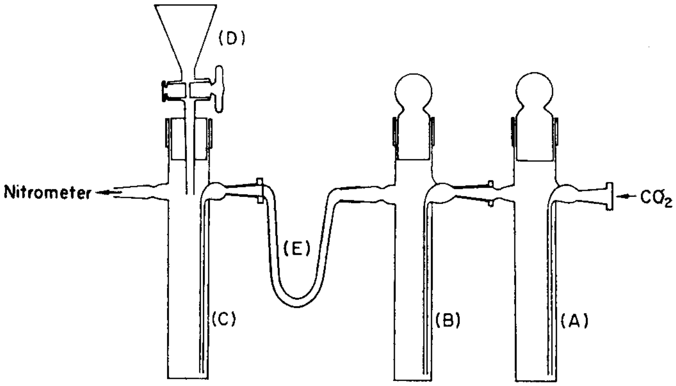


FIG. 1.—Apparatus for gasometric determination of the nitrates and the nitramines. (A) and (B) purification vessels; (C) reduction vessel; (D) funnel; (E) polythene tubing (150 mm).

Procedures

Mercury reduction method. Introduce 3–5 mg of the ground dried sample into reaction vessel *C*, and add 5 drops of mercury. Displace the air with carbon dioxide till no air bubbles are collected in the nitrometer, then introduce about 3 ml of concentrated sulphuric acid through funnel *D*. Shake vigorously till no more gas bubbles are evolved. Record the volume (V_1) of the nitric oxide gas obtained as well as the time of reduction. Allow the gas to stand in the nitrometer for the same period of time and read the volume again (V_2). The difference ($V_1 - V_2$) corresponds to the amount of nitric oxide soluble under the experimental conditions. The total volume ($2V_1 - V_2$) is equivalent to the nitrogen from nitrate or nitramine. Carry out a blank and calculate the nitrogen content.

Iron(II) *reduction method.* Introduce 3–5 mg of the sample into reaction vessel *C*, add excess of powdered iron(II) sulphate and deaerate the system with carbon dioxide. Introduce about 5 ml of 30% sulphuric acid through funnel *D* and heat gently until the brown colour disappears and the solution turns yellowish green. Continue as above.

Titanium(III) *reduction method.* Introduce 3–5 mg of the sample reaction into vessel *C*. Add 3 ml of concentrated hydrochloric acid to the sample and then about 5 ml of 0·3*M* titanium(III) sulphate through funnel *D*. Continue as described for mercury reduction.

Hydroquinone reduction method. Introduce 3–6 mg of the finely powdered sample into reaction vessel *C* followed by about twice as much solid hydroquinone and a few mg of ammonium molybdate. Assemble the apparatus and displace the air with carbon dioxide. Mix the contents thoroughly by shaking the reaction vessel. Add 5 ml of 6*M* hydrochloric acid through funnel *D*. Boil gently till no more gas is liberated. Continue as described for mercury.

Calculation

% Nitramine- or nitrate-nitrogen = $17{\cdot}08\ (2V_1 - V_2 - v)\ (P - p)/(273 + T)\ W$ where V_1 and V_2 ml are the nitrometer readings, v ml is the blank, P mbar is the atmospheric pressure, p mbar is the vapour pressure of the potassium hydroxide solution at T°C (the average temperature of the room and of the solution in the nitrometer), and W mg is the sample weight.

RESULTS AND DISCUSSION

Preliminary studies

In the preliminary studies, two main sources of error were found: (*i*) the source of the carbon dioxide and (ii) the solubility of nitric oxide in concentrated potassium hydroxide solution. Distinctly oxygen-free carbon dioxide is required. The solid carbon dioxide technique described by Ingram,[7] with addition of two pyrogallol traps, suits the present purpose. The solubility of nitric oxide is dependent on the amount of air dissolved in the potassium hydroxide solution, and on the time of contact between the gas and this solution. Although the gas solubility is negligible on the macroscale in the Schultze-Tiemann method, it becomes a serious source of error on both the semimicro and the micro scales. Mustafa and Dawoud's method[8] for the semimicro determination of glycerine nitrate does not give the reported accuracy (error +0·03%) unless the solubility correction is applied. This is in agreement with the finding of Gay Lussac and others[9] that nitric oxide reacts with concentrated potassium hydroxide solution to give potassium nitrite and nitrous oxide.

The error due to gas solubility was measured by recording the reaction time for every experiment, and the decrease in the gas volume in the same period of time. The decrease in volume was added to the original volume measured. This correction was valid because the solubility of the gas was found to increase linearly with time during the first 15 min of contact between the gas and the alkali solution. The gas solubility ranges from nil to about 0·05 ml/mg of sample, depending on the reaction conditions. In most cases 0·01 ml/mg of sample (14% N) was obtained, but as the alkali solution became exhausted the gas solubility increases to reach a maximum of 0·05 ml/mg of sample. The alkali solution should then be renewed.

Reaction conditions

The original macro-scale mercury method suffers from many disadvantages:[5,10] (*a*) the large amount of mercury used (10–15 kg), (*b*) possibility of explosion due to the large volume of gas produced, (*c*) the dissolution of the sample outside the nitrometer may give low results, (*d*) possibility of breaking the nitrometer by the vigorous shaking, (*e*) need to renew the mercury for every experiment.

The micro-method overcomes these disadvantages. Only 5–10 drops of mercury are used, the sample is dissolved inside the reaction vessel, and the volume of gas produced is so small that no explosion or breaking of the simple reaction vessel is possible.

In the micro-scale reduction with iron(II) the sample is mixed with excess of powdered iron(II) salt (at least 10-fold excess for nitramines) and either 30–90% sulphuric acid or 10–30% hydrochloric acid is added. With titanium(III) reduction, 0·3*M* titanium sulphate is added to the nitrate sample in concentrated hydrochloric acid.

Reduction of a typical nitrate with hydroquinone in different media shows that halogen acids (*e.g.*, hydrochloric and hydrobromic) are the best media for quantitative reduction, and that molybdenum(VI) catalyses the reaction, the molybdenum being rapidly reduced to Mo(V) by hydroquinone in acid solution on warming and the Mo(V) oxidized to Mo(VI) by nitrate, in the catalytic cycle.

$$C_6H_4(OH)_2 + 2Mo(VI) \rightarrow C_6H_4O_2 + 2Mo(V) + 2H^+$$
$$NO_3^- + 4H^+ + 3Mo(V) \rightarrow NO + 2H_2O + 3Mo(V)$$

Similar behaviour by molybdenum is known in the reduction of Methylene Blue with hydrazine.[11]

In the absence of molybdenum(VI) no more than 60% reduction was obtained after boiling for 10 min (Fig. 2). Ammonium vanadate and tungstate had a very low catalytic effect.

Mechanism of the reaction

Reduction of nitrate esters or nitramines with mercury–sulphuric acid mixture can proceed by protonation of the oxygen atom of the nitrate or of the nitrogen atom of the nitramine, followed by bond fission to give the nitronium ion NO_2^+,

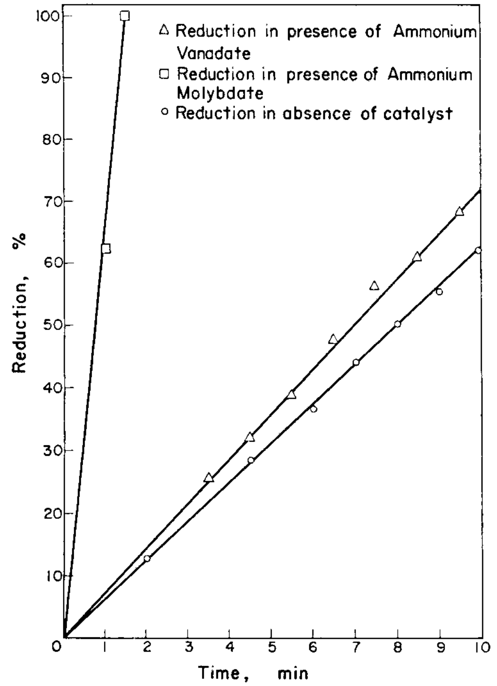
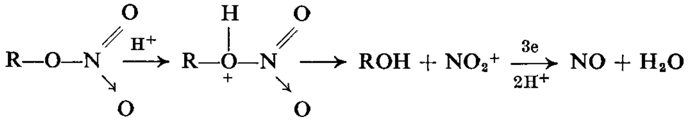


FIG. 2.—The catalytic effect of ammonium molybdate on the reduction of potassium nitrate with hydroquinone.

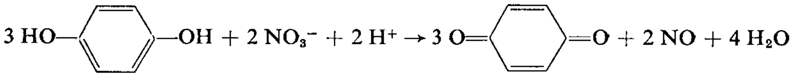
which takes up three electrons and two protons to give water and nitric oxide.



$$R{-}O{-}\overset{O}{\underset{O}{N}} \xrightarrow{H^+} R{-}\overset{H}{\underset{+}{O}}{-}\overset{O}{\underset{O}{N}} \longrightarrow ROH + NO_2^+ \xrightarrow[2H^+]{3e} NO + H_2O$$

For verification of this reaction route, a nitrate sample was dissolved in sulphuric–salicylic acid mixture; nitrosalicylic acid was isolated[12] and titrimetrically determined quantitatively, *in situ*, on the macro-scale with titanium(III) sulphate (*cf.* Part I).[6] It is well established that the nitration reaction proceeds *via* NO_2^+, and the formation of nitrosalicylic acid is a clear indication of the formation of NO_2^+ as intermediate product.[13]

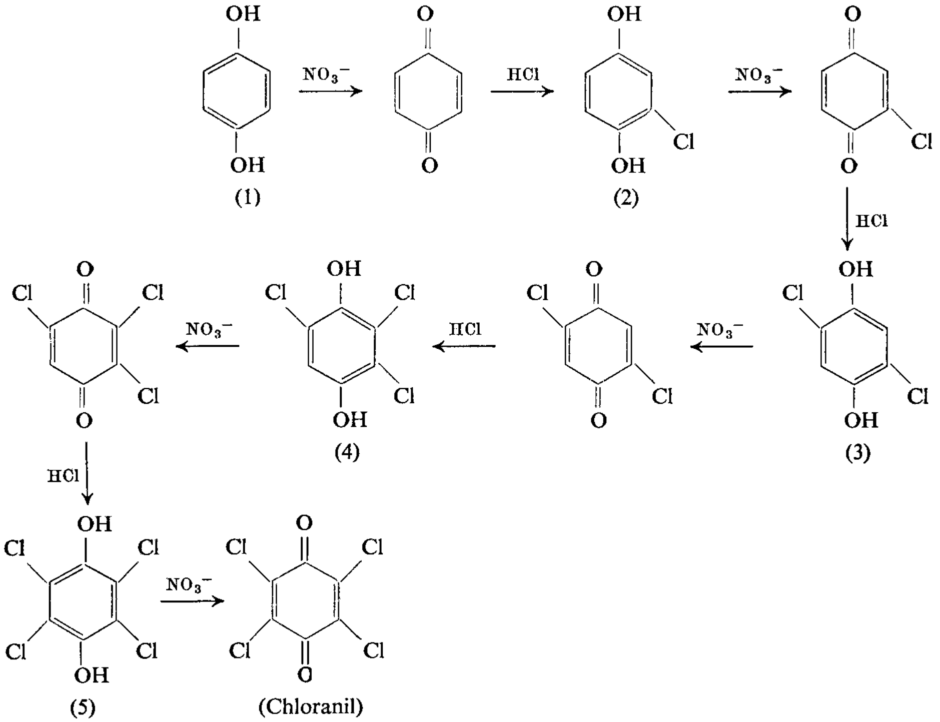
The reaction of hydroquinone with nitrates in the presence of hydrochloric acid was thought, at the outset of this work, to be a simple oxidation-reduction as follows:



Accordingly, each mole of nitrate is expected to consume 1·5 moles of hydroquinone for quantitative liberation of nitric oxide. Contrary to this expectation the reaction is not so simple. When various mole-ratios of hydroquinone and nitrate were used and degree of reduction was calculated from the volume of nitric oxide produced, quantitative reduction was obtained even with 0·3 mole-ratio instead of the expected

1·5 mole-ratio (Fig. 3). With 0·2 and 0·1 mole-ratio the degrees of reduction are 77·5 and 36% respectively instead of the expected 13·3 and 6·7%, showing that the efficiency of hydroquinone in the reduction of the nitrate is 5 times that expected.

The explanation of these results is that hydroquinone is regenerated in the reaction medium. It is known that quinones undergo a 1:4 addition reaction with hydrochloric acid to give chlorohydroquinone.[14] Consequently, the quinone produced from the first stage of oxidation will react with the hydrochloric acid in the medium to give chlorohydroquinone, which is reoxidized by nitrate to give chlorobenzoquinone. The latter will add hydrochloric acid again and the processes of oxidation and hydrochloric acid addition will proceed successively till the fully chlorinated quinone chloranil is formed.



This scheme shows that 1 mole of hydroquinone results in altogether 5 moles of hydroquinone and its chloro-derivatives. Moreover, hydroquinone and its chlorinated derivatives have nearly the same oxidation potential.[15,16] The proposed mechanism is supported by the following facts. When tetrachlorohydroquinone was used as reductant a minimum mole-ratio of chlorohydroquinone to nitrate of 1·5 was needed for complete reduction. When the reaction product from a 0·3 mole-ratio of hydroquinone to nitrate was isolated, crystallized from acetic acid and dried, it was found to be chloranil (m.p. and mixed m.p. with an authentic specimen, and comparison of infrared spectra).

Decomposition time

The time required for full reduction of nitrates and nitramines was measured for all four reductants. With the mercury method, inorganic and organic nitrates and

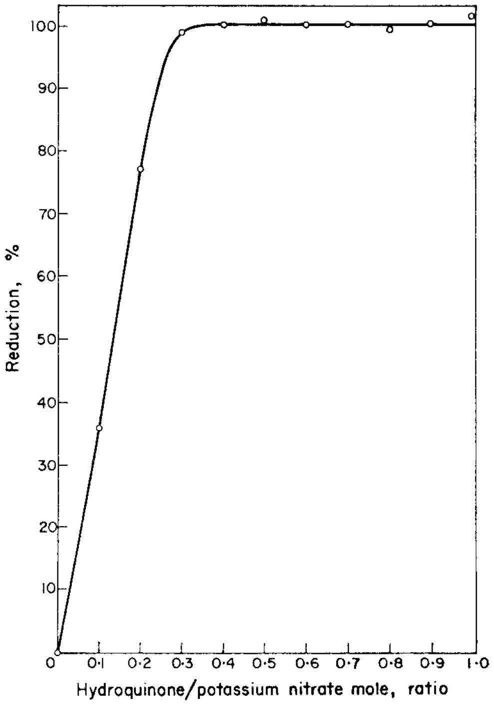


FIG. 3.—Reduction of potassium nitrate with different mole-ratios of hydroquinone.

primary nitramines are quantitatively reduced within 3–4 min; nitrate esters require 4–6 min. With iron(II) reduction, as the acid concentration increases, the decomposition time decreases, but the acid concentration has little effect on the period required for reduction with titanium(III). Reduction with hydroquinone requires boiling for 3 min (Fig. 2).

Interferences

Organic compounds containing different types of nitrogen group were subjected to the mercury, iron(II), titanium(III) and hydroquinone methods of reduction. Nitro (*e.g.*, dinitrobenzene), nitroso (*e.g.*, nitrosonaphthol), azo (*e.g.*, azobenzene), azoxy (*e.g.*, azoxybenzene), amide (*e.g.*, acetamide), imide (*e.g.*, phthalimide), amine (*e.g.*, *p*-aminobenzoic acid), oxime (*e.g.*, dimethyloxime), cyanide (*e.g.*, benzyl cyanide) and ammonium compounds (*e.g.*, ammonium acetate) show no interference with all four methods. Some azides (*e.g.*, isopropylidene hippuric azide) give nitrogen, and some *N*-nitroso compounds (*e.g.*, cupferron) give nitric oxide.

Aromatic derivatives interfere in the mercury method. For this reason nitron nitrate gives no gases when analysed, because of nitration of the aromatic moiety of the nitron molecule. Obviously, the mercury method is not suitable for nitrate or nitramine samples containing aromatic residues or additives.

However, with both the iron(II) and titanium(III) methods, the aromatic residue does not interfer under certain conditions, such as the nature and concentration of the acid used as medium. With 70% sulphuric acid, recovery is 30–40%, whereas with 50% acid solution it is 90%. The low recoveries are due to the formation of an appreciable amount of NO_2^+ which acts as a nitrating agent. On the other hand, quantitative recoveries are obtained with 30% sulphuric acid or hydrochloric acid. No effect due to the presence of an aromatic moiety was observed with hydroquinone reduction method when 6*M* hydrochloric acid was used.

RESULTS

Typical results obtained by all four methods are collected in Table I. With mercury as reductant the mean recovery is 99·3% and the mean absolute error is 0·1%.

TABLE I.—RESULTS FOR GASOMETRIC METHODS

Sample	Nitrate-nitrogen, % calculated	Nitrate-nitrogen found, %			
		Hg	Fe(II)	Ti(III)	$C_6H_4(OH)_2$
Pentaerythritol tetranitrate	17·72	17·7	18·0	—	—
		17·8	17·3		
Cellulose trinitrate	14·14	14·1	13·5	—	—
		14·2	13·8		
RDX	18·92	18·7	18·3	—	—
		18·8	18·6		
Nitroguanidine	13·46	13·3	13·4	—	—
		13·2	13·3		
Nitrobiuret	9·46	9·4	9·4	—	—
		9·4	9·3		
Potassium nitrate	13·85	13·9	13·9	13·6	13·9
		13·8	14·0	13·7	13·9
Urea nitrate	11·38	11·3	11·4	11·1	11·3
		11·3	11·4	11·2	11·5
Guanidine nitrate	11·47	11·2	11·5	11·3	11·6
		11·4	11·4	11·2	11·5
Nitron nitrate	3·73	nil	3·8	3·6	3·9
			3·8	3·5	3·6

With nitrate esters and secondary nitramines, iron(II) reduction gave results with poor concordance (error ±0·7%). This may be due to incomplete solubility and/or hydrolysis of the sample in the reaction medium. Attempts to dissolve these samples, before reduction, in acetic acid or highly polar solvents (*e.g.*, dimethylsulphoxide, dimethylformamide and *N*-methylpyrrolidone) slightly improved the results. However, nitrate salts and nitramines were satisfactorily analysed, the mean recovery being 100% with a mean absolute error of ±0·1%.

Use of titanium(III) as reducing agent is limited to organic and inorganic salts of nitric acid. There is a biased (*cf.* Table I) absolute error of −0·2%, which may be due to either incomplete or over-reduction to give some products other than nitric oxide[17] (*cf.* Part I[6]).

The hydroquinone method can be successfully applied to the determination of inorganic and organic salts of nitric acid, recovery 100·1%, mean absolute error 0·1%, but nitramines and nitrate esters give low recoveries, 40–60%.

The applications, advantages, limitations, and errors of all the methods in Parts I and II are summarized in Table II.

TABLE II.—MICRODETERMINATION OF THE NITRATES AND THE NITRAMINES

Method	Procedure	Application	Advantages	Limitations	Error %
TITRIMETRIC	Iron(II)–acid reduction	Organic and inorganic salts of nitric acid and nitrate esters	No interference from nitramines or other nitrogen groups	No reaction with the nitramines	±0·1
	Iron(II)–titanium(III) reduction mixture	Organic and inorganic salts of nitric acid, nitrate esters, primary and secondary, nitramines	The only accurate titrimetric procedure for nitramines		±0·2
	Titanium(III) reduction	Organic and inorganic salts of nitric acid, and nitrate esters	Useful for the determination of total nitrate and nitro groups in admixture	Other nitrogen groups (*e.g.*, nitro, azo, nitroso, azoxy and hydrazo) interfere	±0·2
	Trans-nitration with salicylic acid	Organic and inorganic salts of nitric acid, nitrate esters, primary and secondary nitramines			±0·3
GASOMETRIC	Mercury–acid reduction		Short reduction, time *e.g.*, 3 min is sufficient	Not suitable with samples containing aromatic moiety	±0·1
	Iron(II)–acid reduction	Organic and inorganic salts of nitric acid and primary nitramines	No interference with samples containing aromatic moiety		±0·2
	Titanium(III)–acid reduction			Not suitable with nitrate esters and nitramines	−0·2
	Hydroquinone–acid reduction	Organic and inorganic salts of nitric acid			±0·1

Zusammenfassung—Vier gasometrische Mikromethoden werden beschrieben, die auf der Reduktion von Nitraten oder Nitraminen zu Stickstoffmonoxid mittels Quecksilber, Eisen(II), Titan(III) und Hydrochinon in sauren Medien beruhen. Die Quecksilbermethode wird in Abwesenheit aromatischer Verbindungen für Nitratester und sekundäre Nitramine empfohlen, die Methode mit Eisen(II) für primäre Nitramine und Nitratsalze in Gegenwart aromatischer Verbindungen. Reduktionen mit Titan(III) und Hydrochinon sind bei Nitratsalzen in Gegenwart von Aromaten ebenfalls erfolgreich, jedoch liefern sie mit Titan(III) weniger genaue Ergebnisse. Die Reduktionsbedingungen, der Mechanismus, Anwendungen und Einschränkungen werden abgehandelt.

Résumé—On décrit quatre micro-méthodes gazométriques basées sur la réduction de nitrates ou nitramines en bioxyde d'azote par le mercure, le fer(II) le titane(III) et l'hydroquinone en milieux acides. La méthode au mercure est recommandée pour les esters nitriques et les nitramines secondaires en l'absence de composés aromatiques. La méthode au fer(II) est conseillée pour les nitramines primaires et les sels nitriques en la présence de composés aromatiques. Les réductions au titane(III) et à l'hydroquinone sont aussi couronnées de succès avec les sels nitriques en la présence d'une groupement aromatique mais la première donne des résultats moins précis. On décrit les conditions de réduction, le mécanisme, les applications et limitations.

REFERENCES

1. G. Lung, *Chem. News*, 1878, **38,** 18; *Dingler's Polytech. J.*, 1878, **228,** 448; *cf.* Ref. (2).
2. A. Marshall, *Explosives*, Vol. 2, p. 721, Churchill, London, 1932.
3. V. Planchon, *Ann. Chim. Anal.*, 1915, **20,** 189.
4. R. Gootz and H. Tunger, *Z. Physiol. Chem.*, 1935, **233,** 67.
5. P. Elving and W. McElroy, *Anal. Chem.*, 1942, **14,** 84.
6. W. I. Awad and S. S. M. Hassan, *Talanta*, 1969, **16,** 1383.
7. G. Ingram, *Methods of Organic Elemental Microanalysis*, p. 111. Chapman and Hall, London, 1962.
8. A. Mustafa and A. Dawoud, *Analyst*, 1963, **88,** 809.
9. J. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. III, p. 432. Longmans, London, 1947.
10. A. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 2nd Ed., p. 810. Longmans, London, 1957.
11. R. Lang, *Z. Anal. Chem.*, 1948, **128,** 165.
12. H. Stalcup and R. Williams, *Anal. Chem.*, 1955, **27,** 543.
13. E. Gould, *Mechanism and Structure in Organic Chemistry*, p. 419. Holt, Rinehart and Winston, New York, 1964.
14. J. Cason, in R. Adams, *Organic Reactions*, Vol. IV, p. 322. Wiley, New York, 1949.
15. J. Conant, *J. Am. Chem. Soc.*, 1927, **49,** 293.
16. J. Conant and L. Fieser, *ibid.*, 1923, **45,** 2194.
17. L. Milligan and G. Gillette, *J. Phys. Chem.*, 1924, **28,** 744.

Talanta, 1969, Vol. 16, pp. 1403 to 1419. Pergamon Press. Printed in Northern Ireland

AN INVESTIGATION OF THE DIETHYLDITHIOCARBAMATES OF PALLADIUM, INCLUDING THE DETERMINATION OF THEIR STABILITY CONSTANTS

G. B. BRISCOE and S. HUMPHRIES
Department of Chemistry, The University of Aston in Birmingham,
Gosta Green, Birmingham 4, England

(*Received* 9 *September* 1968. *Accepted* 17 *March* 1969)

Summary—The reaction of palladium with copper diethyldithiocarbamate has been studied and two complexes isolated: palladium diethyldithiocarbamate and palladium chloride diethyldithiocarbamate. The spectra of both complexes have been examined. The extraction constants and partition coefficients between chloroform and water have been determined, the former by the use of other strong complexing reagents as masking agents for palladium. The stability constants and the exchange constant for the two complexes have been calculated.

NEUTRON-ACTIVATION analysis of trace amounts of metals can be simplified by using the technique of substoichiometric solvent extraction. This involves the use of a chelating agent, the quantity of which is chosen so as to separate only part of the metal present. The complex formed must be strong in order that the reagent reacts totally with the metal. It is also desirable that the complex is more readily extracted than the complexes formed by most other metals, in order that the separation may be as selective as possible.

The complexing agents known to form stronger complexes with palladium than most other common metals, are diethyldithiocarbamic acid and dithizone. The latter was considered unsuitable owing to the formation of an insoluble secondary dithizonate when the metal is in excess.[1] Diethyldithiocarbamic acid promised to be more useful and in this paper the extraction of palladium diethyldithiocarbamate complexes into chloroform has been studied in detail in order that the conditions suitable for a substoichiometric separation may be predicted.

THEORY

The normal reaction of palladium with copper diethyldithiocarbamate is:

$$\mathrm{Pd^{2+}_{(aq)} + Cu(DDC)_{2(org)} \rightleftharpoons Pd(DDC)_{2(org)} + Cu^{2+}_{(aq)}} \tag{1}$$

where DDC is taken to represent the diethyldithiocarbamate ion and the subscripts "aq" and "org" to represent an aqueous and an immiscible organic phase respectively. However, under substoichiometric conditions, *i.e.*, in the presence of excess of metal, a further reaction takes place:

$$\mathrm{Pd(DDC)_{2(org)} + Pd^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \rightleftharpoons 2PdCl(DDC)_{(org)}} \tag{2}$$

In order to carry out a substoichiometric determination it is necessary that a given amount of the reagent shall extract a fixed amount of metal from any solution in which the metal is in excess.[2] Therefore we can use either complex, but only if we can be sure that it is the only species present. Obviously palladium chloride diethyldithiocarbamate could not be formed if extraction were to be carried out from chloride free solution; a difficult condition to maintain in real analysis. It is preferable therefore, that conditions be investigated under which the two complexes are formed, and which are also readily obtained in practice.

The extraction constants for the two complexes are given by:

$$K_A = \frac{[\mathrm{Pd(DDC)_2}]_{\mathrm{org}}}{[\mathrm{Pd}^{2+}][\mathrm{DDC}^-]^2} \tag{3}$$

and

$$K_B = \frac{[\mathrm{PdCl(DDC)}]_{\mathrm{org}}}{[\mathrm{Pd}^{2+}][\mathrm{DDC}^-][\mathrm{Cl}^-]} \tag{4}$$

(the subscript (aq) has been omitted for simplicity). By combining equations (3) and (4) we get K_E, the constant for reaction (2) and the exchange constant for the two complexes:

$$K_E = \frac{[\mathrm{PdCl(DDC)}]^2_{\mathrm{org}}}{[\mathrm{Pd(DDC)_2}]_{\mathrm{org}}[\mathrm{Pd}^{2+}][\mathrm{Cl}^-]^2} = \frac{K_B{}^2}{K_A}\,. \tag{5}$$

It would appear from this equation that chloride ions favour the formation of palladium chloride diethyldithiocarbamate. But chloride ions also complex strongly with palladium(II) ions giving a series of species $\mathrm{Pd(Cl)}_n^{(n-2)-}$ where $n = 1$–6. This means that the concentration of Pd^{2+} ions decreases rapidly with increasing chloride ion concentration and a convenient way to calculate this effect is to use the α-coefficient as used by Ringbom:[3]

$$\alpha_{\mathrm{Pd}} = [\mathrm{Pd}']/[\mathrm{Pd}^{2+}] \tag{6}$$

where $[\mathrm{Pd}'] = [\mathrm{Pd}^{2+}] + [\mathrm{PdCl}^+] + [\mathrm{PdCl_2}] + [\mathrm{PdCl_3}^-] + [\mathrm{PdCl_4}^{2-}] + [\mathrm{PdCl_5}^{3-}] + [\mathrm{PdCl_6}^{4-}]$. The values of α_{Pd} for various chloride ion concentrations were calculated from the stability constants for all these chloro-species[4] (Fig. 1).

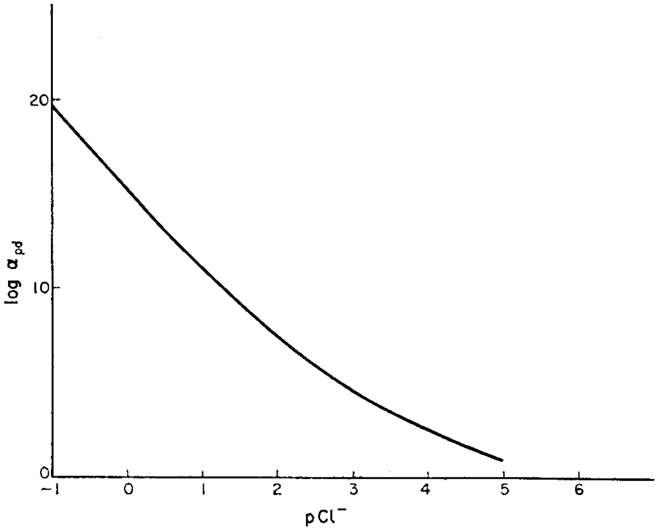


FIG. 1.—Variation of α_{Pd} with chloride ion concentration.

By substitution for $[Pd^{2+}]$, equation (5) becomes:

$$K_E = \frac{[PdCl(DDC)]^2_{org}\alpha_{Pd}}{[Pd(DDC)_2]_{org}[Pd'][Cl^-]^2}. \qquad (7)$$

which implies that it should be possible to determine the value of K_E by varying the chloride ion concentration.

It was found that reaction (2) can be slowed down by the addition of chloride ions (see *Experimental: Procedures* and Fig. 3) under such conditions that reaction (2) does not occur to any detectable extent, even after several hours shaking; however, once palladium chloride diethyldithiocarbamate had been formed (under different conditions), the reaction could not be reversed at all, even by shaking with concentrated hydrochloric acid. Thus, it follows from equation (7) that for $[Cl^-] = 10M$ (concentrated hydrochloric acid) and $\alpha_{Pd} = 10^{19.5}$ (Fig. 1),

$$\frac{[PdCl(DDC)]^2_{org}}{[Pd(DDC)_2]_{org}[Pd']} > 10^4$$

because there must be less than 1% palladium diethyldithiocarbamate present (limit of detection) and $[Pd'] = [Pd(DDC)_2]_{org}$.

Hence $K_E > 10^4 \times 10^{19.5}/10^2$, *i.e.*, $\log K_E > 21$ and is too large to be determined in this manner.

In order to determine K_E it was necessary to use a stronger complexing agent and EDTA was chosen for the purpose. At low pH values we assumed the following equation:[8]

$$2PdCl(DDC)_{(org)} + 2H^+ + Y^{4-} \rightleftharpoons H_2PdY + Pd(DDC)_{2(org)} + 2Cl^- \qquad (8)$$

where H_4Y = EDTA.

The constant K_1 for the reaction is given by:

$$K_1 = \frac{[Pd(DDC)_2]_{org}[H_2PdY][Cl^-]^2}{[H^+]^2[PdCl(DDC)]^2_{org}[Y^{4-}]} = \frac{K_2}{K_E} \qquad (9)$$

where K_2 is the stability constant of the species H_2PdY, given by:

$$K_2 = \frac{[H_2PdY]}{[H^+]^2[Pd^{2+}][Y^{4-}]}. \qquad (10)$$

The concentration of Y^{4-} ions can be calculated by using the α-coefficient again:

$$\alpha_Y = [Y']/[Y^{4-}] \qquad (11)$$

where $[Y'] = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^-] + [H_4Y]$, *i.e.*, the total equilibrium concentration of EDTA in all its forms.

In order to calculate the concentration of the EDTA complex, H_2PdY, we need to take the complexing power of the chloride ions into account. Rearranging equation (10) and substituting for $[Y^{4-}]$ from equation (11) we get:

$$[Pd^{2+}] = \frac{[H_2PdY]\alpha_Y}{[H^+]^2[Y']K_2}, \qquad (12)$$

and combining this expression with equation (6) gives:

$$\frac{[\mathrm{Pd}']}{\alpha_{\mathrm{Pd}}} = \frac{[\mathrm{H_2PdY}]\alpha_{\mathrm{Y}}}{[\mathrm{H^+}]^2[\mathrm{Y}']K_2}. \tag{13}$$

If we denote the concentration of all the palladium in the aqueous phase by $[\mathrm{Pd_{aq}}]$ then:

$$[\mathrm{Pd_{aq}}] = [\mathrm{H_2PdY}] + [\mathrm{Pd}'] \tag{14}$$

and substituting for $[\mathrm{Pd}']$ from (13) gives:

$$[\mathrm{Pd_{aq}}] = [\mathrm{H_2PdY}] + \frac{[\mathrm{H_2PdY}]\alpha_{\mathrm{Y}}\alpha_{\mathrm{Pd}}}{[\mathrm{H^+}]^2[\mathrm{Y}']K_2}. \tag{15}$$

By rearranging:

$$[\mathrm{H_2PdY}] = \frac{[\mathrm{Pd_{aq}}]}{1 + \dfrac{\alpha_{\mathrm{Y}}\alpha_{\mathrm{Pd}}}{[\mathrm{H^+}]^2[\mathrm{Y}']K_2}}. \tag{16}$$

By substituting (11) and (16) in (9) the expression for K_1 becomes:

$$K_1 = \frac{[\mathrm{Pd(DDC)_2}]_{\mathrm{org}}[\mathrm{Pd_{aq}}][\mathrm{Cl^-}]^2\alpha_{\mathrm{Y}}}{[\mathrm{H^+}]^2[\mathrm{PdCl(DDC)}]^2_{\mathrm{org}}[\mathrm{Y}']\left(1 + \dfrac{\alpha_{\mathrm{Y}}\alpha_{\mathrm{Pd}}}{[\mathrm{H^+}]^2[\mathrm{Y}']K_2}\right)}. \tag{17}$$

However, if K_2 is very large in comparison with $\alpha_{\mathrm{Y}}\alpha_{\mathrm{Pd}}$ the expression in parenthesis approaches unity and equation (17) simplifies to:

$$K_1 = \frac{[\mathrm{Pd(DDC)_2}]_{\mathrm{org}}[\mathrm{Pd_{aq}}][\mathrm{Cl^-}]^2\alpha_{\mathrm{Y}}}{[\mathrm{H^+}]^2[\mathrm{PdCl(DDC)}]^2_{\mathrm{org}}[\mathrm{Y}']}. \tag{18}$$

Under the conditions used, (18) was assumed and verified by varying $[\mathrm{H^+}]$, $[\mathrm{Cl^-}]$ and $[\mathrm{Y}']$ independently as follows.

(*i*) By keeping $[\mathrm{H^+}]$ constant, adding no extra chloride ions and having the volume of the aqueous phase twice that of the organic, so that equation (18) becomes:

$$K_1 = \frac{[\mathrm{Pd(DDC)_2}]^4_{\mathrm{org}}\alpha_{\mathrm{Y}}}{2[\mathrm{PdCl(DDC)}]^2_{\mathrm{org}}[\mathrm{H^+}]^2[\mathrm{Y}']}. \tag{19}$$

Hence a logarithmic plot of $[\mathrm{Pd(DDC)_2}]^2/[\mathrm{PdCl(DDC)}]$ *vs.* $[\mathrm{Y}']$ should have a slope of 0·5 and an intercept of $\frac{1}{2}\log 2K_1[\mathrm{H^+}]^2/\alpha_{\mathrm{Y}}$. Experimentally a slope of 0·47 was obtained.

(*ii*) By keeping $[\mathrm{Y}']$ constant, adding no extra chloride ions and having the volume ratio as before, so that equation (19) holds and a logarithmic plot of $[\mathrm{Pd(DDC)_2}]^4\alpha_{\mathrm{Y}}/[\mathrm{PdCl(DDC)}]^2$ *vs.* $[\mathrm{H^+}]$ should have a slope of 2. Experimentally a slope of 2·2 was obtained.

(*iii*) By keeping $[\mathrm{Y}']$ and $[\mathrm{H^+}]$ constant, and varying $[\mathrm{Cl^-}]$ so a logarithmic plot of $[\mathrm{Pd(DDC)_2}]^2\alpha_{\mathrm{Y}}/[\mathrm{PdCl(DDC)}]^2[\mathrm{H^+}]^2$ *vs.* $[\mathrm{Cl^-}]$ should have a slope of -2. Experimentally a slope of $-2{\cdot}2$ was obtained.

In chloride solution equation (10) becomes:

$$K_2 = \frac{[H_2PdY]\alpha_{Pd}\alpha_Y}{[Pd'][Y'][H^+]^2}\,. \tag{20}$$

Hence, K_2 can be found by varying $[H^+]$ or $[Y']$ and measuring the ratio $[H_2PdY]$:$[Pd']$.

The individual extraction constants can be found by determining K_A. This was done by using potassium cyanide as a masking agent, the reaction involved being:

$$Pd(DDC)_2 + 4CN^- \rightleftharpoons Pd(CN)_4^{2-} + 2(DDC^-) \tag{21}$$

The constant for the reaction is given by:

$$K_3 = \frac{[Pd(CN)_4^{2-}][DDC^-]^2}{[Pd(DDC)_2]_{org}[CN^-]^4} = \frac{K_5}{K_A} \tag{22}$$

where

$$K_5 = [Pd(CN)_4^{2-}]/[Pd^{2+}][CN^-]^4 \tag{23}$$

is the stability constant $(\beta_4)^4$ of the cyanide complex. It was considered reasonable to assume $Pd(CN)_4^{2-}$ to be the predominating species under conditions of excess of cyanide and high pH. This was verified by plotting log $[Pd(CN)_4^{2-}][DDC^-]^2/[Pd(DDC)_2]$ against log $[CN^-]$: a slope of 4·05 was obtained.

To obtain K_5, potassium cyanide was used at low pH to reverse reaction (2), giving the overall reaction:

$$2PdCl(DDC)_{(org)} + 4CN^- \rightleftharpoons Pd(DDC)_{2(org)} + Pd(CN)_4^{2-} + 2Cl^-. \tag{24}$$

The constant for this reaction is given by:

$$K_6 = \frac{[Pd(DDC)_2]_{org}[Pd(CN)_4^{2-}][Cl^-]^2}{[PdCl(DDC)]^2[CN^-]^4} = \frac{K_5}{K_E}\,. \tag{25}$$

The stability constant for hydrogen cyanide is given by:[4]

$$K_{HCN} = \frac{[HCN]}{[H^+][CN^-]} = 10^{9 \cdot 2}. \tag{26}$$

Therefore at pH values of less than 10, equation (25) becomes:

$$K_6 = \frac{[Pd(DDC)_2]_{org}[Pd(CN)_4^{2-}][Cl^-]^2 K_{HCN}^4 [H^+]^4}{[PdCl(DDC)]_{org}^2[HCN]^4}\,. \tag{27}$$

At low pH values where the cyanide ion concentration is very small it is possible that $Pd(CN)_4^{2-}$ is no longer the predominant species and the lower complexes may be involved. However, a logarithmic plot of

$$\frac{[Pd(DDC)_2][Cl^-]^2[Pd(CN)_4^{2-}]}{[PdCl(DDC)]^2} \; vs. \; \frac{[HCN]}{[H^+]}$$

gave a slope of 4·3, indicating that our assumption was justified under the conditions used.

EXPERIMENTAL

Apparatus

Nucleonic equipment. The scintillation counter used for the measurement of the palladium-103 activity was a 76 × 76 mm NaI(Tl) well-type crystal associated with a single-channel gamma-ray spectrometer. In all experiments counting was carried out in a 10–50 keV channel, at least 10^4 counts being accumulated in each case.

The chlorine-36 activity was measured by means of a liquid scintillation spectrometer using NE 220 scintillator.

Spectrophotometers. Absorbances were measured with a Unicam SP 600 spectrophotometer and spectra with a Uvispek H 700.

Reagents

These were prepared from analytical reagent grade chemicals.

Copper diethyldithiocarbamate solution. Sodium diethyldithiocarbamate was recrystallized by dissolving it in acetone and adding a large excess of ether. After drying under vacuum the crystals were dissolved in distilled water, excess of copper sulphate solution was added and the resulting precipitate of copper diethyldithiocarbamate was extracted with chloroform. The concentration of the resulting solution was checked by absorbance measurements at 436 nm, after dilution where necessary, and solutions of the required concentration were prepared by dilution with chloroform.

Palladium chloride solutions. Prepared by dissolving finely divided palladium metal in *aqua regia.* The resulting solution was evaporated to dryness with hydrochloric acid, many times, to remove the nitric acid, and finally diluted to the required strength with water.

These solutions were standardized against EDTA by the back-titration method developed by MacNevin and Kriege.[5] This method was found to give as satisfactory results as the dimethylglyoxime precipitation method.[6]

Radioisotopes. The isotopes used were palladium-103 and chlorine-36. Palladium solutions in chloroform had to be evaporated to dryness before counting, as the 20-keV rhodium γ-ray, used to detect the palladium-103, is strongly absorbed by solvents containing chlorine.

Palladium diethyldithiocarbamate solution. Prepared by shaking $10^{-3}M$ palladium chloride in $2M$ hydrochloric acid with a substoichiometric amount of $5 \times 10^{-4}M$ copper diethyldithiocarbamate in chloroform, for 5 min. The organic phase, filtered through a dry No. 41 Whatman paper, was $5 \times 10^{-4}M$ in palladium diethyldithiocarbamate.

Palladium chloride diethyldithiocarbamate solution. Prepared by shaking $10^{-3}M$ palladium chloride in $1M$ sulphuric acid with a substoichiometric amount of $5 \times 10^{-4}M$ copper diethyldithiocarbamate in chloroform, for 5 min. The organic phase, filtered through a dry No. 41 Whatman paper, was $10^{-3}M$ in palladium chloride diethyldithiocarbamate.

Procedures

The kinetics of the extraction of palladium as the diethyldithiocarbamate. A $10^{-3}M$ palladium chloride solution labelled with either palladium-103 or chlorine-36 was extracted with a fixed substoichiometric amount of $5 \times 10^{-4}M$ copper diethyldithiocarbamate in chloroform. The molar ratio, $[PdCl_2]/[Cu(DDC)_2]$ was approximately four. The ratio of aqueous to organic phase was kept constant at two. The hydrogen ion and chloride ion concentrations were varied by the addition of sulphuric acid, hydrochloric acid and sodium chloride solutions. The course of the reaction was followed by shaking a series of test solutions for various lengths of time and measuring the activity of a 3-ml aliquot of the organic phase (Figs. 2 and 3).

The results of this study (see *Results and Discussion*) lead to conditions suitable for the preparation of palladium diethyldithiocarbamate and palladium chloride diethyldithiocarbamate.

Spectra. The absorbance of $2{\cdot}5 \times 10^{-5}M$ palladium diethyldithiocarbamate solution in chloroform was measured in a 10-mm cell against pure chloroform, at intervals of 10 nm over the wavelength range 200–500 nm. This procedure was repeated with $2{\cdot}5 \times 10^{-5}M$ palladium chloride diethyldithiocarbamate in chloroform (Fig. 4).

Partition coefficients. Both the palladium diethyldithiocarbamate and palladium chloride diethyldithiocarbamate were treated in the same way.

Ten ml of a solution of the appropriate complex in chloroform were shaken with 500 ml of distilled water. The aqueous layer was filtered through a No. 42 Whatman paper and shaken with 10 ml of chloroform. The first and second organic layers were filtered through dry No. 41 Whatman papers and the concentration of the complex was determined by absorbance measurements at 350 nm, after dilution where necessary.

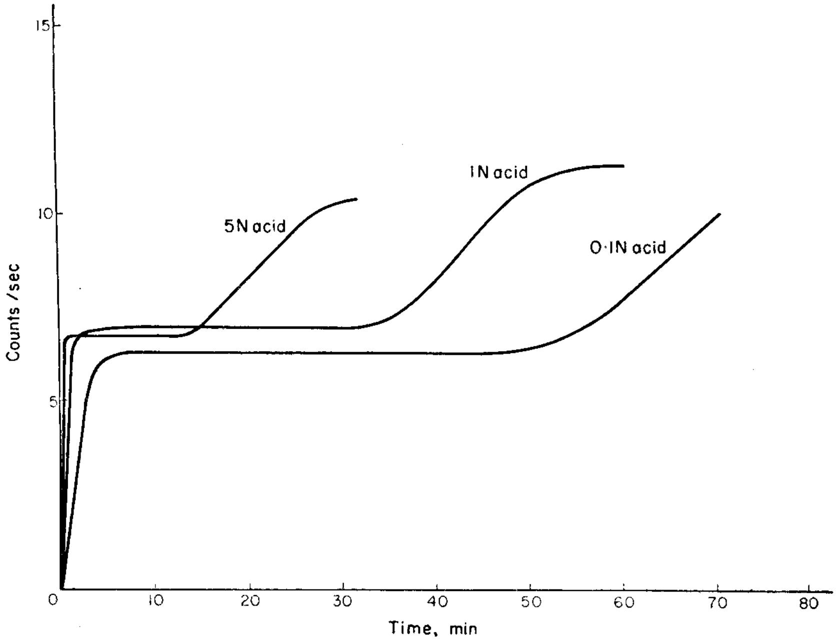


FIG. 2.—Effect of hydrogen ion concentration on the extraction rate of palladium as the diethyldithiocarbamates.
$10^{-3}M$ palladium chloride; $5 \times 10^{-4}M$ copper diethyldithiocarbamate

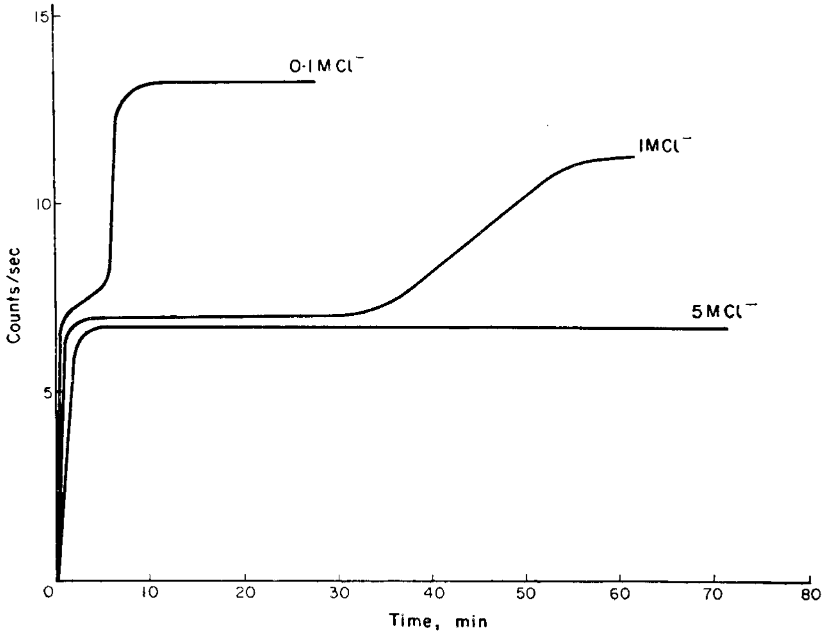


FIG. 3.—Effect of chloride ion concentration on the extraction rate of palladium as the diethyldithiocarbamates.
$10^{-3}M$ palladium chloride; $5 \times 10^{-4}M$ copper diethyldithiocarbamate

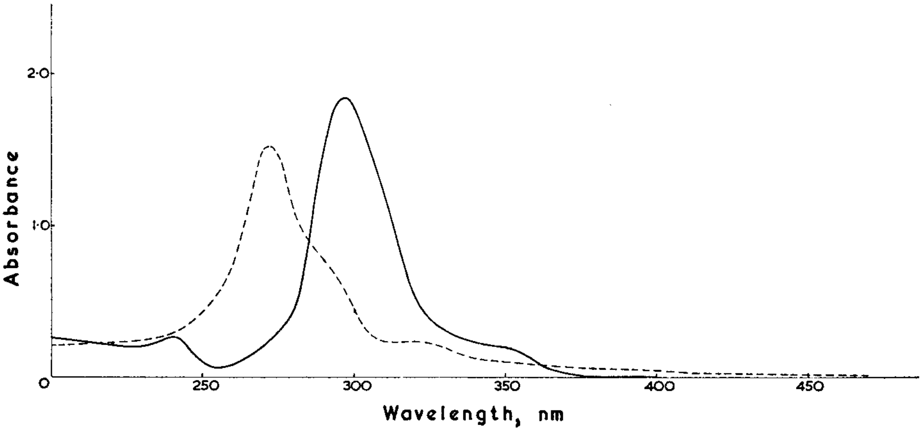


Fig. 4.—Spectra of palladium diethyldithiocarbamate and palladium chloride diethyldithiocarbamate.
——— $2{\cdot}5 \times 10^{-5}M$ palladium diethyldithiocarbamate
– – – – $2{\cdot}5 \times 10^{-5}M$ palladium chloride diethyldithiocarbamate

Determination of K_1. A series of aqueous solutions was prepared, having varied compositions.

1. EDTA (disodium salt) only, over the concentration range 10^{-3}–$10^{-4}M$.
2. A fixed $10^{-3}M$ EDTA concentration with sulphuric acid or perchloric acid added to give a pH range of 1–3.
3. A fixed $10^{-3}M$ EDTA concentration with hydrochloric acid added to give chloride ion concentrations of 10^{-2}–$10^{-3}M$. The pH remained fairly constant, owing to the buffering effect of the EDTA.

To 10 ml of the appropriate aqueous phase were added 5 ml of $10^{-3}M$ palladium chloride diethyldithiocarbamate in chloroform, labelled with palladium-103. The mixture was shaken for 20–30 min, and the organic phase filtered through a dry No. 41 Whatman paper. The activity of a 3-ml aliquot was determined and the absorbances at 350 and 400 nm were measured. The initial activity of the organic phase was determined by counting a 3-ml aliquot of the original palladium chloride diethyldithiocarbamate solution in chloroform.

Determination of K_2. The spectrophotometric properties of the $PdCl_4^{2-}$ ion were investigated by scanning a palladium chloride solution containing excess of chloride ions. The peak[7] at 470 nm was found to be unchanged over a chloride ion concentration range of 0·5–2*M* and a pH range of 0–3. It also obeyed Beer's law over the $PdCl_4^{2-}$ concentration range of 5–80 × $10^{-4}M$.

The spectrophotometric properties of the palladium–EDTA complex, H_2PdY, produced by reacting a palladium chloride solution with excess of EDTA at pH 1–3, were found to be less ideal. The peak[8] at 390 nm obeyed Beer's law only approximately. However, it was quite possible to separate the peaks at 390 and 470 nm and hence calculate the concentrations of the species $PdCl_4^{2-}$ and H_2PdY in a mixture.

A series of test solutions was prepared by diluting 2 ml of approximately $10^{-2}M$ palladium chloride to 10 ml with EDTA solutions of varying concentrations from 10^{-4}–$10^{-2}M$. The pH was adjusted with hydrochloric acid over the range 0–2 and the chloride ion concentration was made up to 1*M* with sodium chloride. The reactions were allowed to come to equilibrium (*ca.* 1 hr) and the absorbances at 390 and 470 nm were measured. The concentrations of the $PdCl_4^{2-}$ and H_2PdY were calculated by comparison with absorbance measurements carried out under conditions where either EDTA alone or chloride alone was present.

Determination of K_3. To 5-ml portions of 5 × $10^{-4}M$ palladium diethyldithiocarbamate in chloroform, labelled with palladium-103, were added 10 ml of an aqueous phase, 0·1–1*M* in potassium cyanide. The mixture was shaken for 3–4 hr, and the organic phase was filtered through a dry No. 41 Whatman paper. The activity of a 3-ml aliquot was determined and the absorbance at 350 nm was measured. The initial activity of the organic phase was determined by counting a 3-ml aliquot of the original labelled palladium diethyldithiocarbamate solution in chloroform.

Determination of K_6. The pH of 10-ml portions of $10^{-2}M$ potassium cyanide was adjusted, over the range from −0·30 to 0·7 with perchloric acid. These were shaken for 10 min with 5-ml portions of $10^{-3}M$ palladium chloride diethyldithiocarbamate in chloroform, labelled with palladium-103. The organic phase was filtered through a dry No. 41 Whatman paper and the activity of a 3-ml aliquot determined. The initial activity of the organic phase was determined by counting a 3-ml aliquot of the original labelled palladium chloride diethyldithiocarbamate solution in chloroform.

RESULTS AND DISCUSSION

The nature of the palladium diethyldithiocarbarbamate complexes and the kinetics of their formation

A typical rate curve, produced when a palladium chloride solution labelled with palladium-103 is extracted with a fixed substoichiometric amount of copper diethyldithiocarbamate in chloroform, is shown in Fig. 5. The first plateau (*a*) corresponds to a palladium to diethyldithiocarbamate ratio of 1:2 in the organic phase, while the final plateau (*b*) corresponds to a ratio of 1:1. If the original palladium chloride solution is labelled with chlorine-36 and extractions are carried out under identical conditions to those previously used, then a rate curve as illustrated in Fig. 6 is produced. By comparing Figs. 5 and 6 it can be seen that while the 1:2 complex ([Pd]/[DDC]) is present, no chloride is extracted into the organic phase. However, when the 1:1 complex ([Pd]/[DDC]) is formed a plateau occurs in Fig. 6 corresponding to a diethyldithocarbamate to chloride ratio of 1:1 in the organic phase.

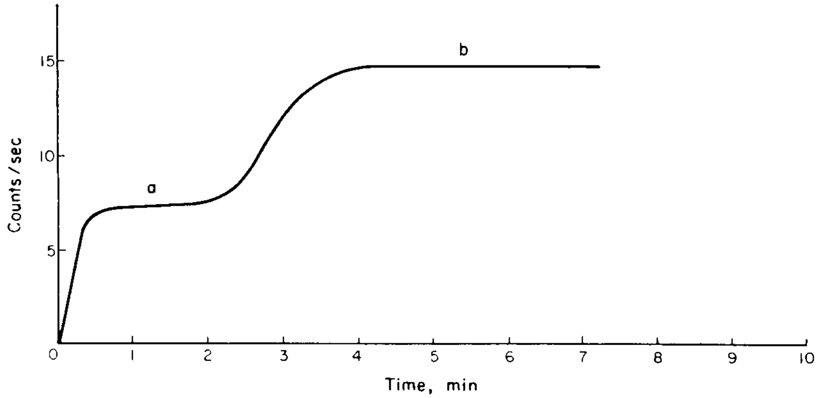


FIG. 5.—Palladium-103 extracted into the organic phase as a function of time of extraction.
$10^{-3}M$ palladium chloride in $10^{-2}M$ sodium chloride extracted with $5 \times 10^{-4}M$ copper diethyldithiocarbamate.

These results indicate that under these substoichiometric conditions two complexes are formed consecutively, having empirical formulae $Pd(DDC)_2$ for the first and PdCl (DDC) for the second. The first complex has the same spectrum (Fig. 4) and composition as that formed under the normal conditions of solvent extraction, *i.e.*, copper diethyldithiocarbamate in excess over palladium chloride, and has been reported by many authors.[9–14]

The shape of the rate curve (Fig. 5) suggests that the production of palladium chloride diethyldithiocarbamate [equation (2)] is autocatalytic in nature. This was shown to be so by the addition of small amounts of a previously prepared palladium chloride diethyldithiocarbamate solution in chloroform to the reaction mixture just after the formation of the palladium diethyldithiocarbamate (Fig. 7).

Investigating the effect of hydrogen ion and chloride ion concentration on the rates of the two reactions showed that increasing the hydrogen ion concentration of

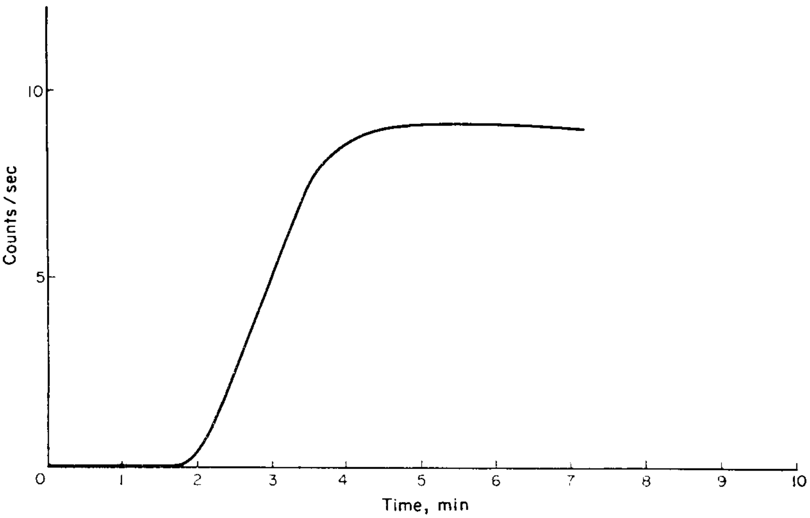


FIG. 6.—Chlorine-36 extracted into the organic phase as a function of time of extraction. $10^{-3}M$ palladium chloride in $10^{-2}M$ sodium chloride extracted with 5 × $10^{-4}M$ copper diethyldithiocarbamate

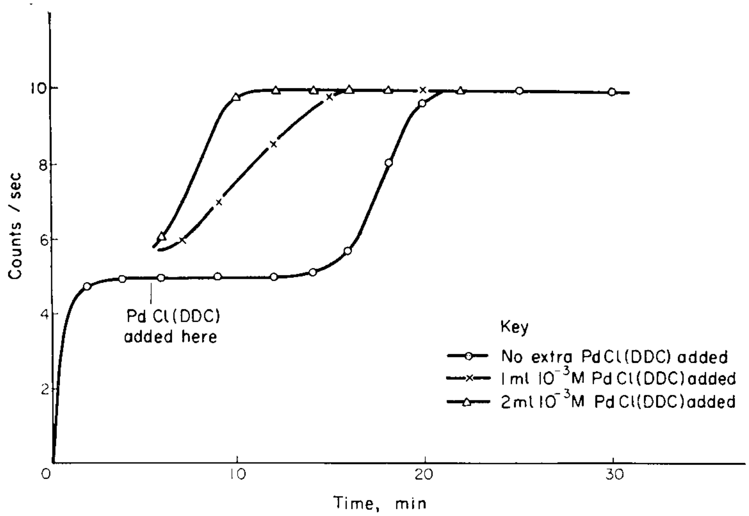


FIG. 7.—Palladium-103 extracted into the organic phase showing the effect of the addition of palladium chloride diethyldithiocarbamate on the rate of the reaction. 2 × $10^{-3}M$ palladium chloride in 1M hydrochloric acid extracted with 5 × $10^{-4}M$ copper diethyldithiocarbamate

the aqueous phase increased the rate of both reactions (Fig. 2) while increasing the chloride ion concentration of the aqueous phase slowed both reactions (Fig. 3). However, in the case of chloride ions the second reaction was affected far more than the first, indeed to such an extent that in the presence of very high chloride ion concentrations (4–5*M*) the second reaction did not occur at all. This meant that conditions for the aqueous phase could be selected for the complete production of either complex, *i.e.*, high hydrogen ion and chloride ion concentrations for the palladium diethyldithiocarbamate; high hydrogen ion but low chloride ion concentrations for the palladium chloride diethyldithiocarbamate.

Spectra and extinction coefficients

The spectra of the two complexes are shown in Fig. 4. Both absorb strongly in the ultraviolet region but are visibly distinguishable because, in chloroform solution, palladium diethyldithiocarbamate is pale yellow, while palladium chloride diethyldithiocarbamate is orange.

The molar absorptivity of palladium chloride diethyldithiocarbamate in chloroform is $6{\cdot}10 \times 10^3$ l.mole.$^{-1}$ mm^{-1} at the absorption maximum of 272 nm, and that of palladium diethyldithiocarbamate is $7{\cdot}30 \times 10^{-3}$ at the absorption maximum of 297 nm.

At 350 nm both complexes have the same molar absorptivity with respect to diethyldithiocarbamate. This enables a mixture of the two complexes to be resolved semiquantitatively by measuring the total diethyldithiocarbamate concentration at 350 nm and the palladium chloride diethyldithiocarbamate concentration at 400 nm.

Partition coefficients

The partition coefficients of both complexes between chloroform and water were calculated from the measured concentrations of the complexes in two successive organic extracts, using the expression:

$$P = \frac{V_{aq}}{V_{org}}\left(\frac{C_{org1}}{C_{org2}} - 1\right)$$

where $P = \dfrac{\text{concentration of the complex in the organic phase}}{\text{concentration of the complex in the aqueous phase}}$,

V_{aq} and V_{org} are the volumes of the aqueous and organic phases, and C_{org1} and C_{org2} are the concentrations of the complex in the first and second organic phases. This method is that of Sandell.[15]

The values of P obtained are 330 for palladium chloride diethyldithiocarbamate (mean of three determinations) and $7{\cdot}00 \times 10^4$ for palladium diethyldithiocarbamate (mean of two determinations). Both are sufficiently high for the complexes to be suitable for a substoichiometric solvent extraction procedure.

Determination of K_1 [*equation* (18)]

The concentrations of the two complexes present in the organic phase after equilibration with an aqueous phase of varying EDTA, hydrogen ion and chloride ion concentrations (see *Experimental*), were calculated from the expressions:

$$[\mathrm{Pd(DDC)_2}] = \left(1 - \frac{A}{A_s}\right) \times 10^{-3}$$

and

$$[\mathrm{PdCl(DDC)}] = \frac{A}{A_s} \times 10^{-3} - [\mathrm{Pd(DDC)_2}],$$

where the original measured activity of the organic phase is represented by A_s and the final activity by A. The absorbance measurements of the organic phase at 350 and 400 nm were used to check these concentrations. This enabled the term $[\mathrm{Pd_{aq}}]$ to be calculated. Under the conditions used all the palladium in the aqueous phase would be present as the species H_2PdY and hence, from a knowledge of the original EDTA concentration, the term $[Y']$ could be calculated. The results, shown in Table I, give a mean value for log K_1 of 14·5 (standard deviation = 0·25).

TABLE I.—DETERMINATION OF K_1

$\mathrm{pPd(DDC)_2}$	pPdCl(DDC)	$\mathrm{pPd_{aq}}$	$\mathrm{pCl^-}$	pH	pY′	log α_Y	log K_1
Variation of [Y′]							
3·456	3·523	3·757	3·456	3·60	4·602	9·4	14·12
3·392	3·721	3·693	3·392	3·60	4·328	9·4	14·50
3·371	3·830	3·672	3·371	3·60	3·947	9·4	14·42
3·358	3·907	3·660	3·358	3·60	3·701	9·4	14·37
3·351	3·921	3·658	3·356	3·60	3·553	9·4	14·27
3·347	4·000	3·648	3·347	3·60	3·536	9·4	14·45
3·343	4·036	3·644	3·343	3·70	3·321	9·2	14·32
3·337	4·097	3·638	3·337	3·80	3·249	9·0	14·39
3·323	4·301	3·620	3·323	3·60	3·118	9·4	14·73
3·323	4·301	3·623	3·323	3·85	3·060	8·9	14·67
Variation of [H⁺]							
3·323	4·301	3·623	3·323	3·85	3·060	8·9	14·67
3·490	3·454	3·790	3·490	2·20	3·050	13·0	14·10
3·378	3·790	3·678	3·378	2·00	3·102	13·6	14·47
3·680	3·255	3·980	3·680	1·35	3·040	16·0	14·23
3·497	3·304	3·798	3·497	1·20	3·047	16·5	14·27
3·830	3·152	4·131	3·830	0·35	3·033	19·9	14·32
Variation of [Cl⁻]							
3·344	4·027	3·644	3·344	3·65	3·112	9·3	14·10
3·347	4·000	3·648	2·839	3·50	3·075	9·6	14·99
3·374	3·812	3·674	2·616	3·44	3·071	9·7	14·99
3·433	3·582	3·733	2·472	3·36	3·031	9·9	14·71
3·450	3·538	3·750	2·360	3·22	3·000	10·2	14·80
3·520	3·402	3·821	2·276	3·10	3·000	10·6	14·71
3·595	3·308	3·896	2·205	2·96	3·000	10·9	14·64
3·625	3·279	3·926	2·084	2·88	3·000	11·0	14·62
4·131	3·070	4·432	2·003	2·22	3·000	12·9	14·21

The ionic strength was not kept constant in these experiments. Attempts to maintain a constant ionic strength, even with sodium perchlorate, resulted in an interference with the reaction. However, variations in ionic strength can be corrected for by using the Davies[16] equation. In this case the ionic strength was never greater than 10^{-2}, corresponding to a maximum correction of less than 5%. Therefore ionic strength effects were ignored.

Determination of K_2 [*equation* (20)]

From the absorbance measurements at 390 and 470 nm the concentrations of the two species $PdCl_4^{2-}$ and H_2PdY were calculated from the equations:

$$[PdCl_4^{2-}] = 2 \times 10^{-3} \times (Ad - (cB)/ad - bc)$$
$$[H_2PdY] = 2 \times 10^{-3} \times (aB - Ab)/(ad - bc)$$

where a = absorbance of $2 \times 10^{-3}M$ $PdCl_4^{2-}$ solution at 470 nm
b = absorbance of $2 \times 10^{-3}M$ $PdCl_4^{2-}$ solution at 390 nm
c = absorbance of $2 \times 10^{-3}M$ H_2PdY solution at 470 nm
d = absorbance of $2 \times 10^{-3}M$ H_2PdY solution at 390 nm
A = measured absorbance at 470 nm
B = measured absorbance at 390 nm.

The total palladium concentration was $2 \times 10^{-3}M$. From a knowledge of these concentrations the terms [Pd′] and [Y′] were determined. Fig. 1 was used to obtain the value of α_{Pd} and hence K_2 was calculated. The results, shown in Table II, give a mean value for log K_2 of 38·0 (standard deviation = 0·14).

TABLE II.—DETERMINATION OF K_2

pPd′	pH_2PdY	pH	log α_Y	log α_{Pd}	pY′	log K_2
2·742	3·745	1·30	16·1	15·5	4·699	37·90
2·824	3·337	1·33	16·0	15·5	4·398	38·05
2·939	3·071	1·40	15·8	15·5	3·824	37·79
3·444	2·851	1·41	15·8	15·5	3·229	37·94
3·824	2·752	1·43	15·7	15·5	2·910	38·04
4·222	2·730	1·50	15·4	15·5	2·670	38·06
4·301	2·719	1·55	15·2	15·5	2·510	37·89
2·759	3·921	0·50	19·2	15·5	3·430	37·97
2·767	3·569	0·50	19·2	15·5	3·137	38·04
2·845	3·244	0·50	19·2	15·5	2·845	38·15
2·991	3·131	0·50	19·2	15·5	2·513	38·07
3·009	2·963	0·50	19·2	15·5	2·408	38·15
3·180	2·879	0·50	19·2	15·5	2·246	38·25
3·260	2·821	0·50	19·2	15·5	2·071	38·21
3·495	2·750	0·50	19·2	15·5	1·739	38·18

In these experiments the ionic strength was maintained at a constant value of 1, in sodium chloride, for two reasons.

1. At lower chloride ion concentrations a mixture of palladium–chloride complexes is produced, making spectrophotometric measurements more difficult.
2. Lowering the chloride ion concentration, and hence α_{Pd}, would mean using higher acidities, which would in any case increase the ionic strength.

In order to compare this value of K_2 with the value of K_1 determined at low ionic strengths it was necessary to correct K_2. This was done by using activity coefficients calculated by the Davies[16] equation. This gave a correction factor of 8·8 giving a corrected value of 39·0 for log K_2.

Determination of K_3 [*equation* (22)]

The concentration of palladium diethyldithiocarbamate in the organic phase was determined from the activity measurement and the absorbance at 350 nm. By assuming that all the palladium in the aqueous phase was present as the species $Pd(CN)_4^{2-}$, the concentrations of this ion and of the cyanide and diethyldithiocarbamate ions were also determined. The results, shown in Table III give a mean value for log K_3 of −7·7 (standard deviation = 0·09).

TABLE III.—DETERMINATION OF K_3

pCN^-	$pPd(CN)_4^{2-}$	$pPd(DDC)_2$	$pDDC^-$	log K_3
1·000	5·000	3·332	5·000	−7·67
0·699	4·569	3·340	4·569	−7·57
0·699	4·602	3·347	4·602	−7·66
0·523	4·409	3·374	4·409	−7·76
0·301	4·131	3·452	4·131	−7·74
0·301	4·155	3·444	4·155	−7·82
0	3·839	3·678	3·839	−7·84
0	3·836	3·661	3·836	−7·85
0	3·818	3·708	3·818	−7·75

As, in all cases, the pH was greater than 10, no correction was required for protonation of cyanide ions. However, the ionic strength varied from 0·1 to 1·0 in potassium cyanide. The Davies[16] equation yields a constant correction factor of 0·6 for this range, giving a corrected value of −8·0 for log K_3.

Determination of K_6 [*equation* (27)]

The concentrations of palladium chloride diethyldithiocarbamate and palladium diethyldithiocarbamate in the organic phase were determined as in the determination of K_1. Again all the palladium in the aqueous phase was present as the $Pd(CN)_4^{2-}$ ion. Thus by use of the value of 9·2 for log K_{HCN} [equation (26)] the results, shown in Table IV, give a mean value for log K_6 of 37·5 (standard deviation = 0·36).

TABLE IV.—DETERMINATION OF K_6

pPdCl(DDC)	$pPd(DDC)_2$	$pPd(CN)_4^{2-}$	pCl^-	pHCN	pH	log K_6
4·301	3·301	3·602	3·301	2·0	0·7	37·10
3·699	3·398	3·699	3·398	2·0	0·3	37·11
3·481	3·481	3·777	3·481	2·0	0	37·54
3·398	3·602	3·903	3·602	2·0	−0·18*	37·90
3·301	3·523	3·824	3·523	2·0	−0·30*	37·91

* Calculated pH values.

The Davies[16] equation was again used to give a constant correction factor of 0·6 over the experimental range of ionic strength. The corrected value thus obtained for log K_6 is 37·3.

The experimental results obtained therefore give:

$$\log K_1 = 14{\cdot}5$$

$$\log K_2 = 39{\cdot}0$$

$$\log K_3 = -8{\cdot}0$$

$$\log K_6 = 37{\cdot}3$$

The exchange constant K_E

From equation (9):

$$\log K_E = \log K_2 - \log K_1$$

$$= 24{\cdot}5.$$

The stability constants for the two complexes

From equation (25):

$$\log K_5 = \log K_6 + \log K_E$$

$$= 61{\cdot}8.$$

From equation (22):

$$\log K_A = \log K_5 - \log K_3$$

$$= 69{\cdot}8.$$

From equation (5):

$$2 \log K_B = \log K_E + \log K_A$$

$$= 94{\cdot}3$$

$$\therefore \log K_B = 47{\cdot}2.$$

The stability constant of palladium diethyldithiocarbamate is given by:

$$K_{Pd(DDC)_2} = \frac{[Pd(DDC)_2]}{[Pd^{2+}][DDC^-]^2}$$

corresponding to the reaction

$$Pd^{2+} + 2DDC^- \rightleftharpoons Pd(DDC)_2$$

in the aqueous phase.

The extraction constants, K_A and K_B, together with the partition coefficients of the complexes, can now be used to calculate the stability constants, for $[Pd(DDC)_2]_{aq} = [Pd(DDC)_2]_{org}/P_{Pd(DDC)_2}$. If $P_{Pd(DDC)_2}$ is the partition coefficient of palladium diethyldithiocarbamate and $P_{PdCl(DDC)}$ is that of palladium chloride diethyldithiocarbamate, both between chloroform and water, then $K_{Pd(DDC)_2} = K_A/P_{Pd(DDC)_2}$ and $K_{PdCl(DDC)} = K_B/P_{PdCl(DDC)}$, giving $\log K_{Pd(DDC)_2} = 64{\cdot}9$ and $\log K_{PdCl(DDC)} = 44{\cdot}6$.

Summary of the constants determined in this paper

Palladium diethyldithiocarbamate

Extraction constant into chloroform, $\log K_A = 69{\cdot}8$.
Partition coefficient between chloroform and water, $\log P_{Pd(DDC)_2} = 4{\cdot}9$.
Stability constant (β_2), $\log K_{Pd(DDC)_2} = 64{\cdot}9$.
Molar absorptivity at 297 nm, $\varepsilon_{Pd(DDC)_2} = 7{\cdot}30 \times 10^3$ l. mole.$^{-1}$ mm^{-1}.

Palladium chloride diethyldithiocarbamate:

Extraction constant into chloroform, $\log K_B = 47{\cdot}2$.
Partition coefficient between chloroform and water, $\log P_{PdCl(DDC)} = 2{\cdot}5$.
Stability constant $\log K_{PdCl(DDC)} = 44{\cdot}6$.
Molar absorptivity at 272 nm, $\varepsilon_{PdCl(DDC)} = 6{\cdot}10 \times 10^3$ l. mole.$^{-1}$ mm^{-1}.

$Pd(CN)_4^{2-}$ *complex*
Stability constant (β_4), $\log K_5 = 61{\cdot}8$.

H_2PdY *complex* (Y = EDTA)
Stability constant (β_{12}), $\log K_2 = 39{\cdot}0$.

The use of the complexes in a substoichiometric solvent extraction procedure for palladium

For the purpose of substoichiometric solvent extraction the constants of interest are the extraction constants of the complexes, K_A and K_B, and the exchange constant, K_E. In the absence of any interfering species, anionic or cationic, palladium chloride diethyldithiocarbamate will be completely formed provided that sufficient time is allowed for equilibrium to be reached and sufficient chloride ions are present.

In the presence of interfering metal ions both reactions will go to completion, unless the interfering metal has an extraction constant comparable with or greater than K_A. In the presence of strong complexing agents, one or both of the reactions may be prevented. Of all the reagents known to complex strongly with palladium only potassium cyanide was found to prevent both reactions. However, it is expected that several reagents will prevent only the second reaction [equation (2)]. For this to occur the conditional stability constant[3] of the complex formed with palladium must lie between the values of K_E and K_A. (For a complexing agent A the conditional stability constant is defined as $K = [PdA]/[Pd][A']$ where $[A']$ is the total concentration of A in all its forms.) Both EDTA and potassium cyanide at certain pH values fall into this category.

Under the conditions used in activation analysis (*i.e.*, with mg-amounts of carriers) palladium chloride diethyldithiocarbamate is of limited value because (*a*) its formation is more subject to interference than is that of palladium diethyldithiocarbamate and (*b*) in the chloride ion concentrations which are likely to be used in real analysis, *i.e.*, $>1M$, it is formed very slowly.

Work is now in progress to develop methods for the substoichiometric determination of traces of palladium by neutron-activation and radioactive isotope-dilution analysis, using these complexes.

Acknowledgements—The authors wish to thank The University of Aston in Birmingham for the provision of a research assistantship (S. H.) which enabled the work reported to be carried out.

Zusammenfassung—Die Reaktion von Palladium mit Kupferdiäthyldithiocarbamat wurde untersucht und zwei Komplexe isoliert Palladiumdiäthyldithiocarbamat und Palladiumchloriddiathyldithiocarbamat. Die Spektren beider Komplexe wurden gemessen. Die Extraktionskonstanten und Verteilungskoeffizienten zwischen Chloroform und Wasser wurden bestimmt, die ersten unter Verwendung starker Komplexbildner zur Maskierung von Palladium. Die Stabilitätskonstanten und die Austauschkonstante der beiden Komplexe wurden berechnet.

Résumé—On a étudié la réaction du palladium avec le diéthyldithiocarbamate de cuivre et l'on a isolé deux complexes: diéthyldithiocarbamate de palladium et diéthyldithiocarbamate-chlorure de palladium. On a examiné les spectres des deux complexes. On a déterminé les constantes d'extraction et les coefficients de partage entre le chloroforme et l'eau, les premiers par l'emploi d'autres réactifs complexants forts comme agents de dissimulation du palladium On a calculé les constantes de stabilité et la constante d'échange pour les deux complexes.

REFERENCES

1. G. Iwantscheff, *Das Dithizon und seine Anwendung in der Mikro und Spurenanalyse*, p. 115. Verlag Chemie, Weinheim, 1958.
2. J. Růžička and J. Starý, *At. Energy Review, I.A.E.A. Vienna*, 1964, **2**, 3.
3. A. Ringbom, *Complexation in Analytical Chemistry*, Chap. 2. Interscience, New York, 1963.
4. L. G. Sillén and A. E. Martell, *Stability Constants of Metal-ion Complexes*, Spec. Publn. No. 17, Chemical Society, London, 1964.
5. W. M. MacNevin and O. H. Kriege, *Anal. Chem.*, 1955, **27**, 535.
6. R. Belcher and A. J. Nutten, *Quantitative Inorganic Analysis*, Butterworths, London, 1960.
7. A. J. Cohen and N. Davidson, *J. Am. Chem. Soc.*, 1951, **73**, 1955.
8. W. M. MacNevin and O. H. Kriege, *ibid.*, 1955, **77**, 6149.
9. M. Bobtelsky and J. Eisenstadter, *Anal. Chim. Acta*, 1957, **16**, 479.
10. H. Bode, *Z. Anal. Chem.*, 1955, **144**, 165.
11. K. Glen and R. Schwab, *Angew. Chem.*, 1950, **62**, 326.
12. W. Beyer and R. D. Ott, *Mikrochim. Acta*, 1965, 1130.
13. L. Malatesta, *Gazz. Chim. Ital.*, 1938, **68**, 195.
14. J. T. Pyle and W. D. Jacobs, *Anal. Chem.*, 1964, **36**, 1796.
15. R. W. Geiger and E. B. Sandell, *Anal. Chim. Acta*, 1953, **8**, 197.
16. C. W. Davies, *Ion Association*, Butterworths, London, 1962.

Talanta, 1969, Vol. 16, pp. 1421 to 1429. Pergamon Press. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM(IV), IRIDIUM(IV) AND PLATINUM(IV) AND SEPARATION AND DETERMINATION OF PALLADIUM(II) AND RUTHENIUM(III) IN THE PRESENCE OF OTHER PLATINUM METALS, WITH OXIMIDOBENZOTETRONIC ACID AS REAGENT

G. S. MANKU, A. N. BHAT and B. D. JAIN
Department of Chemistry, University of Delhi, Delhi-7, India

(*Received* 9 *January* 1968. *Revised* 15 *October* 1968. *Accepted* 3 *November* 1968)

Summary—Oximidobenzotetronic acid is suggested as a reagent for the spectrophotometric determination of osmium(IV), iridium(III), iridium(IV), platinum(IV) and for separation and determination of palladium(II) and ruthenium(III) in the presence of other platinum metals. Iridium(III) and (IV) can be estimated when present together.

IRIDIUM is one of the minor constituents of most platinum metal ores, and there is thus a need for sensitive and accurate methods for its determination. The available spectrophotometric methods for the determination of iridium have recently been reviewed by Beamish.[1] The use of perchloric acid–phosphoric acid[2] appears to be most suitable for the determination of 6–100 ppm of iridium; for 0·5–4·0 ppm the use of leuco-Crystal Violet has been recommended.[3] For the separation and estimation of ruthenium in presence of other platinum metals, no suitable reagent has been reported.[4,5] Iridium must be absent[6] when dimethylglyoxime is used for the separation and gravimetric determination of palladium. Ruthenium, along with osmium, can be separated from other platinum metals as the tetroxide by distillation, but the separation is not quantitative in the presence of chloro-complexes.[4]

Oximidobenzotetronic acid (OBTA, or 3-nitroso-4-hydroxycoumarin) has already been used as a gravimetric reagent for cobalt(II),[7] iron(II)[8] and palladium(II)[9] and as a spectrophotometric reagent for iron(II)[10], cobalt(II),[11] ruthenium(III),[12] and rhodium(III).[12] Its complexes with some bivalent metal ions[13] and lanthanon(III) ions[14] have been investigated in solution. On studying the reaction of OBTA with other platinum metals, it was observed that on boiling sodium chloroiridate(IV) solution with ethanolic OBTA, a wine-red colour is produced instantaneously at pH 10–12, but a brown-black colour results when potassium chloro-osmate(IV) solution is boiled with OBTA at pH 1·5–3·5. With chloroplatinic(IV) acid, there is slow development of a bright yellow colour (turning deep red at pH 12) on heating with an ethanol or acetone solution of OBTA. The present communication deals with spectrophotometric studies of these complexes and the spectrophotometric determination of these metal ions with the help of OBTA. As these complexes have been found to be anionic in nature, and precipitation of palladium(II) is quantitative even in presence of other platinum metals, the use of OBTA for the separation and gravimetric estimation of palladium, and then for the separation of ruthenium(III) (a neutral OBTA complex) by ion-exchange followed by spectrophotometric estimation, has also been investigated.

Osmium(VI), in the form of potassium osmate(VI), and platinum(II) as sodium chloroplatinate(II), do not give any coloured products with this reagent. Iridium(III), as sodium chloroiridate(III), gives a brownish red colour under conditions similar to those used for iridium(IV); the absorption spectra obtained in alkaline conditions are similar, but the molar absorptivities are different, so iridium(IV) and iridium(III) can be determined simultaneously.

Since OBTA undergoes some change when heated, the nature of the coloured complexes was not investigated.

EXPERIMENTAL

Reagents

Oximidobenzotetronic acid was prepared from 4-hydroxycoumarin,[15] and a freshly prepared ethanolic solution of it was used for all the investigations. Stock solutions of the platinum metal salts were made from ruthenium(III) trichloride, sodium chlororhodate(III), palladium(II) nitrate, potassium chloro-osmate(IV), sodium chloroiridate(III), chloroiridic(IV) acid and chloroplatinic(IV) acid in 1M hydrochloric acid and were standardized by gravimetric[16,17] and spectrophotometric methods.[18] For ion-exchange studies, Amberlite ion-exchange resins were used. All chemicals used were analytical reagent grade. The pH of the solutions was adjusted with dilute solutions of hydrochloric acid, sodium hydroxide or potassium hydroxide and measured with a pH-meter.

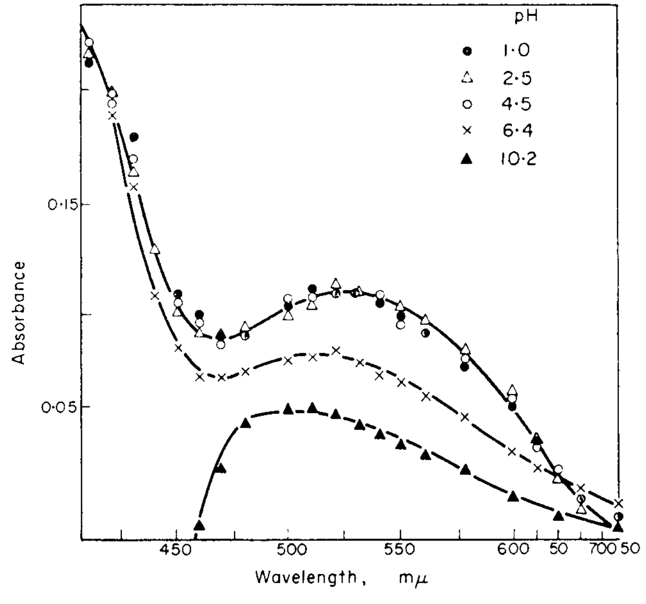


FIG. 1.—Absorption spectra of osmium(IV) complex [5 ppm Os(IV)] at different pH values.

Absorption spectra of the complexes

Osmium(IV). A 10-fold excess of OBTA was added to potassium chloro-osmate(IV) solution at pH 2·1 and the solution was boiled for *ca.* 1 min. The absorption spectrum of the resultant brownish-black solution, measured against a reagent blank (Fig. 1) showed a single absorption maximum at 520–540 nm over the pH range 1·0–10·4. OBTA has neglible absorbance at 520 nm.

Iridium(IV). A 10-fold excess of OBTA was added to chloroiridic(IV) acid and the pH of the resultant solution was raised to $\sim$12. The resultant pale yellow solution turned deep wine-red when heated to boiling. Under these conditions in the absence of OBTA, iridium(IV) is reduced to metallic iridium and precipitated. The absorption spectrum of this wine-red solution (against a reagent blank) showed that at pH $>$ 8·0 there was an absorption maximum at 470–480 nm, but none in the visible

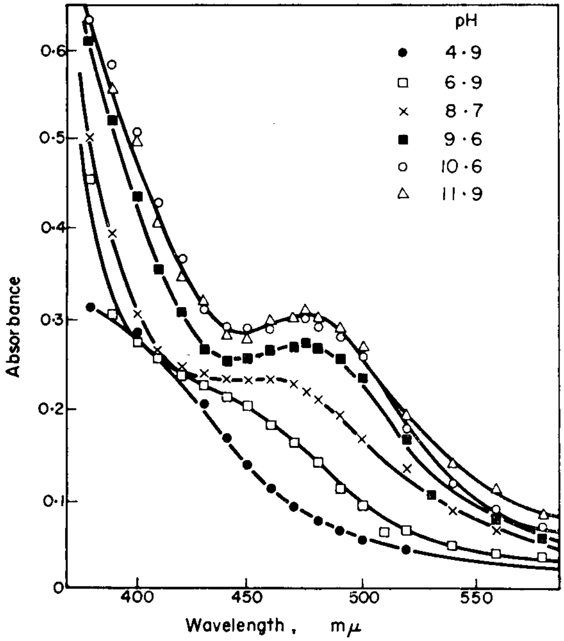


FIG. 2.—Absorption spectra of iridium(IV) complex [6·5 ppm Ir(IV)] at different pH values.

region of the spectrum if the pH was <8·0 (Fig. 2). OBTA and chloroiridate(IV) have negligible absorbance at 576 nm.

Iridium(III). With iridium(III) a brownish red colour is produced with OBTA under the conditions used for iridium(IV). The wavelength of maximum absorption shifts from 410 nm at pH 4·3 (yellowish brown solution) to 480 nm at pH > 9·0 (reddish brown solution), the curves passing through an isosbestic point at 445 nm (Fig. 3). This indicates the formation of two complexes (since the absorption due to iridium(III) is negligible under the experimental conditions). For the analytical determination of iridium(III) only the reddish-brown complex was used and the wavelength chosen was 480 nm, the reagent showing negligible absorbance at this wavelength.

Platinum(IV). The absorption spectrum of the yellow solution obtained by heating chloroplatinic(IV) acid with a 10-fold excess of OBTA at pH 3·5, in a boiling water-bath for 45 min, is shown in Fig. 4 (reagent as blank). Over the pH range 2·0–8·1, the yellow solution showed an absorption maximum at 425 nm but at higher pH the solution turned red and exhibited an absorption maximum at 480–490 nm (isobestic point at 450 nm). The absorption due to chloroplatinate(IV) under these conditions was negligible. It was concluded that two complexes were formed.

RESULTS

Effect of variation in conditions

Except for the platinum(IV), the complexes were formed instantaneously on boiling, and colour development was maximal within 15 sec. For platinum(IV) at pH 3·5, however, heating in a boiling water-bath for 35 min was necessary, and for iridium(IV) at pH 2, complex formation required heating in a boiling water-bath for 60 min. The osmium(IV), iridium(III), iridium(IV) and platinum(IV) complexes at pH 2·1, 12, 12 and 3·5 respectively, were found to be stable for 60, 30, 10 and 40 min respectively when kept in a boiling water-bath, whereas at room temperature (30°) these complexes showed no change in absorbance for 24 hr, 4 days, 50 min and 24 hr respectively.

The effect of pH on the absorbance of the complexes is shown in Fig. 5. The

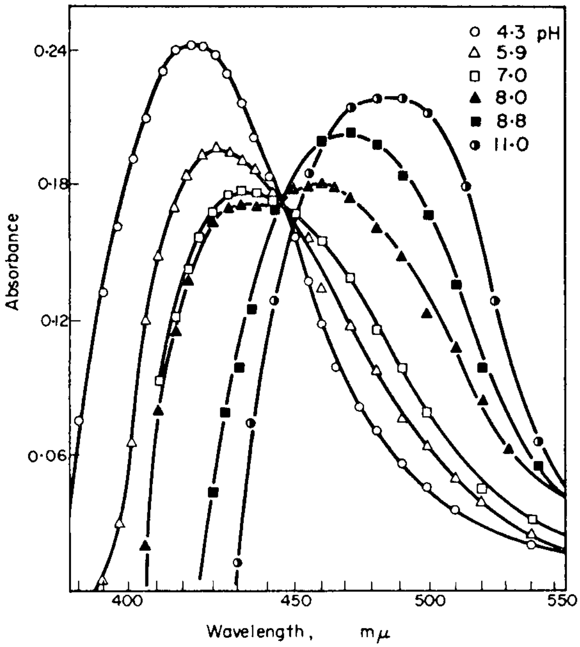


FIG. 3.—Absorption spectra of iridium(III) complex [9·5 ppm Ir(III)] at different pH values.

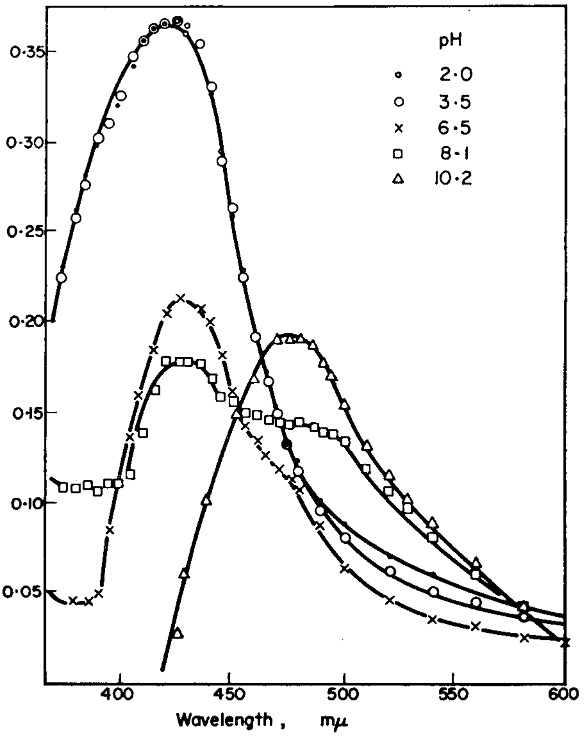


FIG. 4.—Absorption spectra of platinum(IV) complex [27 ppm Pt(IV)] at different pH values.

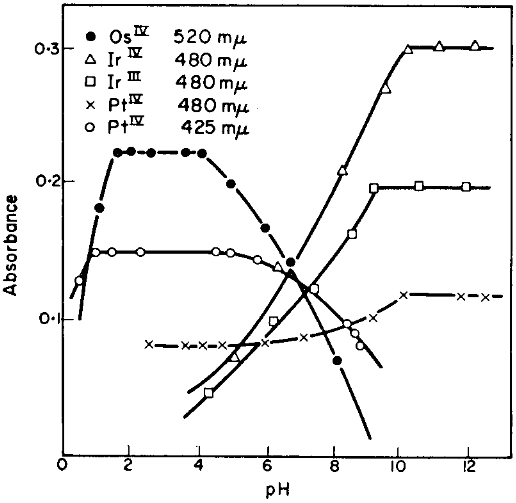


FIG. 5.—Effect of pH on the absorbance of the complexes of Os(IV), Ir(III) and (IV) and Pt(IV).

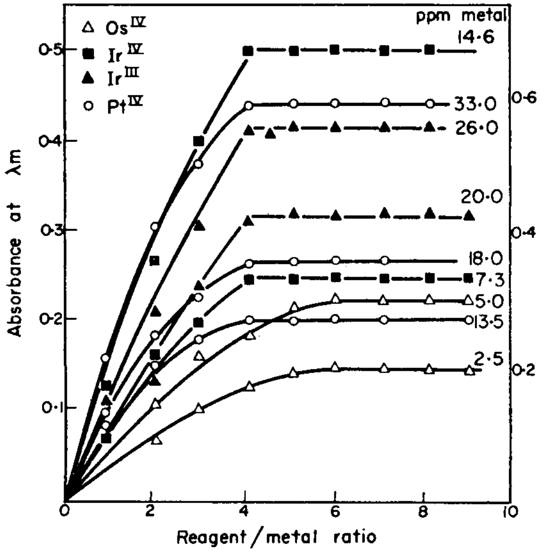


FIG. 6.—Effect of reagent concentration on the formation of the platinum metal complexes.

optimum pH ranges for analytical purposes are: osmium(IV) 1·1–5·0; iridium(IV) 10·0–12·0; iridium(III) > 9·3; platinum(IV) 1·6–4·0 or >10·2.

For full colour development under the conditions prescribed, the minimum reagent:metal concentration ratio required was found to be 6 for osmium(IV) and 4 for iridium(III), iridium(IV) and platinum(IV) (Fig. 6).

Even in the presence of a 10-fold excess of OBTA, a minimum concentration of 20 μg of iridium(IV) per ml was necessary for full colour development, the solution subsequently being diluted for measurement. Similarly, minimum concentrations of

15 μg/ml and 10 μg/ml were found for rhodium(III) and ruthenium(III) respectively. For osmium(IV) and platinum(IV), however, no such phenomenon was observed.

Properties of the complexes

The Lambert-Beer law was found to be valid for the ranges 1·0–12·0 μg/ml [osmium(IV)], 1·5–18·0 μg/ml [iridium(IV)], 1·0–10 μg/ml [iridium(III)] and 7·0–70 μg/ml [platinum(IV)]. The molar absorptivities were $8{\cdot}3 \times 10^2$ at 520 nm for osmium(IV); $9{\cdot}05 \times 10^2$ for iridium(IV) and $4{\cdot}5 \times 10^2$ for iridium(III) at 480 nm (at pH 12); $2{\cdot}56 \times 10^2$ for the yellow platinum(IV) complex at 425 nm and $1{\cdot}41 \times 10^2$ for the red platinum(IV) complex at 490 nm, all in l. mol^{-1}. mm^{-1}.

TABLE I.—INTERFERENCES DUE TO FOREIGN IONS IN THE SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM(IV) 9·8 ppm, IRIDIUM(IV) 10·7 ppm AND PLATINUM 10·3 ppm BY OBTA.

Foreign ion taken	Maximum tolerated, *ppm*, for spectrophotometric determination of		
	Os	Ir	Pt
Ruthenium(III)	0·5	0·5	3·5
Rhodium(III)	55	11	1·5
Palladium(II)	17	17	1
Osmium(IV)	—	128	16
Iridium(IV)	26	—	11
Platinum(IV)	62	34·5	—
Iron(II)	0·5	0·5	0·5
Cobalt(II)	0·5	0·5	0·5
Nickel(II)	2000	2000	100
Lead(II)	1000	1000	1000
Chromium(III)	2000	2000	2000
Sulphate	10000	10000	10000
Nitrate	10000	20000	20000
Chloride	9000	7000	7000
Perchlorate	9000	7000	7000

The osmium(IV) complex was only partially extracted by the following solvents: benzene, toluene, xylene, nitrobenzene, ethyl acetate, chloroform, ethyl methyl ketone, cyclohexanol and ether; the iridium(III) or (IV) complexes could not be extracted by any of the solvents listed above. The yellow platinum(IV) complex could not be extracted by benzene, toluene, xylene, nitrobenzene or ethyl acetate, and was only partially extracted by chloroform, ethyl methyl ketone, isobutyl methyl ketone, cyclohexanol and ether.

Interferences

The maximum amount of foreign ions that can be tolerated in the spectrophotometric estimation of osmium(IV), iridium(IV) and platinum(IV) with OBTA as reagent are given in Table I.

Determination of iridium(III) and iridium(IV)

Since both iridium(III) and iridium(IV) form coloured complexes with OBTA under similar conditions, but the molar absorptivities differ at all wavelengths, the amount of the metal in each oxidation state can be estimated in a mixture by measurement, at two wavelengths, of the total absorbances A_n of the solutions obtained by heating the chloroiridate complexes with OBTA at pH 10–12, and solution of the necessary simultaneous equations. Suitable wavelengths are 445, 480 and 500 nm. Typical results are given in Table II; their accuracy is limited by the precision with which the molar absorptivities are known.

Ion-exchange studies

When solutions of the osmium(IV), iridium(IV) and platinum(IV) complexes were passed through IRC 50(H) and IRA 401 (OH) resins, these complexes were exchanged by the anion-exchanger, showing that at higher pH values the complexes are anionic species. As the complex of rhodium(III) has already been reported[12] to be anionic and that of ruthenium(III) to be neutral,[12] ruthenium(III) can be separated from osmium(IV), iridium(IV), platinum(IV) and rhodium(III) by ion-exchange resin.

TABLE II.—DETERMINATION OF IRIDIUM(III) AND IRIDIUM(IV) IN THE PRESENCE OF EACH OTHER

Taken, *ppm*		Absorbance at pH 12			Found, *ppm*	
Ir(III)	Ir(IV)	445 *nm*	480 *nm*	500 *nm*	Ir(III)	Ir(IV)
11·0	1·1	0·245	0·315	0·275	11·0	1·0
11·0	2·1	0·295	0·365	0·320	10·9	2·0
9·8	3·2	0·335	0·405	0·350	10·0	3·3
7·4	4·3	0·345	0·405	0·345	7·5	4·5
8·6	5·4	0·385	0·450	0·385	8·3	5·0
6·1	6·4	0·400	0·455	0·390	6·3	6·2
4·9	7·5	0·460	0·495	0·420	5·0	7·5
3·7	8·6	0·485	0·505	0·450	3·4	9·0
2·5	9·6	0·495	0·540	0·455	2·5	9·6
1·2	10·7	0·510	0·550	0·465	1·0	10·5

$$\left.\begin{array}{r}\text{Molar absorption of iridium(III) complex at 445 nm} = 3{\cdot}5 \times 10^2\\ \text{at 480 nm} = 4{\cdot}5 \times 10^2\\ \text{at 500 nm} = 4{\cdot}0 \times 10^2\\ \text{Molar absorption of iridium(IV) complex at 445 nm} = 8{\cdot}8 \times 10^2\\ \text{at 480 nm} = 9{\cdot}5 \times 10^2\\ \text{at 500 nm} = 8{\cdot}0 \times 10^2\end{array}\right\} \text{l. mole}^{-1}\text{. mm}^{-1}\text{.}$$

The usual oxidation states of platinum metals in their chloro-complexes are rhodium(III), ruthenium(III) and (IV), palladium(II) and (IV), osmium(IV), iridium(III) and (IV) and platinum(II) and (IV). However, on repeated digestion with hydrochloric acid during the dissolution of the platinum metals, palladium(IV) is reduced to palladium(II), and ruthenium(IV) when boiled with ethanol in presence of hydrochloric acid is reduced to ruthenium(III).

Since in the gravimetric estimation of palladium(II) with OBTA, other platinum metals do not interfere,[9] palladium can be separated by precipitation, followed by ion-exchange separation of ruthenium(III).

Because sulphuric acid is often used for the removal of rhodium from other platinum metals, the effect of fuming the platinum metal solutions with concentrated sulphuric acid before their colour reaction with OBTA was also studied. It was found that precipitation of palladium(II) by OBTA is quantitative even when the solutions are fumed for up to 4 hr with sulphuric acid. Complex formation with platinum(IV) and ruthenium(III) is not in any way effected by the fuming, but with rhodium(III) and iridium(IV) the complex formation reaction is retarded, and takes $\sim$1 hr for complete colour development at pH $\sim$ 4·0. The absorption spectra of the rhodium(III) and iridium(IV) complexes at pH 12 do not change, though the molar absorptivity becomes slightly higher. Fuming, however, completely destroys the ability of osmium(IV) to form the OBTA complex.

The relative standard deviation was 3·5% for the spectrophotometric determination of the platinum metals after they had been fumed with sulphuric acid for 4 hr.

Recommended procedures

Osmium(IV). To 5 ml of chloro-osmate(IV) solution containing 25–300 μg of osmium at pH 1–4 add a 10-fold excess of OBTA in ethanol and boil the solution vigorously for 1 min. Cool, dilute to 25 ml so that the final ethanol concentration is 30% v/v and measure the absorbance at 520 nm against water as reference.

Iridium(III) and (IV). To 1 ml of the solution containing 30–400 μg of iridium as the chloro-complexes add a 10-fold excess of OBTA in ethanol, raise the pH to 12 and boil for a few seconds. Cool, dilute the dark red solution to 25 ml (ending with 30% v/v ethanol and pH > 10) and measure its absorbance at 470–480 nm against reagent as blank. If both iridium(III) and iridium(IV) are present, measure the absorbance at two wavelengths, and determine their concentration by solving the simultaneous equations.

TABLE III.—SEPARATION AND DETERMINATION OF RUTHENIUM(III) IN PRESENCE OF OSMIUM(IV), IRIDIUM(IV), PLATINUM(IV) AND RHODIUM(III)

Ru(III) taken, μg	Foreign ions added, μg				Ru(III) found, μg	Error, %
	Os(IV)	Ir(IV)	Pt(IV)	Rh(III)		
283	—	—	—	—	286	1·1
283	325	—	—	—	288	1·8
283	1625	—	—	—	288	1·8
283	—	535	—	—	286	1·1
283	—	2140	—	—	284	0·4
283	—	—	1150	—	282	0·4
283	—	—	2875	—	282	0·4
283	—	—	—	550	288	1·8
283	—	—	—	275	285	0·7
141	469	67	72	619	141	0·0
141	375	134	144	550	139	1·4
141	282	201	288	413	142	0·7
141	198	335	431	275	139	1·4
141	93	468	575	138	138	2·2
141	140	669	719	69	138	2·2

Platinum(IV). To 5 ml of chloroplatinate(IV) solution at pH 3·5 add a 10-fold excess of the reagent and heat in a boiling water-bath for 45 min, cool, and dilute to 25 ml (final medium 30% ethanol). Measure the absorbance at 425 nm against a reagent blank.

Palladium and ruthenium. Precipitate and estimate palladium(II) within acidity range 0·5–0·75*N*, using OBTA as described earlier[9] but keeping the ruthenium(III) concentration < 200 ppm. Evaporate to a paste the filtrate mixed with sulphuric–nitric acid mixture, to destroy the organic matter, expel nitric acid by repeated heating with hydrochloric acid, and then complex ruthenium by the addition of excess of an ethanolic solution of OBTA. Heat for 30 min, raise the pH to 10–12 and pass the solution through a column of IRA 410. Collect the effluent and wash the resin column with water till the effluent is colourless. Dilute to known volume, bring the pH of the solution to $\sim$2·0 and measure the ruthenium absorbance at 520 nm.

Typical results for palladium and ruthenium are shown in Tables III and IV.

TABLE IV.—SEPARATION AND DETERMINATION OF PALLADIUM(II) AND RUTHENIUM(III) IN PRESENCE OF OTHER PLATINUM METALS

Taken								Found	
Pd(II) *mg*	Ru(III) *μg*	Rh(III) *μg*	Os(IV) *μg*	Ir(III) *μg*	Ir(IV) *μg*	Pt(II) *μg*	Pt(IV) *μg*	Pd *mg*	Ru *μg*
8·45	283	550*	469*	728*	335*	120	288	8·46	277
4·23	1130	550	469	728	669	360	288	4·22	1120
7·61	283	550	469	728	335	240	288	7·56	281
5·29	566	550	469	728	669	360	288	5·89	558

* Added as the oxides after precipitation of Pd.

REFERENCES

1. F. E. Beamish, *The Analytical Chemistry of the Noble Metals*, pp. 418–26. Pergamon, Oxford, 1966.
2. G. H. Ayres and Q. Quick, *Anal. Chem.*, 1950, **22**, 1403.
3. G. H. Ayres and W. T. Bolleter, *ibid.*, 1957, **29**, 72.
4. F. E. Beamish, *op. cit.*, p. 39.
5. *Idem*, *op. cit.*, p. 366.
6. W. R. Schoeller and A. R. Powell, *The Analysis of Minerals and Ores of Rare Elements*, 3rd Ed., p. 349. Griffin, London, 1955.
7. G. S. Manku, A. N. Bhat and B. D. Jain, *Anal. Chim. Acta*, 1967, **39**, 128.
8. *Idem*, *Proc. Indian Acad. Sci.*, *Sec. A*, 1968, **68**, 88.
9. *Idem*, *Anal. Chim. Acta*, 1967, **39**, 369.
10. A. N. Bhat and B. D. Jain, *ibid.*, 1961, **25**, 343.
11. *Idem*, *J. Indian Chem. Soc.*, 1961, **38**, 779.
12. G. S. Manku, A. N. Bhat and B. D. Jain, *Talanta*, 1967, **14**, 1229.
13. *Idem*, *Current Sci.* (*India*), 1968, **37**, 461.
14. G. S. Manku, R. D. Gupta, A. N. Bhat and B. D. Jain, *J. Less-Common Metals*, 1968, **16**, 343.
15. R. Anschütz, *Ann. Chem.*, 1909, **367**, 169.
16. A. I. Vogel, *Text Book of Quantitative Inorganic Analysis*, 3rd Ed., p. 510. Longmans, London, 1962.
17. R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.*, 1935, **57**, 2565.
18. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 1st Ed., pp. 346, 358, 384, 388. Interscience, New York, 1944.

Zusammenfassung—Oxinidobenzotetronische Säure wird als Reagens für die spektralphotometrische Bestimmung von Osmium(IV), Iridium(III), Iridium(IV), Platinum(IV) und zur Trennung und Bestimmung von Palladium(II) und Ruthenium(III) bei Vorhandensein von anderen Platinum Metallen vorgeschlagen. Wenn Indium(III) und (IV) gemeinsam vorhanden sind, kann eine Schätzung gemacht werden.

Résumé—L'acide oxymidobenzotétronique est suggéré comme un réactif pour la détermination spectrophotométrique de l'osmium(IV), l'iridium(III), l'iridium(IV), le platine(IV) et pour la sépration et la détermination du palladium(II) et du ruthenium(III) en présence d'autres métaux de platine. L'iridium(III) et (IV) peuvent être évalués quand ils sont présents ensemble.

Talanta, 1969, Vol. 16, pp. 1431 to 1434. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

Rapid spectrophotometric determination of cobalt after extraction using oximidobenzotetronic acid

(*Received* 30 *January* 1969. *Accepted* 1 *April* 1969)

OF A large number of reagents proposed for spectrophotometric determination of cobalt,[1–4] nitroso-R-salt has been recommended.[4] Many other reagents have recently been proposed for this determination, including quinoxaline-2,3-dithiol[5] (Pd, Pt interfere, interference due to Cu and Fe is eliminated by their extraction into acetylacetone), Chrome Azurol S[6] (Cu^{2+}, Ni^{2+}, SO_4^{2-}, NH_4^+, Al^{3+}, Cr^{3+}, Sn^{2+}, Zr^{4+} interfere), tartaric acid in presence of hydrogen peroxide[7] (Mg^{2+}, Ca^{2+}, Fe^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+} interfere), bis(2-pyridyl)ethyleneglycol[8] (neither sensitive nor specific), *S*-2-(3-mercaptoquinoxalinyl)thiuronium chloride[9] which in ammonia buffer (pH 10) is hydrolysed to quinoxaline-2,3-dithiol (Ag^+, Cu^{2+}, Pd^{2+}, Hg^{2+}, Bi^{3+}, Sn^{2+}, Pt^{2+} interfere), Monochrome Green S[10] (equal amounts of Fe and Cu can be tolerated), phenylguanylurea,[11] phenylbiguanidine,[11] (carboxymethylthio) succinic acid[12] and Chromotrope 2R[13] (no interference data reported). Condensation products of formyl oxines with 1,3,3-trimethyl-2-methylene indoline,[14] Schiff's bases derived from aromatic *o*-aminoketones and ethylenediamine,[15] and substituted triazines related to 6-cyano-2,2′-bipyridine[16] have also been tested but though very sensitive are not very selective. Reagents for which interferences can be reduced by extraction of the cobalt chelate include thenoyltrifluoroacetone (several ions interfere when benzene–acetone mixture is used as solvent,[17] but only Cu^{2+} is reported to interfere in a modified procedure with xylene[18]), Dalzin[19] (Bi^{3+}, Hg^{2+}, Pd^{2+} always interfere, tolerance for Ag^+, Cu^{2+}, Ni^{2+} is low), salicylaldoxime[20] (separation from Ni at pH 6) and Hyamine 1622 in presence of thiocyanate[21] (ions complexed by thiocyanate interfere, but interference by Fe^{3+} and Cu^{2+} is removed by use of thiosulphate and sulphur dioxide respectively).

There is thus a need for specific and sensitive reagents for the estimation of cobalt in the presence of other elements, especially nickel, iron, copper and palladium. In the case of phenanthrene quinone monoxime[22] and 2,2′-dipyridyl ketone oxime,[23] the interference due to other ions (including Cu^{2+}, Ni^{2+}, Fe, Bi^{3+}, Pd^{2+} and some platinum metals) has been overcome by modification of the method; in the case of dithiocarbamic acid,[24] separation by ion-exchange chromatography has been suggested.

Oximidobenzotetronic acid (OBTA, 3-nitroso-4-hydroxycoumarin) has already been used[25–28] for determination of a number of metals. The $Co(OBTA)_3$ complex precipitated on addition of ethanolic OBTA solution to cobalt(II) solution is soluble in chloroform, benzene, diethyl ether, ethyl acetate and isopentanol. This communication deals with extraction of the complex into these solvents. Since the deep blue iron(II) complex is not soluble in benzene,[27] cobalt(II) and iron(II) can be separated by use of a benzene solution of OBTA, and determined spectrophotometrically in the organic and aqueous phases respectively.

EXPERIMENTAL

Reagents

Fresh solutions of OBTA prepared from 4-hydroxycoumarin[29] were used. A cobalt(II) solution prepared from analytical grade cobalt sulphate heptahydrate or cobalt nitrate heptahydrate was standardized gravimetrically as anthranilate, or as cobalt sulphate after precipitation as the 1-nitroso-2-naphthol complex.

For interference studies, chlorides, nitrates or sulphates of the metals were used, and sodium or potassium salts for the anions.

Procedure

Extract 20 ml of cobalt(II) solution (containing 6–60 μg of Co) at an appropriate pH (3·5–8·5) with two 7–8 ml portions of 0·005*M* benzene solution of OBTA and dilute the combined extracts to 25 ml. Measure the absorbance of the organic phase at 430 nm against reagent solution. Shaking for 1 min is adequate.

RESULTS AND DISCUSSION

The spectral characteristics and optimum pH ranges for various solvents are given in Table I, and the partition coefficients are given in Table II. Chloroform and benzene are the best solvents.

The precision and accuracy were determined from 10 replicate analyses. There was no systematic error, and the relative standard deviation was inversely proportional to the cobalt concentration, ranging from 2% at the 0·5-ppm cobalt level to 0·5% at the 2·5-ppm level. Two extractions with equal volumes of benzene or chloroform were sufficient for complete extraction.

TABLE I.—SPECTRAL CHARACTERISTICS OF COBALT–OBTA COMPLEX IN SOME ORGANIC SOLVENTS

Solvent	λ_{max} *nm*	ε *l. mole^{-1}. mm^{-1}*	Conc. range for which Beer's law is valid, *ppm*	Optimum pH range
Chloroform	410	$1{\cdot}68 \times 10^3$	0·2–3·0	3·0–9·0
Benzene	430	$1{\cdot}82 \times 10^3$	0·2–3·0	3·5–8·8
Ethyl acetate	420	$0{\cdot}95 \times 10^3$	0·5–6·0	5·0–7·2
Diethyl ether	415	$1{\cdot}47 \times 10^3$	0·3–4·5	4·5–7·8
Isopentanol	400	$1{\cdot}10 \times 10^3$	0·4–6·0	—

TABLE II.—LOGARITHM OF THE PARTITION COEFFICIENTS OF OBTA (log p) AND ITS COBALT COMPLEX (log p_3) BETWEEN DIFFERENT ORGANIC SOLVENTS AND 0·10*M* SODIUM PERCHLORATE AT 20°C

Solvent	log p				log p_3		
	Method (*a*)	Method (*b*)	Method (*c*)	Average	Method (*a*)	Method (*b*)	Average
Chloroform	1·69	1·64	1·68	1·67	3·15	3·10	3·13
Benzene	1·60	1·62	1·54	1·59	2·66	2·60	2·63
Ethyl acetate	1·11	1·18	1·12	1·14	1·60	1·52	1·56
Diethyl ether	0·97	1·02	1·01	1·00	1·38	1·32	1·35
Isopentanol	0·85	0·93	0·92	0·90	0·68	0·70	0·69

(*a*): Duncan and Thomas's method.[30]
(*b*): Irving and Bell's method.[31]
(*c*): Dyrssen's two-phase titration method.[32]

Effect of diverse ions

With benzene as the organic solvent, 200-fold amounts (relative to cobalt) of the following ions did not interfere: Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Zn^{2+}, Pb^{2+}, Fe^{2+}, UO_2^{2+}, Be^{2+}, Pd^{2+}, Pt^{2+}, Al^{3+}, Cr^{3+}, Ce^{3+}, La^{3+}, γ^{3+}, Gd^{3+}, In^{3+}, Tl^{3+}, Ti^{4+}, Zr^{4+}, Th^{4+}, Cl^-, Br^-, I^-, F^-, NO_3^-, ClO_4^-, $CH_3CO_2^-$, S^{2-}, $S_2O_3^{2-}$, SO_4^{2-}, SO_3^{2-}, $(COO)_2^{2-}$, VO_3^-, WO_4^{2-}, SeO_4^{2-}, TeO_3^{2-}, MoO_4^{2-}, $PtCl_6^{2-}$, $IrCl_6^{2-}$, $OsCl_6^{2-}$, $RuCl_6^{3-}$, $RhCl_6^{3-}$, $IrCl_6^{3-}$, tartrate; a 100-fold amount of citrate and 50-fold amount of phosphate also did not interfere.

The interference due to Ni^{2+} and Cu^{2+} could be eliminated either by measuring the absorbance at 480–500 nm where their chelates had negligible absorption, or by scrubbing the organic phase with aqueous ammonia at pH 8 or hydrochloric acid at pH 2, which decomposed the nickel and copper chelates but not the cobalt chelate. Even minute quantities of CN^-, EDTA, Ce^{4+}, VO^{2+} and Fe^{3+} caused serious interference. However, the deep blue iron(II)–OBTA complex was not extracted into benzene, so iron(II) and cobalt(II) could be separated, and each estimated in the appropriate phase. Typical results are given in Table III.

Composition and stability constant

The molar composition of the cobalt–OBTA complex, determined by the method of continuous variations applied to a two-phase system,[33] and by the usual equimolar solutions method, was found to be 3:1 OBTA:Co, the same as that reported for the complex precipitated from aqueous ethanol.[26] When the isolated solid complex was dissolved in chloroform or benzene, an absorption spectrum identical with that of the extracted complex was observed.

Table III.—Separation and determination of cobalt(II) and iron(II) with OBTA in benzene solution

Taken, μg		Found, μg	
Cobalt(II)	Iron(II)	Cobalt(II)	Iron(II)
7·3	112·0	7·2	111·0
14·6	100·8	14·4	101·0
21·9	89·6	21·8	89·9
29·2	78·4	29·3	78·2
36·5	67·2	36·8	67·0
43·8	56·0	43·8	56·4
51·1	44·8	51·0	44·8
58·4	33·6	58·6	33·3
65·7	22·4	65·9	22·4
73·0	11·2	72·6	11·2

Wavelength for cobalt (in benzene) = 430 nm.
Wavelength for iron (in aqueous phase) = 625 nm.

The stability constant (β_3) was determined from the extraction data at different pH values,[34] chloroform, benzene, ethyl acetate and diethyl ether being used as solvents. The average value was log $\beta_3 = 14{\cdot}1 \pm 0{\cdot}2$ at 20° (0·10*M* sodium perchlorate medium).

Department of Chemistry
University of Delhi
Delhi-7, India

G. S. Manku
A. N. Bhat
B. D. Jain

Summary—A spectrophotometric method based on the extraction of cobalt with benzene solutions of oximidobenzotetronic acid (OBTA) is proposed for the estimation of 0·2–3·0 ppm of cobalt. The 3:1 OBTA:Co complex containing cobalt(III) has its absorption maximum at 430 nm; its molar absorptivity in benzene is 1·82 × 10^3 l. mole^{-1}. mm^{-1}. Since the blue iron(II) complex is not extracted into benzene, iron(II) and cobalt(II) can be separated and determined spectrophotometrically.

Zusammenfassung—Ein spektrophotometrisches Verfahren, das auf der Extraktion von Kobalt mit benzolischen Lösungen von Oximidobenzotetronsäure beruht, wird zur Bestimmung von 0,2–3,0 ppm Kobalt vorgeschlagen. Der 3:1(OBTA:Co)-Komplex, der Kobalt(III) enthält, hat sein Absorptionsmaximum bei 430 nm; sein molarer Extinktionskoeffizient in Benzol beträgt 1,82 · 10^3 l mol^{-1} mm^{-1}. Da der blaue Eisen(II)-Komplex nicht in Benzol extrahiert wird, können Eisen(II) und Kobalt(II) getrennt und spektrophotometrisch bestimmt werden.

Résumé—On propose une méthode spectrophotométrique basée sur l'extraction du cobalt par des solutions benzéniques d'acide oximidobenzotétronique pour l'estimation de 0,2–3,0 ppm de cobalt. Le complexe 3:1 OBTA:Co contenant le cobalt(III) a son maximum d'absorption à 430 nm; son coefficient d'absorption moléculaire dans le benzène est 1,82 × 10^3 l.mole^{-1}mm^{-1}. Le complexe blue du fer(II) n'étant pas extrait en benzène, on peut séparer et déterminer spectrophotométriquement les fer(II) et cobalt(II).

REFERENCES

1. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Ed., p. 409. Interscience, New York, 1959.
2. F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, Vol. II, p. 352. Van Nostrand, Princeton, 1964.

3. W. J. Williams, *Talanta*, 1958, **1,** 88.
4. G. Charlot, *Colorimetric Determination of Elements*, Elsevier, New York, 1964.
5. R. W. Burke and J. H. Yoe, *Anal. Chem.*, 1962, **34,** 1378.
6. Y. Horiuchi and H. Nishida, *Bunseki Kagaku*, 1967, **16,** 576.
7. H. Basinska and K. Polak, *Chem. Anal.* (*Warsaw*), 1967, **12,** 253.
8. A. N. Bhat, R. D. Gupta and B. D. Jain, *Proc. Indian Acad. Sci. A*, in press.
9. J. A. W. Dalziel and A. K. Slawinski, *Talanta*, 1968, **15,** 367.
10. V. V. Bagrew and Yu. A. Zolotov, *ibid.*, 1968, **15,** 988.
11. F. Capitan and F. Salinas, *ARS Pharm.*, 1967, **8,** 195; *Chem. Abstr.*, 1968, 1969, **68,** 18245x.
12. B. C. Nair and H. L. Nigam, *Indian J. Chem.*, 1967, **5,** 212.
13. O. Prakash and S. P. Mushran, *Chim. Anal.*, (*Paris*), 1967, **49,** 473.
14. F. Przystal, T. Rodolf and J. P. Philips, *Anal. Chim. Acta*, 1968, **41,** 391.
15. E. Uhlemann and W. Wischnewski, *ibid.*, 1968, **42,** 247.
16. A. A. Schilt and K. R. Kluge, *Talanta*, 1968, **15,** 475.
17. A. K. De and M. S. Rahaman, *Anal. Chim. Acta*. 1962, **27,** 253.
18. *Idem*, *ibid.*, 1966, **34,** 233.
19. N. K. Dutt and P. K. De, *J. Indian Chem. Soc.*, 1967, **44,** 98.
20. I. Dahl, *Anal. Chim. Acta*, 1968, **41,** 9.
21. N. Gunderson and E. Jacobson, *ibid.*, 1968, **42,** 330.
22. K. C. Trikha, Mohan Katyal and R. P. Singh, *Talanta*, 1968, **15,** 977; K. C. Trikha, *Ph.D. Thesis*, Delhi University, 1969.
23. W. J. Holland and J. Bozic, *Talanta*, 1968, **15,** 843.
24. O. Grossmann and H. Grosse-Ruyken, *Z. Anal. Chem.*, 1967, **233,** 14.
25. A. N. Bhat and B. D. Jain, *Anal. Chim. Acta*, 1961, **25,** 343; *J. Indian Chem. Soc.*, 1961, **38,** 779.
26. G. S. Manku, A. N. Bhat and B. D. Jain, *Anal. Chim. Acta*, 1967, **39,** 128.
27. *Idem*, *Proc. Indian Acad. Sci. A*, 1968, **68,** 88.
28. *Idem*, *Anal. Chim. Acta*, 1967, **39,** 369; *Talanta*, 1967, **14,** 1229; *Talanta*, 1969, **16,** 1421.
29. R. Anschütz, *Annalen*, 1909, **367,** 169.
30. J. F. Duncan and F. G. Thomas, *J. Chem. Soc.* 1960, 2814.
31. H. Irving and C. F. Bell, *ibid.*, 1952, 1216.
32. D. Dyrssen, *Svensk. Chim. Tidskr.*, 1952, **64,** 213.
33. J. Starý, *Solvent Extraction of Metal Chelates*, Pergamon, Oxford, 1964.
34. F. J. C. Rossotti and H. Rossotti, *Determination of Stability Constants*, McGraw-Hill, New York, 1961.

Talanta, 1969, Vol. 16, pp. 1434 to 1436. Pergamon Press. Printed in Northern Ireland

Precipitation of manganese ammonium phosphate from homogeneous solution

(*Received* 28 *January* 1969. *Accepted* 6 *March* 1969)

ACCORDING to the literature it is expedient to allow metal ammonium phosphate precipitates to stand for half a day before filtration. The precipitate recrystallizes and becomes easier to filter off. Precipitation from homogeneous solution (PFHS) is well known as a technique for achieving coarse-grained precipitates, but has seldom been tried in the case of metal ammonium phosphate precipitates.

In most PFHS methods the reagent is generated in the solution by hydrolysis, oxidation, reduction or synthesis. Alternatively, the reagent may be in the solution, and the ion to be determined is present as a complex which is then decomposed. MacNevin and Dunton[1] decomposed the iron(III)–EDTA complex by oxidation with hydrogen peroxide at constant pH, to precipitate hydrous iron(III) oxide. Cartwright systematically studied the decomposition of various metal–EDTA complexes by hydrogen peroxide,[2] and he explored the possibilities for PFHS,[2] but pointed out that the method had poor selectivity.[3] Metal ions which are not masked by EDTA and form precipitates instantaneously cannot be precipitated from homogeneous solution by this method. Of metal ammonium phosphates Cartwright found only $MgNH_4PO_4$ not to precipitate at pH 8 within 10 min. Taking into account the solubility product of the precipitate and the stability constant of the metal–EDTA complex, we can conclude that of precipitates with similar solubilities, the one with the least stable EDTA complex will be preferentially precipitated.

We have studied the possibilities of the precipitation of metal ammonium phosphates by decomposing the metal–EDTA complex with hydrogen peroxide.

EXPERIMENTAL

Reagents

Mn, Zn and Cd stock solutions. Prepared from $MnSO_4 \cdot 4H_2O$, $ZnSO_4 \cdot 7H_2O$ and $Cd(NO_3)_2$ and containing about 1 g of metal ion in 100 ml; standardized by precipitation[5] as the ammonium phosphate.

$(NH_4)_2HPO_4$ solution, 20%. Neutralized with 2*M* ammonia to the phenolphthalein end-point.

NH_4Cl solution, 10%. Neutralized with 2*M* ammonia to the Phenol Red end-point.

H_2O_2 solution, 30%. Neutralized with 2*M* ammonia to the Phenol Red end-point

All solutions were made from analytical grade reagents.

Procedure

Manganese, zinc and cadmium were complexed with excess of EDTA, then the precipitant was added and the metal ammonium phosphate formed by decomposing the complex by boiling with hydrogen peroxide. The solution containing manganese became turbid in about 1 hr, those containing zinc and cadmium about 3 hr later. Boiling was continued for various times, then the precipitates were collected on sintered-glass crucibles, and washed and dried at 100° (130° for zinc).

RESULTS

The amounts of precipitate formed in different times are given in Fig. 1. As indicated by the figure, $MnNH_4PO_4 \cdot H_2O$ is precipitated practically completely in 1 hr. The rates of precipitation of $ZnNH_4PO_4$ and $CdNH_4PO_4 \cdot H_2O$ are similar in the first 2 hr, but $ZnNH_4PO_4$ is precipitated quantitatively in 6 hr whereas $CdNH_4PO_4 \cdot H_2O$ is only 95% precipitated even in 8 hr.

These results are in agreement with the observation of Cartwright[4] that there is a loose correlation between the stability constant of the complex and the rate of precipitation. At pH 5 the apparent stability constants (log *K*) are Mn 7·19, Zn 9·90, Cd 9·86.

The particle size of all three precipitates was about two orders of magnitude greater than that of the precipitates obtained by the usual methods. The Mn and Cd precipitates consisted of longish shining sheets, and the Zn precipitate of prisms and needles.

Determination of manganese(II)

The method was found satisfactory for the gravimetric determination of 50–150 mg of manganese. To the solution of manganese(II) 0·1*M* EDTA is added in about 50% excess, and the solution is made just acidic to Methyl Red, and diluted to about 70 ml. Then 10 ml each of 10% ammonium chloride solution, 20% diammonium hydrogen phosphate solution and 30% hydrogen peroxide solution are added. The beaker is covered with a watch-glass and the solution gently boiled. Water is added from time to time to replace that lost by evaporation. The precipitate is collected on a sintered-glass crucible, porosity 3, washed with saturated manganese ammonium phosphate solution and dried at 100° for 2 hr. The precipitate can be collected when the mixture has cooled to 60°.

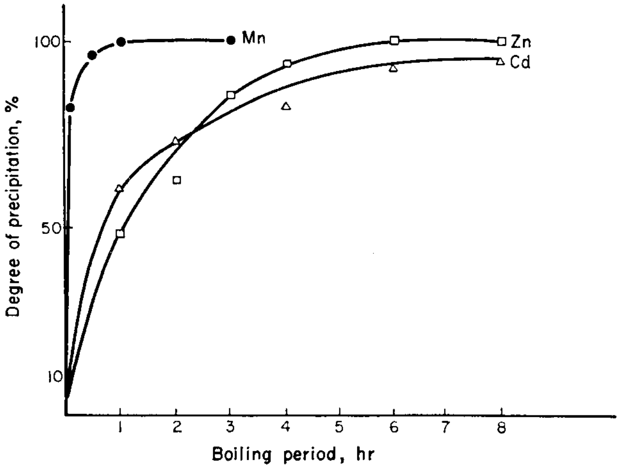


FIG. 1.—Rates of precipitation of metal ammonium phosphates.

Typical results for solutions containing 50, 100 and 150 mg of manganese had a relative standard deviation of 0·3–0·4% and mean errors of +0·1%, −0·2% and −0·3% respectively.

Institute for General and
Analytical Chemistry
Technical University, Budapest

É. Buzágh-Gere
L. Erdey

Summary—Precipitation of manganese, zinc and cadmium ammonium phosphates from homogeneous solution by decomposition of metal EDTA complexes by boiling with hydrogen peroxide in presence of phosphate has been investigated. Precipitation of Cd is not quantitative, but of Mn is complete in 2 hr, and of Zn in 6 hr.

Zusammenfassung—Die Fällung von Mangan-, Zink- und Cadmiumammoniumphosphat aus homogener Lösung durch Zersetzung von Metall-EDTA-Komplexen durch Kochen mit Wasserstoffperoxid in Gegenwart von Phosphat wurde untersucht. Die Fällung von Cd verläuft nicht quantitativ; die von Mn ist nach 2 hr, die von Zn nach 6 hr vollständig.

Résumé—On a étudié la précipitation des phosphates doubles d'ammonium et de manganèse, zinc et cadmium en solution homogène par décomposition de complexes métal-EDTA par ébullition avec de l'eau oxygénée en présence de phosphate. La précipitation de Cd n'est pas quantitative, mais celle de Mn est complète en 2 h et celle de Zn en 6 h.

REFERENCES

1. W. M. MacNevin and M. L. Dunton, *Anal. Chem.*, 1954, **26**, 1246.
2. P. F. S. Cartwright, *Analyst*, 1961, **86**, 688, 692.
3. *Idem. ibid*, 1967, **92**, 319.
4. *Idem, ibid.*, 1962 **87**, 163.
5. L. Erdey, *Gravimetric Analysis*, Part II, Pergamon Press, Oxford, 1965.

Talanta, 1969, Vol. 16, pp. 1436 to 1439. Pergamon Press. Printed in Northern Ireland

Determination of europium in minerals and rocks by neutron activation and γγ-coincidence spectrometry

(*Received* 6 *March* 1969. *Accepted* 2 *April* 1969)

Several neutron activation procedures for the determination of europium in geological material have appeared in the literature. Most methods have been based on radiochemical separation procedures used after decomposition of the sample. Recently instrumental methods based on measurement of 13 y ^{152}Eu, with Ge(Li) detectors, have been applied to rocks.[1,2] The 9·2 hr isomer of ^{152}Eu has been used in analysis of minerals rich in rare earths, either an NaI(Tl) detector[3] or a Ge(Li) detector[4] being used.

The aim of the present work was to develop a simple method for the routine determination of europium in connection with a rare earth prospecting programme. As no satisfactory Ge(Li) detector system was available in the laboratory when the present work started, it was decided to try $\gamma\gamma$-coincidence spectrometry following neutron activation of the samples.

Although $\gamma\gamma$-coincidence measurements represent a comparatively specific system for the determination of certain components in complex radionuclide mixtures, this technique has not been extensively used in activation analysis of geological material. Procedures for the determination of copper,[5-7] iridium and selenium,[8] and caesium and cobalt[9] have been described, but no applications to rare earth elements have been published so far.

TABLE I.—INTERFERENCE FROM EQUAL AMOUNTS OF SOME ELEMENTS IN THE DETERMINATION OF EUROPIUM BASED ON 9·3 hr ^{152m}Eu.*

	Single NaI detector, measurement of 41 keV X-ray[3]	$\gamma\gamma$-Coincidence 122–841 keV, (gate: 122 keV)
^{152m}Eu	100	100
^{153}Sm	13	0·012†
^{160}Tb	0·08	0·008
^{166}Ho	3·1	<0·0002
^{169}Yb–^{175}Yb	0·3	<0·01
^{177}Lu	0·6	<0·0002
^{56}Mn	—	0·015
^{72}Ga	—	0·22
^{140}La	—	0·025

* The values refer to measurements 24 hr after a 15-min irradiation.

† Probably due to ^{152m}Eu impurity.

Establishment of experimental conditions

Three radioactive europium isotopes are formed by thermal neutron activation of Eu, *i.e.*, 9·3 hr ^{152m}Eu, 13 y ^{152}Eu, and 16 y ^{154}Eu. In the present work, where a rapid aquisition of data was essential, the analysis was based on the short-lived ^{152m}Eu. This nuclide decays partly by β^--emission to ^{152}Gd (75 %), and partly by electron capture (EC) to ^{152}Sm (25 %). The actual possibilities of coincidence measurements are associated with the EC-branch, either by coincidence between the 41-keV *K* X-ray originating from the EC process and a subsequent γ-ray (abundances 14, 11 and 10 % for the 122, 841 and 963 keV γ-rays respectively), or by 122-keV and 841-keV γ-rays in cascade (abundance 7 %).

Testing of the various coincidences and evaluation of the various interferences to be expected from other radionuclides indicated the 122 keV-841 keV coincidence to be the best choice for the measurements. The possible interference from other rare earths emitting γ-rays in the 120 keV region was investigated, and the results are given in Table I, in comparison with similar figures obtained by a method previously used in the laboratory, based on NaI γ-spectrometry.[3] Nuclides having a γ-ray at about 840 KeV coincident with one or more other γ-rays would constitute a possible interference, by coincidences between a back-scattered or Compton-scattered γ-ray and a γ-ray totally absorbed in the detector. The most probable interfering nuclides of this kind, which were considered to be 2·58 hr ^{56}Mn, 14·2 hr ^{72}Ga and 40·2 hr ^{140}La, were also tested. As shown in Table I, the elements investigated can usually be disregarded as sources of error, provided that the measurements are performed about 24 hr after the irradiation.

Angular correlation measurements in the region 90–180° showed that maximum intensity of the 122 keV–840 keV coincidence was obtained at an angle of 90° between the two detector axes, the relative counting rates being 100, 97, 89, 81 and 79 at 90°, 110°, 135°, 160° and 180°, respectively, as the angle between the detector axes.

EXPERIMENTAL

Counting equipment

The detectors used were Harshaw integral line detectors with 50 × 50 mm NaI(Tl) crystals. They were mounted on a rack which made it possible to change the angle between the central axes of the detectors continuously in the range 90–180°. The detectors were connected *via* Hamner charge-sensitive amplifiers to a Hamner coincidence unit consisting of two linear double-delay line amplifiers, two jitter-free pulse-height analysers and a fast coincidence unit with a variable resolving time in the range 10–150 nsec. The output of the coincidence unit was used to gate a Tullamore 400-channel pulse-height analyser.

Samples and standards

As test material, five samples were selected which were considered to be representative of the series to which the method was to be applied. They were three apatites, a hematite and an iron-rich carbonatite. For standards, aliquots of dilute europium solutions were evaporated to dryness on small polyethylene sheets and sealed in flat polyethylene bags; 10-mg samples of the test materials were weighed into flat polyethylene bags.

Irradiation and measurement

Samples and standards were irradiated for 15 min in the reactor JEEP II (Kjeller, Norway) at a thermal neutron flux of about 2×10^{11} n. mm^{-2}. sec^{-1}. The gamma-activity measurements were carried out 20–28 hrs after the irradiation. The samples were mounted in a perspex sample holder placed in the central axis of the detectors, which were kept at an angle of 90° relative to each other. During measurements the distance between detectors and sample was so adjusted that the dead time of the multichannel analyser in no case exceeded 40% when the pulses from either detector were fed *via* the preamplifier directly into the analyser. The counting time used was ordinarily 10 min. The area of the 0·841 MeV photopeak was evaluated according to the method of Covell.[10]

Shielding effects

As some rare earth elements show strong neutron absorption, the results of the present work may be subjected to errors associated with shielding effects. The following experiments were carried out to study this point:

The test samples were analysed for samarium, europium and dysprosium, partly by analysis of 10-mg aliquots of the solid samples, and partly by analysis of dilute solutions of each sample. The method employed for this was γ-spectrometry with an NaI-detector.[8] No significant difference between the results was observed, indicating that shielding effects were of minor importance in the concentration range covered by the test samples. This conclusion is supported by calculations according to the method described by Högdahl,[11] for the shielding effect due to gadolinium homogeneously distributed in a 10 mg sample. It appears that this element, which is likely to cause the most serious errors, may be present in concentrations up to 1000 ppm and still give less than 5% error due to thermal neutron shielding.

The possible self-shielding effect of europium was studied by adding known amounts of europium to the carbonatite test sample. The europium was added in increments of 50 ppm up to a maximum of 200 ppm, and the total content determined by the coincidence method for each addition. A plot of the total europium concentration as a function of the amount added gave a straight line which was extrapolated to zero addition. This gave a value of 37 ppm, which is in good agreement with the mean value 38·6 ppm for this sample. The result of this experiment indicates that the self-shielding effect of europium can be neglected in the concentration range studied.

RESULTS AND DISCUSSION

Results for the europium content of the test samples are shown in Table II. The precision of the results is about 5%.

As shown in Table I, the interference from other elements by the present method is quite low. Interference from other rare earth elements should be insignificant in most geological samples. For samples with europium content of the same order as those analysed in the present work, possible interference from other elements can also be neglected in most cases. Neutron shielding effects also seem to be of little importance.

TABLE II.—EUROPIUM CONTENT OF FIVE TEST SAMPLES (*ppm*)

	Kodal apatite	Karlshus apatite	ödegaarden apatite	Hematite	Iron-rich carbonatite
	57·7	12·6	50·3	50·8	37·0
	55·8	13·2	49·3	56·3	40·5
	58·6	12·0	46·9	50·5	38·5
	61·0	12·1	50·5	52·6	38·2
	53·3	12·4	43·5	57·9	42·3
	60·3	13·9	47·0	59·1	37·8
	57·2	14·2	48·9	52·4	37·3
	55·2	12·5	47·2	50·8	39·4
	58·8	13·6	45·8	52·1	38·1
	53·9	12·8	47·6	51·0	36·9
Mean, *ppm*	57·2	12·9	47·7	53·4	38·6
Relative standard deviation, %	4·7	5·9	4·5	6·1	4·4

The present $\gamma\gamma$-coincidence method has proved to be a convenient method for the rapid determination of europium in a large series of mineral and rock samples, mostly in the 10–150 ppm concentration range. The sensitivity of the method for routine application is about 5 ppm. By extension of the counting period to several hours, europium concentrations below 1 ppm can be determined. In this case, however, the interference from ^{56}Mn and ^{72}Ga becomes important. In such cases use of a method based on a rapid radiochemical separation is recommended.

Institutt for Atomergi
Kjeller, Norway

O. B. MICHELSEN
E. STEINNES

Summary—Neutron activation followed by $\gamma\gamma$-coincidence measurements of 9·3 hr ^{152}Eu is shown to be a convenient method for routine determination of europium in minerals and rocks. In the concentration range 10–150 ppm the method is free of interference from other elements, and neutron shielding effects do not interfere seriously in the analysis. The precision of the method is about 5 %.

Zusammenfassung—Neutronenaktivierung und anschließende $\gamma\gamma$-Koinzidenzmessungen von ^{152}Eu(9,3 h) wird als bequeme Methode zur Routinebestimmung von Europium in Mineralien und Gesteinen angegeben. Im Konzentrationsbereich 10–150 ppm ist die Methode frei von Störungen durch andere Elemente; Neutronenabschirmeffekte stören bei der Analyse nicht wesentlich. Die Genauigkeit ist ungefähr 5 %.

Résumé—On montre que l'activation par neutrons suivie de mesures de coïncidence $\gamma\gamma$ de ^{152}Eu 9,3 h est une méthode commode pour le dosage de routine de l'europium dans les minerais et roches. Dans le domaine de concentrations 10–150 ppm, la méthode est exempte d'interférence d'autres éléments, et les influences de protection de neutron n'interfèrent pas sérieusement dans l'analyse. La précision de la méthode est d'environ 5 %.

REFERENCES

1. J. C. Cobb, *Anal. Chem.*, 1967, **39**, 127.
2. G. E. Gordon, K. Randle, G. G. Goles, J. B. Corliss, M. H. Beeson and S. S. Oxley, *Geochim. Cosmochim. Acta*, 1968, **32**, 369.
3. E. Steinnes, Institutt for Atomenergi Kjeller, Norway, *Rept.* **KR-120**, 1967.
4. F. M. Graber, H. R. Lukens and J. K. Mac Kenzie, *Trans. Am. Nucl. Soc.* 1967, **10**, 26.
5. L. Gorski, *Talanta*, 1964, **11**, 1135.
6. O. B. Michelsen and E. Steinnes, *ibid.*, 1968, **15**, 574.
7. R. Wölfle, U. Herpers and W. Herr, *Z. Anal. Chem.*, 1968, **233**, 241.
8. W. Herr and R. Wölfle, *ibid.*, 1965, **209**, 213.
9. L. P. Greenland, *U.S. Geol. Surv. Prof. Paper* **600-B**, 1968, 76.
10. D. F. Covell, *Anal. Chem.*, 1959, **31**, 1785.
11. O. T. Högdahl, *Proc. IAEA Conf. Radiochemical Methods of Analysis*, Vienna, 1965, p. 23.

Talanta, 1969, Vol. 16, pp. 1439 to 1441. Pergamon Press. Printed in Northern Ireland

Voltammetric oxidation of anthraquinones in acetonitrile and nitromethane

(*Received* 28 *March* 1969. *Accepted* 3 *April* 1969)

IT IS well known that quinones are reduced polarographically and voltammetrically in aprotic solvents in one-electron steps to the singly and doubly charged anions.[1] Fodiman and Levin[2] have used such reduction waves in the polarographic determination of anthraquinone derivatives. It has recently been observed in our laboratory that anthraquinones, but not benzoquinones, naphthaquinones and phenanthraquinones, can also be oxidized voltammetrically in acetonitrile and nitromethane to the singly charged cations. The voltammetric oxidations of anthraquinones have, therefore, been studied in some detail to ascertain if these reactions can be of use to the analytical chemist. The results of these investigations are now reported.

EXPERIMENTAL

Apparatus

A Beckman Electroscan 30 was used for voltammetric investigations with a rotating platinum electrode and for cyclic voltammetry with a stationary platinum electrode. A cell similar to that already described was used.[3]

Reagents

The quinones were recrystallized before use when necessary. Acetonitrile was purified by the method of O'Donnell *et al.*[4] Nitromethane was purified by fractional freezing.[3] Tetraethylammonium perchlorate was dried in a vacuum oven at 60° before use.

Recording of voltammograms and cyclic voltammograms

These were obtained for anthraquinones in $0{\cdot}1M$ solutions of tetraethylammonium perchlorate in acetonitrile or nitromethane at 25°. Voltammograms were recorded, a voltage scan-rate of 0·24 V/min and a platinum cylindrical microelectrode rotated at 600 rpm being used. Cyclic voltammograms were obtained by use of the same electrode, not rotated, and a scan-rate of 0·04 V/sec.

RESULTS

The voltammetric ranges were from +1·8 to −1·5 V *vs.* an aqueous S.C.E. and from +2·1 to −1·3 V *vs.* an aqueous S.C.E., in acetonitrile and nitromethane respectively. Voltammetric data for the oxidation of anthraquinones in acetonitrile and nitromethane are given in Table I. The solutions were approximately $5 \times 10^{-4}M$ in the quinone.

TABLE I.—VOLTAMMETRIC DATA FOR THE OXIDATION OF ANTHRAQUINONES

	Acetonitrile		Nitromethane	
	$E_{1/2}$, *V vs.* aq.S.C.E.	$E_{3/4} - E_{3/4}$ *mV*	$E_{1/2}$, *V vs.* aq.S.C.E.	$E_{3/4} - E_{1/4}$, *mV*
9,10-Anthraquinone	+1·21	56	+1·20	55
1-Amino-9,10-anthraquinone	+1·33	70	+1·30	75
1-Amino-4-hydroxy-9,10-anthraquinone	+1·01	70	+0·96	80
1-Methylamino-9,10-anthraquinone	+1·16	80	+1·15	61
1,4-Dihydroxy-9,10-anthraquinone	+1·53	110	+1·52	125
1,2,4-Trihydroxy-9,10-anthraquinone	+1·26	100	+1·25	130
1,2,5,8-Tetrahydroxy-9,10-anthraquinone	+1·21	110	+1·22	100

Benzoquinones, naphthaquinones and phenanthraquinones were not oxidized before the final rise in current caused by the oxidation of the electrode, the solvent or the perchlorate ion of the base electrolyte.

The values of i_1^{ox}/i_1^{red} were 1·0, 1·1 and 1·3 for 1-amino-9,10-anthraquinone in acetonitrile, 1-amino-4-hydroxy-9,10-anthraquinone in nitromethane and 1,2,4-trihydroxy-9,10-anthraquinone in nitromethane respectively, where i_1^{ox} and i_1^{red} are the limiting currents on the plateaus of the oxidation and first reduction waves respectively.

For 1-amino-9,10-anthraquinone in nitromethane, the limiting current is directly proportional to concentration as expected. Over the range of $(0{\cdot}6\text{–}2{\cdot}5) \times 10^{-4}M$ a graph of limiting current *vs.* concentration was a straight line passing through the origin. The standard deviation of the error in limiting current was 0·11 μA (9 points), which corresponds to a relative standard deviation of 1·0% at a quinone concentration of $2{\cdot}5 \times 10^{-4}M$. The error in limiting current is expressed by i_l (obs) − i_l (calc), where the values of i_l (calc) are points exactly on the straight-line calibration graph of limiting current against concentration.

DISCUSSION

Since the first reduction waves are quite definitely a result of a one-electron reduction, the values of i_1^{ox}/i_1^{red} indicate that the anthraquinones were oxidized to the singly charged quinone radical cations.

Values in excess of unity result if the radical cation reacts rapidly with its environment to produce at least one species which is itself oxidized at potentials on the plateaus of the oxidation waves. Cyclic voltammograms of the anthraquinone solutions showed peaks of the expected shape on the oxidation half-cycles but no peaks on the reduction half-cycles, thus verifying that the singly charged quinone radical cations are unstable and react rapidly with their environment.

As with 1-amino-9,10-anthraquinone, it is likely that other anthraquinones will also produce straight line calibration graphs of limiting current *vs.* concentration.

The results of this study indicate that these voltammetric oxidation waves should be suitable for the determination of anthraquinones in the presence of other quinones. When reduction waves are used, benzoquinones, naphthaquinones and phenanthraquinones interfere in the determination of anthraquinones in aprotic solvent media.

Acknowledgement—We thank the Science Research Council for a grant for the purchase of the Beckman Electroscan 30.

Department of Chemistry
The University
Sheffield
England

M. Ashraf
J. B. Headridge

REFERENCES

1. S. Wawzonek, *Talanta*, 1965, **12,** 1229.
2. Z. I. Fodiman and E. S. Levin, *Zavodsk, Lab.*, 1968, **34,** 141.
3. J. B. Headridge, *Electrochemical Techniques for Inorganic Chemists*, Academic Press, London, 1969.
4. J. F. O'Donnell, J. F. Ayres and C. K. Mann, *Anal. Chem.*, 1965, **37,** 1162.

Summary—The voltammetric oxidation of seven anthraquinones to the singly-charged radical cations has been investigated in acetonitrile and nitromethane. The voltammetric waves can be used for the quantitative determination of anthraquinones. Benzoquinones, naphthaquinones and phenanthraquinones are not oxidized in these solvents.

Zusammenfassung—Die voltammetrische Oxidation von sieben Anthrachinonen zu den einfach geladenen Radikalkationen wurde in Acetonitril und Nitromethan untersucht. Die voltammetrischen Wellen können zur quantitativen Bestimmung von Anthrachinonen verwendet werden. Benzochinone, Naphthochinone und Phenanthrenchinone werden in diesen Lösungsmitteln nicht oxidiert.

Résumé—On a étudié l'oxydation voltammétrique de sept anthraquinones en cations radicaux chargés simplement, en acétonitrile et nitrométhane. On peut utiliser les vagues voltammétriques pour la détermination quantitative d'anthraquinones. Les benzoquinones, naphtoquinones et phénanthrènequinones ne sont pas oxydées dans ces solvants.

Talanta, 1969, Vol. 16, pp. 1441 to 1444. Pergamon Press. Printed in Northern Ireland

Determination of fluoride in potable waters by ion-exchange and potentiometric titration

(*Received* 7 *February* 1969. *Accepted* 4 *April* 1969)

Recently a procedure was described for the micro-determination of fluorine in organic materials by titration using a fluoride-selective ion electrode and thorium(IV) as titrant.[1] In that work, 1-mg samples of fluoride were titrated in ethanol–water medium (80:20) with precision and relative error of about 1%. The present communication describes the extension of this procedure to the determination of fluoride in potable waters, with an ion-exchange step for concentration of fluoride and removal of interfering ions.

Fluoridated water supplies contain a nominal fluoride concentration of 1 mg/l. While direct titration of fluoride at this level is not feasible,[2] direct potentiometric determinations using a total ionic strength adjustment buffer[3] and a system for continuously monitoring fluoride[4] have been reported. For the direct potentiometric measurements, the relative accuracy was about 5%, a substantial improvement over that reported for the classical SPADNS technique.[5]

Water supplies have too low a fluoride concentration for direct titration and typically contain ions which interfere in the titration. Ion-exchange separations of fluoride from phosphate by gradient elution with sodium hydroxide[6] and of fluoride from iron, aluminium, phosphate, and sulphate by stepwise elution with sodium acetate[7] have been described.

This note describes a procedure for the quantitative recovery and titration of 1 mg of fluoride after ion-exchange concentration and separation from 1-litre samples of treated or untreated water. Elution is accomplished with potassium chloride; the precision and relative error of the method are both 1%.

EXPERIMENTAL

Apparatus

The ion-exchange column was made from Pyrex tubing fitted with a glass stop-cock at the bottom. Glass-wool plugs were used to retain the resin. The resin bed dimensions were 100 × 10 mm. Dowex 1 × 4, 50–100 mesh anion-exchange resin was used. All titrations were performed with a Metrohm Automatic Titrator (Model E436), using an Orion Model 94-09 fluoride electrode as the indicator electrode. The remote-junction reference electrode is used.[8] Direct potentiometric fluoride measurements were obtained with this same electrode pair and a Corning Model 12 pH meter. Solutions were prepared from reagent grade chemicals.

Procedure

The technique of titration to a preselected end-point potential in alcoholic medium has been previously described.[1] A sample (1 mg of fluoride) was added to 40 ml of 0·10*N* potassium chloride and the pH was adjusted to 2·0 by dropwise addition of 6*N* nitric acid. Then 40 ml of ethanol were added and the sample was titrated with 0·005*M* thorium nitrate. The end-point potential was taken at the maximum slope and the thorium nitrate was standardized by titration to this value. This potential was then used for all subsequent fluoride titrations.

Column preparation

Ion-exchange resins were prepared by passing 40 ml of 1·0*M* hydrochloric acid through the column and rinsing with distilled water until the effluent was at pH ~ 7. After preparation, 1 litre of the sample water was passed through the column at a flow-rate of about 1 ml/min. The flow-rate did not seem to be critical but was fairly constant over the series of runs. After the sample had passed through, the column was rinsed with distilled water. Fluoride was eluted with 45 ml of 0·1*M* potassium chloride at a flow-rate of 1·0 ml/min. In each case, the first 5 ml of eluate were discarded and the next 40 ml of eluate were collected, adjusted to pH 2·0, and titrated as described above.

RESULTS AND DISCUSSION

This procedure was tested on synthetic samples of fluoride in distilled water and tap-water from the town of Foxboro, Massachusetts. The results are shown in Table I. These data show that the recovery of fluoride from distilled water and the separation and recovery of fluoride from distilled water containing a large added excess of sodium sulphate is quantitative. Foxboro tap-water, an untreated water drawn from surface wells, is not fluoridated. A typical analysis, supplied by Massachusetts Department of Public Health, showed:

Alkalinity (as Na_2CO_3)	10–28 mg/l.
Hardness (as $CaCO_3$)	18–44 mg/l.
Iron	0·00–0·24 mg/l.
Manganese	0·02–1·4 mg/l.
Nitrate	1·0–2·0 mg/l.
Chloride	10·0–18·0 mg/l.

Addition of barium chloride showed detectable sulphate, estimated to be 8 mg/l.

A titration blank showed no titratable fluoride content in this water (*i.e.*, the fluoride electrode potential was slightly more positive than the previously selected end-point potential). The direct

TABLE I.—DETERMINATION OF FLUORIDE IN SYNTHETIC WATERS

1-litre sample of 1 mg of F^- in	Recovery, *mg*
Distilled H_2O	1·02
Distilled H_2O	0·99
Foxboro tap water	1·02
Foxboro tap water	1·00
Foxboro tap water	0·99
Distilled H_2O + 50 mg SO_4^{2-}	0·98
Distilled H_2O + 100 mg SO_4^{2-}	1·00
Distilled H_2O + 100 mg SO_4^{2-}	1·00

TABLE II.—DETERMINATION OF FLUORIDE IN PUBLIC WATERS

Sample	Titration F^- found *mg/l.*	Potentiometry F^- found *mg/l.*
Beverly-Salem, Mass.	1·00	1·10
	1·01	1·08
	0·98	1·06
	1·02	1·04
Mean	1·00	1·07
Providence, R.I.	0·94	1·04
	0·95	0·90
	0·94	0·90
Mean	0·94	0·95

Standard deviation of titration results = 0·013 mg/l.
Standard deviation of potentiometric results = 0·047/l.

potentiometric determination by the procedure described by Frant and Ross,[3] however, showed the fluoride content to be about 0·02 mg/l. When 1-mg amounts of fluoride were added to litre portions of this water and fluoride was determined as above, the results (Table I), corrected for the blank potentiometric value of 0·02 mg, showed no bias when compared with the determination made from the distilled water samples. Precision and relative error is about 1%.

Table II shows the results obtained from determination of fluoride in the fluoridated water supplies of two neighbouring cities of Beverly-Salem, Mass., and Providence, R.I. Both supplies are treated surface-water. Also shown in Table II are the results obtained by the direct potentiometric method. This titration procedure, with its precision and relative error of 1%, improves on direct potentiometry by a factor of about five.

Research Center
The Foxboro Company
Foxboro, Massachusetts, U.S.A.

T. S. LIGHT
R. F. MANNION
K. S. FLETCHER, III

REFERENCES

1. T. S. Light and R. F. Mannion, *Anal. Chem.*, 1969, **41,** 107.
2. D. J. Curran and K. S. Fletcher III, *ibid.*, 1969, **41,** 267.
3. M. S. Frant and J. W. Ross, Jr., *ibid.*, 1968, **40,** 1169.
4. R. H. Babcock and K. A. Johnson, *J. Am. Water Works Assoc.*, 1968, **60,** 953.
5. *Standard Methods for Examination of Water and Wastewater*, 12th Ed., American Public Health Association, New York, 1965.
6. I. Zipkin, W. D. Armstrong, and L. Singer, *Anal. Chem.*, 1957, **29,** 310.
7. H. M. Nielsen, *ibid.*, 1958, **30,** 1009.
8. T. S. Light, in *Analysis Instrumentation*, Vol. 5, L. Fowler, R. G. Harmon, and D. K. Roe, Eds., pp. 73–87. Plenum Press, New York, 1968.

Summary—A procedure is described for the accurate titration of fluoride at the 1 mg/1. level in potable water. The procedure employs an ion-exchange step for concentration of fluoride and removal of interfering ions, and Th(IV) as titrant. Precision and relative error of the method are both 1%.

Zusammenfassung—Eine Vorschrift zur genauen Titration von Fluorid im Bereich um 1 mg/l. in Trinkwasser wird angegeben. Zur Anreicherung von Fluorid und zur Entfernung störender Ionen wird eine Ionenaustausch-Stufe eingesetzt; titriert wird mit Thorium(IV). Genauigkeit und relativer Fehler der Methode betragen beide 1%.

Résumé—On décrit une technique pour le titrage précis du fluorure à la teneur de 1 mg/l dans l'eau potable. La technique utilise un stade d'échange d'ions pour la concentration du fluorure et l'élimination des ions gênants et Th(IV) comme agent de titrage. La précision et l'erreur relative de la méthode sont toutes deux de 1%.

Talanta, 1969, Vol. 16, pp. 1444 to 1447. Pergamon Press. Printed in Northern Ireland

Eine verbesserte Apparatur zur kontinuierlichen trägerfreien Durchflussionophorese

(*Eingegangen am* 19. *February*1969. *Angenommen am* 21. *März* 1969)

DIE von Barrollier, Watzke und Gibian erstmals beschriebene Apparatur zur trägerfreien Durchflußionophorese[1] hat sich besonders nach verschiedenen Modifizierungen und Verbesserungen[2,3] bei kontinuierlichen Trennungen bewährt. Der apparative Aufwand ist aber bei dieser Versuchsanordnung wie auch bei entsprechenden ähnlichen Entwicklungen[4] beträchtlich. Insbesondere die Substanzzufuhr und -abnahme sowie die Konstanthaltung der Durchflußgeschwindigkeit erfordern komplizierte Regeleinrichtungen und diskontinuierlich arbeitende Dosier-und Schlauchpumpen, die oft zu Störungen Anlaß geben.

Auf der Grundlage der bei der Entwicklung der Gegenstromionophorese[5–9] gewonnenen Erfahrungen wird deshalb unter Beibehaltung des Grundprinzips eine in vielen Punkten verbesserte und vereinfachte Versuchsanordnung zur kontinuierlichen Durchflußionophorese beschrieben. Die neue Apparatur ist ganz den Erfordernissen der Trennung temperaturempfindlicher Substanzen angepaßt. Neben der Verkleinerung der Kühlplatten auf ein handliches Format von 300 × 300 mm betreffen die Verbesserungen den Zulauf des Trenngemisches, die Homogenität des elektrischen Feldes, die Regulierung und Konstanthaltung der Durchflußgeschwindigkeit, sowie die Abnahme der getrennten Substanzen.

APPARATUR

Abbildung 1 zeigt schematisch die Gesamtapparatur, Abb. 2 einen Längsschnitt, der insbesondere Einzelheiten der Regulierung der Durchflußströmung erkennen läßt.

Zwei von Kühlflüssigkeit (2) durchflossene Glasplatten (1) der Abmessungen 300 × 300 mm werden durch fünf inkompressible Kunststoffplättchen (14) von 0,3 mm Dicke auf konstantem Abstand gehalten. Die zwischen den Kühlplatten entstehende Ionophoresekammer, eine kapillare Trennfläche, wird nach allen Seiten mit einem Zweikomponentenklebstoff abgedichtet. Die beiden Elektrodentröge stehen über zwei mit Asbestwolle gefüllte, 2 mm breite Diaphragmenspalten, die durch den Kühlraum der Oberplatte führen, mit der Trennfläche in Verbindung.

Der Zulauf des Grundelektrolyten erfolgt durch neun gleichmäßig über die gesamte Rückfront verteilte Polyäthylenschläuche (3) (Durchmesser: innen 1,0 mm, außen 1,5 mm). Sie sind in eingeschliffene Kerben der Oberplatte (16) fest eingekittet und führen über eine Glasharfe zum Vorratsgefäß (4), dessen Flüssigkeitsniveau durch eine vorgeschaltete Mariottesche Flasche konstant gehalten wird. Über sechs mit Kunststoffhülsen versehene Spülbohrungen (5) lassen sich Luftblasen aus der Trennfläche absaugen.

Das Trenngemisch fließt aus dem Niveaugefäß (7) durch einen dünnen Schlauch (15) über eine der drei Bohrungen mit PVC-Hülsen (8) in die Trennfläche. Diese Zuleitung ist von einem 10 mm

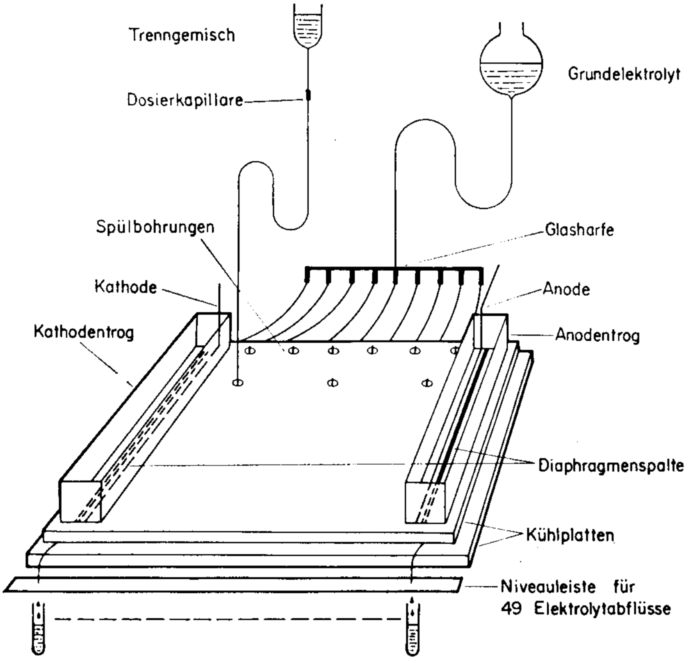


Abb. 1.—Verbesserte Apparatur zur kontinuierlichen Durchflußionophorese.

dicken Kühlschlauch (10) umgeben, der zeischen dem Kühlmantel (9) des Gefäßes (7) und dem Glasansatz (11) einen biegsamen Kühlmantel bildet. Bei Anschluß an einen Kryomaten gelangt das Trenngemisch gekühlt in die Apparatur. Die Zulaufgeschwindigkeit wird durch die Dosierkapillare (6) festgelegt.

An der Abflußseite der Trennkammer sind 49 Polyäthylenschläuche (18) im gleichen Abstand in Kerben (12) eingekittet. Die Schläuche werden wegen der fehlenden Kühlung auf möglichst kurzem

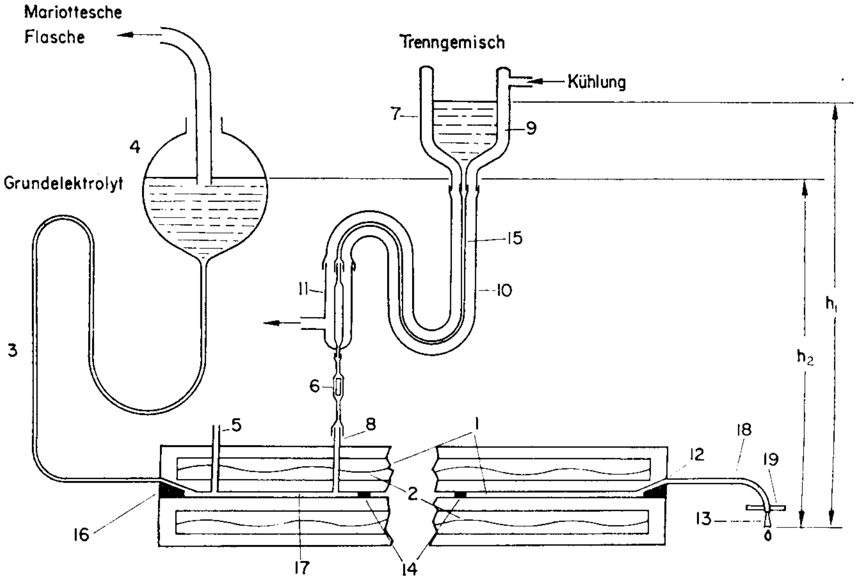


Abb. 2.—Längsschnitt der Apparatur zur kontinuierlichen Durchflußionophorese.

Weg an eine Halterung (19) geführt. Jedes Schlauchende trägt eine Kapillare (13) gleicher Ausflußgeschwindigkeit. Mit der Leiste (19) werden alle Kapillaren in einer Ebene angeordnet, so daß der gleichmäßige Abfluß der getrennten Substanzen und des Grundelektrolyten über die gesamte Breite der Trennfläche gewährleistet ist. Die von den Kapillaren abtropfenden Lösungen werden in gekühlten Reagensgläsern aufgefangen.

Arbeitstechnik

Zur Inbetriebnahme füllt man die Trennfläche blasenfrei mit dem Grundelektrolyten, im allgemeinen einer Pufferlösung der Ionenstärke 0,01 bis 0,05. Um Ionenverarmung in den Diaphragmen zu vermeiden, enthalten die Elektrodentröge den gleichen Puffer, jedoch in der 5–10 fachen Konzentration.

Die Apparatur wird bei konstanter Gleichspannung zwischen 2000 und 3000 V, entsprechend Feldstärken von 8–12 V/mm, betrieben. Die entstehende Joulesche Wärme führt die mit einem Kryomaten umgepumpte Kühlflüssigkeit (Methanol) ab. Bei der Trennung empfindlicher Substanzen soll die Temperatur in der Trennfläche möglichst niedrig sein. Bei einer Stromstärke von etwa 100 mA, entsprechend 200–300 Watt, und einer Kühlsoletemperatur von −5° liegt die Temperatur im Trennspalt bei 0°.

Die Strömungsgeschwindigkeit des Grundelektrolyten und der Trennlösung wird hydrostatisch gesteuert. Dazu ist die sorgfältige Auswahl der Dosierungskapillare (6) und der 49 Ablaufkapillaren (13) erforderlich. Diese Kapillaren werden aus dem konischen Teil der Spitzen ausgezogener dickwandiger Glasrohre herausgeschnitten. Ihre Länge beträgt 10–15 mm, der Außendurchmesser am spitzen Ende 0,7–1 mm, am stumpfen 2–3 mm. Ihre Auslaufgeschwindigkeit wird experimentell bestimmt. Sie darf bei gleichem hydrostatischen Druck für die Ablaufkapillaren maximal um 10% differieren. Die Kapillaren werden durch Eindrücken ihres spitzen Endes in die Polyäthylenschläuche befestigt.

Da die Ausflußmenge von Kapillaren proportional dem hydrostatischen Druck ist, läßt sich die Strömungsgeschwindigkeit in der Trennfläche durch Einstellung des Niveaus h_2 regeln. Die Differenz $(h_1 - h_2)$, die stets positiv sein muß, bestimmt den Durchsatz an Trennlösung. Die Verweilzeit muß auf die Wanderungsgeschwindigkeiten der zu trennenden Ionen und mit den übrigen Arbeitsbedingungen abgestimmt werden.

Kontinuierliche Trennungen

Die beschriebene Apparatur wurde am Beispiel der Trennung einiger Osmiumkomplexe erprobt. Ein Gemisch mit gelben $[OsCl_6]^{2-}$ und blauvioletten $[OsBr_6]^{2-}$ Ionen, deren Beweglichkeiten sich um etwa 12% unterscheiden, wurde unter folgenden Arbeitsbedingungen getrennt:

Grundelektrolyt:	Puffer je 0,01m an CH_3COOH und CH_3COOK
Elektrodenlösung:	Puffer je 0,1m an CH_3COOH und CH_3COOK
Gleichspannung:	2,5 kV
Stromstärke:	50 mA
Kühlsoletemperatur:	−3°
Verweilzeit:	25 Min.

Bei einer Durchsatzleistung von 3–5 ml 0,01n Analysenlösung pro Stunde gelang die vollkommene Entmischung der Komponenten.

In gleicher Weise bewährt sich die Apparatur zur präparativen Isolierung einiger neuer Mehrkernkomplexe des Osmiums.[10,11]

DISKUSSION

Die wichtigsten Vorteile und Verbesserungen der neuen Versuchsanordunung sind:

(1) *Geringe Störanfälligkeit*: Durch den gänzlichen Verzicht auf mechanische Regelelemente und Zusatzgeräte wird die Störanfälligkeit beträchtlich verringert.

(2) *Hohe Konstanz der Durchflußströmung:* Die Verwendung hydrostatisch geregelter Kapillaren garantiert das völlig gleichmäßige Fließen und eine weit bessere Langzeitkonstanz der Strömungsgeschwindigkeit, als das mit rhythmisch arbeitenden Pumpsystemen erreicht werden kann.

(3) *Homogenes elektrisches Feld:* Bei den früher verwendeten einzelnen Diaphragmenbohrungen traten stets gewisse Feldinhomogenitäten auf. In diesen Bereichen kam es wegen Überhitzung häufig zu störenden Gasabscheidungen. Die intensiv gekühlten Diaphragmenspalte gestatten dagegen das Arbeiten bei höheren Strom- und Feldstärken. Dadurch wird die Verweilzeit des Trenngutes in der Apparatur verringert und die Durchsatzleistung gesteigert.

(4) *Trennmöglichkeit für temperaturempfindliche Verbindungen:* Die Stabilität vieler Verbindungen nimmt mit fallender Temperatur zu. Neben der intensiven Kühlung der Apparatur ist deshalb

auch die Zuleitung für das Trenngemisch kühlbar. Die englumigen, kurzen Schläuche des Abnahmeteils werden von den getrennten Substanzen schnell durchströmt. Die ältere Abnahme vorrichtung wies dagegen viel Totvolumen auf. Die verkürzte Trenndauer wirkt zeitabhängigen Störungen infolge Substanzzerfalls entgegen.

(5) *Geringer Aufwand:* Die Herstellung der Versuchsanordnung ist gegenüber Apparaturen vergleichbarer Leistungsfähigkeit weit weniger aufwendig. Sie bedarf keiner besonderen Aufstellvorrichtung und Justierung. Der Betrieb ist sicher und erfordert wenig Wartung.

Wir danken dem Direktor des Instituts, Herrn Prof. Dr. E. Blasius, für häufige Beratung. Für finanzielle Unterstützung danken wir der Deutschen Forschungsgemeinschaft und dem Bundesministerium für Wissenschaftliche Forschung.

Institute für Analytische Chemie und Radiochemie
der Universität des Saarlandes
Saarbrücken, Deutschland

W. PREETZ
H. L. PFEIFER

Zusammenfassung—Bei der beschriebenen Apparatur wird die Konstanthaltung und Steuerung der Durchflußströmung durch hydrostatische Regelung der Auslaufgeschwindigkeit ausgewählter Kapillaren erreicht. Der Verzicht auf mechanische Regelemente und Dosierpumpen verringert die Störanfälligkeit und den apparativen Aufwand. Die Apparatur eignet sich insbesondere für die Trennung temperaturempfindlicher Verbindungen.

Summary—An apparatus is described which achieves constant transverse flow of electrolyte by means of hydrostatic regulation of the flow-rate from selected capillaries. The absence of pumps and mechanical control devices reduces both the expense and the possibility of failure. The apparatus is particularly suitable for the separation of temperature-sensitive compounds.

Résumé—On décrit un appareil qui réalise une circulation transversale constante d'électrolyte au moyen d'une régulation hydrostatique de la vitesse d'écoulement à partir de tubes capillaires sélectionnés. L'absence de pompes et de dispositifs de contrôle mécaniques réduit tant la dépense que la possibilité de défaillance. L'appareil est particulièrement approprié à la séparation de composés sensibles à la température.

LITERATUR

1. J. Barrollier, E. Watzke und H. Gibian, *Z. Naturforsch.*, 1958, **13b**, 75.
2. K. Wiek, *J. Chromatog.* 1964, **13**, 111.
3. E. Blasius und W. Preetz, *Z. Anorg. Allgem. Chem.*, 1965, **335**, 1, 16.
4. K. Hannig, *Z. Anal. Chem.*, 1961, **181**, 244.
5. W. Preetz, *Talanta*, 1966, **13**, 1649.
6. *Idem*, *Naturwissenschaften*, 1967, **54**, 85.
7. W. Preetz und H. L. Pfeifer, *Talanta*, 1967, **14**, 143.
8. *Idem*, *Anal. Chim. Acta*, 1967, **38**, 255.
9. W. Preetz, *Fortschr. Chem. Forsch.*, 1969, **11**, 375.
10. H. L. Pfeifer, *Dissertation*, Univ. d. Saarlandes, Saarbrücken, 1968.
11. W. Preetz, *Habilitationsschrift*, Univ. d. Saarlandes, Saarbrücken, 1968.

Talanta, 1969, Vol. 16, pp. 1447 to 1450. Pergamon Press. Printed in Northern Ireland

Selective complexometric determination of mercury, using thiourea as masking agent

(*Received* 7 *March* 1969. *Accepted* 24 *March* 1969)

COMPLEXOMETRIC methods for the direct determination of mercury are of poor selectivity, owing to co-titration of other metal ions. The usual practice is to determine the sum of mercury and other components and then to decompose the mercury–EDTA complex selectively with masking agents such as thiosemicarbazide[1] or cystein[2] and titrate the liberated EDTA. In all these methods, however, copper causes the most serious interference. Potassium iodide has been suggested by Ueno[3] as the masking agent for determining mercury in the presence of copper in alkaline medium, but then many other ions interfere. Thiosulphate[4] has also been recommended as a selective masking agent in alkaline medium but the interference of copper has not been studied.

The present communication describes the use of thiourea as a masking agent for the selective decomposition of mercury–EDTA complex at pH 5–6. The liberated EDTA is then titrated against standard lead nitrate, with Xylenol Orange (or Methylthymol Blue) as indicator. The main advantage is that copper does not interfere if cooled solutions are titrated.

EXPERIMENTAL

Reagents

EDTA 0·05M. Standardized against pure zinc, with Eriochrome Black T as indicator.

Mercuric nitrate 0·05M. Prepared from reagent grade salt and standardized with 0·05*M* EDTA, Xylenol Orange being used as indicator.

Xylenol Orange and Methylthymol Blue indicators. Aqueous solutions, 0·1%

Thiourea solution, 10%. Reagent grade nitrates of the cations were used for studying interferences.

Determination of mercury in the presence of other cations

To an acidic aliquot of the sample solution containing not more than 50 mg of mercury, add excess of 0·05*M* EDTA. If the solution is only slightly acidic a temporary milkiness appears during the addition of EDTA, but disappears when the excess of EDTA has been added. Dilute the solution to 100 ml with distilled water and add sufficient solid hexamine to adjust the pH to 5–6. Add 0·5 ml of Xylenol Orange indicator and back-titrate the excess of EDTA with 0·05*M* lead nitrate to a sharp colour change from yellow to red-violet. Add 12 ml of 10% thiourea solution (1 ml for each 4 mg of mercury), shake, and titrate the liberated EDTA with 0·05*M* lead nitrate to the same sharp end-point as in the first titration. Methylthymol Blue gives equally sharp end-point colour changes from yellow to blue.

Determination of mercury in the presence of copper

To an acidic aliquot of the sample solution containing not more than 12 mg of copper and 40 mg of mercury add excess of 0·05*M* EDTA and dilute to 100–150 ml with distilled water. Adjust the pH to 5–6 with solid hexamine and add 1 ml of Xylenol Orange indicator. If the solution is blue after the addition of the indicator, EDTA is not in excess, and the titration must be repeated because the indicator is blocked by the free copper. Back-titrate the excess of EDTA with 0·05*M* lead nitrate added dropwise with constant shaking, till a sharp colour change from green-yellow to violet-blue is obtained.

Cool the reaction mixture to below 20° (preferably to 15°), adjust the pH to about 5·5 and add the requisite volume of 10% thiourea solution. Shake for 1 min or so till a clear yellow-green colour reappears. Titrate the liberated EDTA slowly with 0·05*M* lead nitrate to the same end-point as before.

With Methylthymol Blue as indicator the end-point colour change is from yellow-green to blue. The end-points both with and without copper are extremely sharp.

TABLE I.—CATION INTERFERENCE STUDY (AT 35°C).

Ion added, *mg*		0·05*M* EDTA liberated, *ml* Expected	Actual	pH at the end-point
—		4·80	4·80	5·8
—		4·80	4·80	5·2
Ag^+	40	4·80	4·80	5·3
Mn^{2+}	5	4·80	4·81	5·4
Cd^{2+}	22	4·80	4·80	5·5
Fe^{3+}	11	4·80	4·81	5·8
Bi^{3+}	30	4·80	4·80	5·5
Zn^{2+}	52	4·80	4·80	5·6
Co^{2+}	10	4·80	4·80	5·5
Ni^{2+}	42	4·80	4·80	5·4

TABLE II.—EFFECT OF TEMPERATURE AND pH ON THE INTERFERENCE OF COPPER AND ALUMINIUM

Mercury taken, *mg*	Ion added, *mg*		10% Thiourea, *ml*	0·05*M* EDTA liberated, *ml*		pH at end-point	Temp. °*C*
				Expected	Actual		
38·41	—		—	3·82	3·82	5·5	8
	Cu^{2+}	15·7	10	3·82	3·85	5·5	35
				3·82	3·83	5·1	9
				3·82	3·82	5·35	8
		12·6	10	3·83	3·85	5·2	37
				3·83	3·83	5·3	18
		9·4	10	3·83	3·84	5·15	35
				3·83	3·83	5·50	35
19·2		15·7	5	1·92	1·92	5·3	35
		15·7	10	1·92	$1{\cdot}92_5$	5·4	35
39·01	Al^{3+}	5	10	3·89	3·92	5·5	33
				3·89	3·90	5·1	12
				3·89	3·89	5·6	16
		8	10	3·89	3·90	5·4	14

RESULTS AND DISCUSSION

Cation interference

The mercury–EDTA complex is readily decomposed by thiourea at pH 5–6 and at a temperature as low as 8°. Many cations can be tolerated (Table I). Manganese gives some trouble in the end-point detection in both back-titrations. The interference of copper and aluminium can be easily eliminated by the proper control of pH and temperature. High temperature and low pH give slightly higher results. The amounts of mercury and copper present also affect the accuracy of the results. With smaller amounts of mercury larger amounts of copper can be tolerated. The pH of the solution should preferably be kept at about 5·5 and the temperature at about 15°. Typical results are recorded in Table II.

Although calcium and magnesium complex only weakly with EDTA at pH 5–6, they may cause unexpectedly serious interference by making the end-point protracted in the second back-titration (after the addition of thiourea). The pH at the end-point has a pronounced effect on this interference. At the lower limit of the pH range larger amounts of calcium and magnesium can be tolerated. Addition of potassium fluoride solution just before the end-point helps in the toleration of larger

TABLE III.—EFFECT OF pH ON THE INTERFERENCE OF CALCIUM AND MAGNESIUM

Ion added, *mg*		Indicator	pH at end-point	End-point†
Ca^{2+}	4	XO	5·15	S
	4		5·5	P
	8*		5·8	S
	16*		5·8	P
	32*		5·4	S
	32		5·0	S
	32	MTB	5·5	S
Mg^{2+}	4	XO	5·5	P
	10		5·3	S
	34		5·2	S
	19	MTB	5·6	S

* 5% KF added solution just (0·02 ml) before the end-point.
† S = Sharp, P = Protracted.

amounts of calcium. It was interesting to observe that in the presence of calcium and magnesium Methylthymol Blue indicator gives a better performance than Xylenol Orange (Table III). Barium and strontium do not interfere with either of the indicators.

Acknowledgement—Professor Nazar Singh, Head of Chemistry Department, is thanked for providing research facilities.

Department of Chemistry
Punjabi University
Patiala-4, India

Rajinder Pal Singh

Summary—A method is described for selective complexometric determination of mercury, thiourea being used as masking agent. An excess of EDTA is added and the surplus EDTA is back-titrated with lead nitrate, with Xylenol Orange or Methylthymol Blue as indicator (pH 5–6). Thiourea is then added to decompose the mercury–EDTA complex and the liberated EDTA is again back-titrated with lead nitrate. The interference of various cations has been studied.

Résumé—On décrit une méthode pour le dosage complexométrique sélectif du mercure, la thiourée étant utilisée comme agent dissimulant. On ajoute un excès d'EDTA et le surplus d'EDTA est titré en retour par le nitrate de plomb, avec l'Orangé Xylénol ou le Bleu de Méthylthymol comme indicateur (pH 5–6). On ajoute alors de la thiourée pour décomposer le complexe mercure-EDTA et l'EDTA libéré est de nouveau titré en retour par le nitrate de plomb. On a étudié l'interférence de divers cations.

Zusammenfassung—Ein Verfahren zur selektiven komplexometrischen Bestimmung von Quecksilber wird beschrieben, bei dem Thioharnstoff als Maskierungsmittel verwendet wird. Überschüssige EDTA wird zugesetzt und der Überschuß mit Bleinintrat zurücktitriert, wobei Xylenolorange oder Methylthymolblau als Indikator verwendet werden (pH 5–6). Dann wird Thioharnstoff zur Zerlegung des Quecsilber-EDTA-Komplexes zugegeben und die freigesetzte EDTA wiederum mit Bleinitrat zurücktitriert. Die Störung durch verschiedene Kationen wurde untersucht.

REFERENCES

1. J. Körbl and R. Přibil, *Chem. Listy*, 1957, **51**, 667; *Collection Czech. Chem. Commun.*, 1957, **22**, 1771.
2. W. Berndt and J. Šára, *Talanta*, 1961, **8**, 653.
3. K. Ueno, *Anal. Chem.*, 1957, **29**, 1669.
4. P. Curro and G. Calabro, *Atti Soc. Peloritana Sci. Fis. Mat. Nat.*, 1965, **11**, 49; *Chem. Abstr.*, 1966, **65**, 2996*h*.

Talanta, 1969, Vol. 16, pp. i to ii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Metallextraktionen mit aliphatischen Alkoholen: Eugen Gagliardi und Peter Tümmler. (9 *May* 1969)

Spectrophotometric extractive titrations—VII. Titrations with di-2-naphthylthiocarbazone: A. Galik. (5 *June* 1969)

L'Automatisation en analyse per activation neitronique et ses applications a la production industrielle: J. Perdijon. (6 *June* 1969)

Pyridylalpyridylhydrazone (PDP) as spectrophotometric reagent for cobalt: L. Keith Hunt and Harvey Diehl. (20 *June* 1969)

Determination of the molecular weights of esters of ethylenediaminetetraacetic acid (EDTA) and related acids by saponification: D. J. Alner, P. A. Claret and A. G. Osborne. (20 *June* 1969)

Complexometric determination of molybdenum(VI): Rudolf Přibil and Vladimír Veselý. (23 *June* 1969)

Optimum physical and chemical conditions for the Methylene Blue method of estimating gaseous sulphide in the environment: P. K. Zutshi and T. N. Mahadevan. (24 *June* 1969)

Use of a filter in atomic-fluorescence spectroscopy: P. D. Warr. (24 *June* 1969)

Notes upon photometric determination of selenium(IV) with dithizone: N. Jordanov and K. Daskalova. (25 *June* 1969)

Alkaline errors of glass electrodes in non-aqueous solvents: B. Karlberg and G. Johansson. (25 *June* 1969)

Hydrolysis of substituted 8-acetoxyquinolines: E. J. Billo, R. P. Graham and P. G. Calway. (25 *June* 1969)

Polarimetric studies of a few boron–sugar complexes: N. A. Ramaiah and H. R. Srivastava. (26 *June* 1969)

Polarographic behaviour of percapryclic, percapric, perlauric and permyristic acids—I. Ammonium nitrate in methanol–benzene or in dimethyl formamide as supporting electrolyte: I. W. Siddiqui and R. M. Johnson. (27 *June* 1969)

Determination of atmospheric iron particulates by X-ray fluorescence spectroscopy: Jae Y. Hwang. (27 *June* 1969)

Determination of tin in ores and concentrates: D. P. Schweinsberg and B. J. Heffernan. (30 *June* 1969)

Nucleation and crystal growth of copper(II) 8-hydroxyquinolate precipitates from mixed solvents: T. Rihs, M. C. Thurston and L. C. Howick. (30 *June* 1969)

Analytical applications of *m*- and *p*-phenylene-di-(1-tetrazoline-5-thione). Gravimetric determination of ruthenium(III) in presence of large amounts of rhodium(III): G. S. Johar and Umesh Agarwala. (1 *July* 1969)

Determination of composition and conditional stability constant of complex A_mB_n by means of extrapolation method: B. Budesinský and J. Švecová. (5 *July* 1969)

Simultaneous spectrophotometric determination of cobalt, nickel and copper with 2,3-quinoxalinedithiol: R. W. Burke and E. R. Deardorff. (14 *July* 1969)

Exchange reactions of ternary ion-association complexes directly in the organic phase: R. W. Burke. (14 *July* 1969)

Titration of sulfhydryl, using a silver electrode: Taft Y. Toribara and Larysa Koval. (16 *July* (1969)

Reactions of 2′,7′-Bis(acetoxymercuri)fluorescein (AMF) with certain complexing anions: G. Colovos, M. Haro and H. Freiser. (16 *July* 1969)

Solvents for the external heavy atom effect in phosphorimetry: W. J. McCarthy and K. L. Dunlap. (26 *July* 1969)

Détection et dosage de l'oxyde de carbone avec un réactif de couleur: La combinaison d'argent de l'acide *p*-sulfamyle-benzoique: G. Ciuhandu and V. Bockel. (28 *July* 1969)

Spectrophotometric estimation of cobalt(II): *m*-Mercaptoacetamidophenol as a precipitant and sodium hydroxide as a solvent: S. N. Kakkar and N. S. Poonia. (29 *July* 1969)

α-(Phenylazo)-4-nitrobenzylcyanide, new acid-base indicator: László Légrádi. (29 *July* 1969)

A separation scheme for the analysis of multicomponent samples: James S. Fritz and Gary L. Latwesen. (31 *July* 1969)

Catalytic analysis—I. Mechanisms of catalymetric analytical reactions: P. R. Bontchev. (1 *August* 1969)

Complexes formed in chloroform extraction of uranium(VI) with 5,7-dichloro-oxine: Shohachirō Oki and Shigeki Yamauchi. (5 *August* 1969)

End-point evaluation in instrumental titrimetry—II. Confidence intervals in extrapolation of linear titration curves: Pavel Janders and Stanislav Kotrlý. (11 *August* 1969)

Amperometric titration of papaverine hydrochloride by cobalt thiocyanate: I. M. Roushdi, S. A. Soliman and M. H. Sadek. (11 *August* 1969)

Analysis of platinum for certain elemental impurities by neutron-activation assay: H. K. El-Shamy, A. A. Abdel-Rassoul and R. Madbouly. (11 *August* 1969)

Determination of low concentrations of iodine-131 in fast-reactor coolant systems: A. R. Ware, G. Oldham and D. M. Bibby. (11 *August* 1969)

Determination and separation of cerium by photochemical precipitation: M. Das, R. P. Agarwal, A. H. Heyn and M. Z. Hoffman. (11 *August* 1969)

Photometric determination of gold with oxine in the presence of *aqua regia*: M. E. Macovschi. (12 *August* 1969)

Application of the Unterzaucher method to the determination of oxygen in coke: B. P. Kirk and H. C. Wilkinson. (14 *August* 1969)

Determination of manganese and calcium in ores and slags by successive DCTA and EDTA titrations: Yonk Chekhlarova, Pavel Ganev and Ivan Gabrovsky. (18 *August* 1969)

The complexometric determination of manganese in the presence of iron and the alkaline earth metals: Yonka Chekhlarova and Pavel Ganev. (18 *August* 1969)

Cerimetric determination of Erioglaucine A, Eriogreen B and Xylenecyanol FF: N. Venkayeswara Rao and V. V. S. Eswara Dutt. (18 *August* 1969)

Talanta, 1969, Vol. 16, pp. iii to iv. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Practical Statistics for Chemical Research: JOHN D. HINCHEN, Methuen, London, 1969. Pp. vii + 116. 36s. (Also available from Science Paperbacks (18s).)

This is a book which is intended to popularise the use of statistics in the analysis of data, more particularly in the Chemical Industry. The author has experience both in teaching and in industrial quality control and has written about his subject in an unconventional and engaging manner. In addition to the main discussion of statistical methods relevant to research and control there are provided a glossary of terms and a collection of statistical tables.

Chelates in Analytical Chemistry, Vol. 2: Eds. H. A. FLASCHKA and A. J. BARNARD, JR., Dekker, New York, 1969. Pp. xiv + 398. $19.75.

This volume continues the lines laid down in Vol. 1, with monographic articles on arylazo derivatives of chromotropic acid, electrometric titrations with two polarizable electrodes, advances in precipitation methods with chelating agents, applications of Schiff's bases, selectivity of dioximes, and chelation in the chemistry of niobium and tantalum.

Infra-Red Spectra and Structure of Organic Long-Chain Polymers: A. ELLIOT, Arnold, London, 1969. Pp. VIII + 119. 35s.

This is a short work, written by a biophysicist for those interested in molecular biology, polymer technology and related undergraduate and postgraduate courses. Chapter 1, General principles, and Chapter 2, Experimental methods, will be comprehensible to most readers. Chapter 3, Vibration in chain molecules, and Chapter 4, Uses of polarized radiation, are more complicated and will probably involve the reader in some background reading. Chapter 5, Some special topics in the spectroscopy of polymers, reflects the author's interests, and deals with hydrogen bonding, the amide group, frequency shifts associated with conformational changes in polypeptides and proteins, hydrogen-deuterium exchange and the difference between the spectra of crystalline and amorphous polymers. The usefulness of a small book depends on the number and quality of the references. Here the author has done a good job. The diagram on p. 56 could have been made clearer. That however is the only criticism of what is otherwise an excellent book. Molecular biologists and fibre technologists will find it a useful book. Its price and coverage make it a suitable text for certain undergraduate and postgraduate courses.

Electroanalytical Chemistry, Vol. 3: Ed. ALLEN J. BARD. Edward Arnold, London, 1969. Pp. 311. $15.75.

The analytical chemist with an interest in computing techniques will find much to interest him in this volume, one third of which deals with Digital Simulation applied to the solution of problems concerning reactions and physical phenomena at electrodes. The use of smaller analogue computors is also discussed in a chapter on the Application of Controlled-Current Coulometry to Reaction Kinetics, in which the simplicity of the technique and the complexity of the interpretation receive due consideration.

Much useful information is to be found in the chapter on Non-aqueous Solvents for Electrochemical Use in which the properties, uses and purification of 38 solvents are presented. The fourth chapter is a detailed account of the use of the Radioactive-Tracer Method for the Investigation of the Electrical Double-Layer Structure. A considerable number of experimental results obtained by the authors are presented in this review. As with the preceding volumes, the material is attractively presented, and the chapters are well documented. Most analytical and physical chemists will find some stimulating reading here.

New Pathways in Inorganic Chemistry: Eds. E. A. EBSWORTH, A. G. MADDOCK and A. G. SHARPE. Cambridge University Press, Cambridge, 1968. Pp. xxx + 390. £4.

This is a collection of reviews by former students of Professor Emeleus in honour of his 65th birthday. They mainly are concerned with aspects of the chemistry of co-ordination compounds, fluorine-containing compounds, non-aqueous solvents and the solid state. Few of the articles are of direct interest to the analyst but as authorative reviews of aspects of modern inorganic chemistry they provide valuable and, in the main, readable background material.

Activation Analysis Literature Cards: Akadémiai Kiadó, Budapest, Hungary. Unslotted: $0.05 per card; slotted: $0.06 per card.

These cards cover the literature from 1935 to 1968 and will be issued in 1969; the bibliography thus provided will be brought up to date yearly.

Molecular Photochemistry: Ed. A. A. LAMOLA, Dekker, New York, 1969. Annual subscription $35.00 (U.S.A. postal pool); $37.00 (Canada and other foreign countries). Issued quarterly.

Atomic Absorption and Flame Emission Spectroscopy Abstracts: Eds. P. R. MASEK and I. SUTHERLAND, Science & Technology Agency, London, 1969. Annual subscription £24 ($58.00). Issued bimonthly.

Modern Methods for the Separation of Rare Metal Ions: JOHANN KORKISCH, Pergamon, London, 1969. Pp. xii + 620. £7. 10; $20.00.

This is an exhaustive treatise by a world authority on the separation of the rare metals. The book outlines the principal methods which have been developed for carrying out such separations, under the headings of ion exchange, liquid-liquid extraction, distillation and co-precipitation. In a number of succeeding chapters the application of these methods to single metals or groups. of metals is described. This is a definitive work and the field is surveyed up to the year of issue.

Third Ceramic Chemists' Conference (on Silicate Analysis): British Ceramic Research Association Stoke-on-Trent, U.K., 1969. Pp. vii + 59. £2.

The proceedings of the meeting held on 1–2 October 1968, covering lectures and discussions.

Chemist's Guide—Basic Chemical and Physical Data: J. P. JESSON and E. L. MUETTERTIES, Dekker, New York, 1969. Pp. iii + 43. $1.95.

An eclectic compilation of useful data, ranging from the genetic code via basic chemical information to character and correlation tables, but SI units are not used.

The Accuracy of Industrial Ceramic Analysis: H. BENNETT and W. G. HAWLEY, British Ceramic Research Association, Stoke-on-Trent, U.K. Special Publication No. 53, 1966, reprinted 1969. Pp. 60. 30s.

A useful compilation of comparative data on analysis of various ceramic standards.

Ion Exchange and Solvent Extraction of Metal Complexes: Y. MARCUS and A. S. KERTES, Wiley-Interscience, London, 1969. Pp. ix + 1037. 315s.

This work discusses the principles of ion exchange and solvent extraction in a critical, informed and informative way. The style is clear and concise but, for all its size, there are omissions and some important topics are dealt with in a few paragraphs. No analytical procedures are given, because it is considered that they are dealt with adequately in other texts. But analysts will find the background information, supported by 2802 references, of great value. It is a remarkable book, which serious workers in the field should try to acquire.

Analysis of Paper: B. L. BROWNING, Dekker, New York, 1969. Pp. ix + 342. 168s.

The scope of this work has been determined by the wide range of analyses for different purposes, which the author has carried out at The Institute of Paper Chemistry in Wisconsin. It appears to be based on laboratory instruction sheets, so that the procedures are clearly described and should be capable of ready adoption by any analyst.

SUMMARIES FOR CARD INDEXES

A membrane electrode for nitrate and other univalent anions: THOMAS N. DOBBELSTEIN and HARVEY DIEHL, *Talanta*, 1969, **16**, 1341. (Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—A membrane electrode has been developed which is responsive to nitrate and other univalent anions but non-responsive to sulphate and other multivalent anions and to cations other than hydrogen. The membrane is prepared by polymerizing a mixture of phenol, formaldehyde, ammonia and nickel nitrate directly to a film for mounting in the usual cell-with-membrane assembly. Response to hydrogen ion is 0·30 mV per pH unit, to nitrate 0·60 mV per pNO_3 (activity) unit. Based on chemical composition and behaviour, physical properties, and electrical response, a structure and mechanism for exchange with hydrogen ion and nitrate ion and for internal electrical conduction has been postulated. Applications have been made to the determination of nitrate and to the detection of end-points.

Untersuchungen zur Optimierung der Reaktionsbedingungen für die katalytische Jodwirkung auf das System Ce(IV)-arsenige Säure (Eine modifizierte Sandell-Kolthoff-Reaktion): GÜNTER KNAPP und HANS SPITZY, *Talanta*, 1969, **16**, 1353. (Institut für Allgemeine Chemie Mikro- und Radiochemie, Technische Hochschule, Graz, Osterreich.)

Summary—The influence of different acids on the rate of the iodine-catalysed redox reaction between Ce(IV) and As(III) has been investigated. The catalytic activity of iodine in nitric acid solutions is 20 times that in the sulphuric acid solutions which have been used so far. The catalytic reaction in nitric acid is also far less sensitive towards accompanying ions, making the system more useful for the determination of traces of iodine.

Eine Apparatur zur automatischen Jodbestimmung im Nanogrammbereich: GÜNTER KNAPP and HANS SPITZY, *Talanta*, 1969, **16**, 1361. (Institut für Allgemeine Chemie, Mikro- und Radiochemie, Technische Hochschule in Graz, Österreich.)

Summary—On the basis of the Sandell-Kolthoff reaction as modified by Knapp and Spitzy an apparatus for automatic iodine determinations has been developed. This instrument works according to a new principle of measurement and allows the analysis of 40 samples per hour. The detection limit is 0·5 ng of iodine. The sample volume per determination can be up to 4 ml, which corresponds to a concentration limit of 0·12 ng/ml.

МЕМБРАННЫЙ ЭЛЕКТРОД ДЛЯ НИТРАТИОНА И ДРУГИХ ОДНОВАЛЕНТНЫХ АНИОНОВ:

THOMAS N. DOBBELSTEIN and HARVEY DIEHL, *Talanta*, 1969, **16**, 1341.

Резюме—Сконструирован мембранный электрод реагирующий на нитратионы и другие одновалентные анионы, но не реагирующий на сульфатион и другие многовалентные анионы и на катионы кроме водорода. Мембрану приготовляют прямым образованием пленки полимеризацией смеси фенола, формальдегида, аммиака и нитрата никеля и сконструированием обыкновенной ячейки с мембраной. Ответ на водородион равен 0,30 мв для единицы pH, а на нитратион 0,60 мв для единицы pNO_3 (активности). Предложены структура и механизм обмена с ионамы водорода и нитрата и внутренной электропроводимости на основе химического состава и характеристики, физических характеристик и электрического ответа. Электродом пользовались для определения нитратиона и для обнаружения концев титрования.

ОПРЕДЕЛЕНИЕ ОПТИМАЛЬНЫХ УСЛОВИЙ ДЛЯ КАТАЛИТИЧЕСКОГО ДЕЙСТВИЯ ИОДА НА СИСТЕМУ Ce(IV)—МЫШЬЯКОВИСТАЯ КИСЛОТА (ИЗМЕНЕННУЮ РЕАКЦИЮ САНДЕЛЛА-КОЛЬТГОФФА):

GÜNTER KNAPP and HANS SPITZY, *Talanta*, 1969, **16**, 1353.

Резюме—Исследовано влияние различных кислот на скорость катализированной иодом окислительно-восстановительной реакции Ce(IV) с As(III). Каталитическая активность иода в азотнокислых растворах является в 20 раз больше чем в использованных до сих пор сернокислых растворах. Кроме того каталитическая реакция в азотной кислоте гораздо менее чувствительна на сопровождающие ионы, улучшая этим образом применимость системы в определении следов иода.

ПРИБОР ДЛЯ АВТОМАТИЧЕСКОГО ОПРЕДЕЛЕНИЯ НАНОГРАММОВЫХ КОЛИЧЕСТВ ИОДА:

GÜNTER KNAPP and HANS SPITZY, *Talanta*, 1969, **16**, 1361.

Резюме—Сконструирован прибор для автоматического определения иода основан на реакции Санделла-Кольтгоффа, измененной Кнаппом и Шпицием. Прибор применяет новый принцип измерения и позволяет анализировать 40 проб в час. Чувствительность определения 0,5 нг иода. Объем проб может быть до 4 мл, соответствующий предельной концентрации 0,12 нг/мл.

Metal complexes with tropolones: YAG DUTT, R. P. SINGH and MOHAN KATYAL, *Talanta*, 1969, **16**, 1369. (Department of Chemistry, University of Delhi, India.)

Summary—A review of the analytical applications of tropolone and its derivatives.

Microdetermination of nitrates and nitramines—I. Titrimetric methods based on the reduction with iron(II), titanium(III), and a mixture of both: WILLIAM IBRAHIM AWAD and SAAD S. M. HASSAN, *Talanta*, 1969, **16**, 1383. (Research Microanalytical Laboratories, Chemistry Department, Faculty of Science, Ain Shams University, Cairo, U.A.R.).

Summary—Organic and inorganic nitrates are satisfactorily determined on the microscale by reduction with Fe(II). Titanium(III) reduces the nitrates in strongly acidic, citrate-buffered, and acetate-buffered media with the comsumption of 3, 6 and 8 equivalents respectively of Ti(III) per nitrate group. Nitramines are determined by reduction with a mixture of Ti(III) and Fe(II). Determination of nitrates and nitramines by *trans*-nitration with salicylic acid is suitable on the microscale. A new electrolytic reduction automatic microburette was devised for the reduction, storage and use of the titanium(III) solution.

Microdetermination of nitrates and nitramines—II. Gasometric methods based on reduction with mercury, iron(II), titanium(III) and hydroquinone: WILLIAM IBRAHIM AWAD and SAAD S. M. HASSAN, *Talanta*, 1969, **16**, 1393. (Research Microanalytical Laboratories, Chemistry Department, Faculty of Science, Ain Shams University, Cairo, U.A.R.)

Summary—Four gasometric micro-methods based on the reduction of nitrates or nitramines to nitric oxide with mercury, iron(II), titanium(III) and hydroquinone in acid media are described. The mercury method is recommended for nitrate esters and secondary nitramines in the absence of aromatic compounds. The iron(II) method is advocated for primary nitramines and nitrate salts in the presence of aromatic compounds. Reductions with titanium(III) and hydroquinone are also successful with the nitrate salts in the presence of an aromatic moiety but the former gives less accurate results. The reduction conditions, mechanism, applications and limitations are described.

КОМПЛЕКСЫ МЕТАЛЛОВ С ТРОПОЛОНАМИ:

Yag Dutt, R. P. Singh and Mohan Katyal, *Talanta*, 1969, **16**, 1369.

Резюме—Приведен обзор применения в анализе трополона и его производных.

ОПРЕДЕЛЕНИЕ НИТРАТОВ И НИТРАМИНОВ НА МИКРОШКАЛЕ—I. ТИТРИМЕТРИЧЕСКИЕ МЕТОДЫ ОСНОВАННЫЕ НА ВОССТАНОВЛЕНИИ С ЖЕЛЕЗОМ(II), ТИТАНОМ(III) И ИХ СМЕСЬЮ:

William Ibrahim Awad and Saad S. M. Hassan, *Talanta*, 1969, **16**, 1383.

Резюме—Удовлетворительным методом определения органических и неорганических нитратов на микрошкале является восстановление с Fe(II). Титан(III) восстанавливает нитраты в сильнокислых, буфферированных цитратом или ацетатом средах, с расходованием 3,6 или 8 еквивалентов Ti(III) дла каждой нитратгруппы, соответственно. Нитрамины определяют восстановлением с смесью Ti(III) и Fe(II). Определение нитратов и нитраминов методом **транс**-нитрации с использованием салициловой кислоты удается провести на микрошкале. Предложена новая автоматическая микробюретка для электролитического восстановления, хранения и использования раствора Ti(III).

ОПРЕДЕЛЕНИЕ НИТРАТОВ И НИТРАМИНОВ НА МИКРОШКАЛЕ—II. ГАЗОМЕТРИЧЕСКИЕ МЕТОДЫ ОСНОВАННЫЕ НА ВОССТАНОВЛЕНИИ С РТУТЬЮ, ЖЕЛЕЗОМ(II), ТИТАНОМ(III) И ГИДРОХИНОНОМ:

William Ibrahim Awad and Saad S. M. Hassan, *Talanta*, 1969, **16**, 1393.

Резюме—Описаны четыре газометрических микрометода основанные на восстановлении нитратов или нитраминов в окись азота с ртутью, железом(II), титаном(III) и гидрохиноном в кислых средах. Ртутный метод рекоммендуется для эфиров азотной кислоты и вторичных нитраминов в отсутствии ароматических соединений. Метод пользующийся железом(II) применен для первичных нитраминов и солей азотной кислоты в присутствии ароматических соединений. Восстановление с титаном(III) и гидрохиноном также применимо в случае солей азотной кислоты в присутствии ароматических соединений но первым методом получаются менее точные результаты. Описаны условия восстановления, механизмы, применения и недостатки методов.

An investigation of the diethyldithiocarbamates of palladium, including the determination of their stability constants: G. B. Briscoe and S. Humphries, *Talanta*, 1969, **16**, 1403. (Department of Chemistry, The University of Aston in Birmingham, Gosta Green, Birmingham 4, England.)

Summary—The reaction of palladium with copper diethyldithiocarbamate has been studied and two complexes isolated: palladium diethyldithiocarbamate and palladium chloride diethyldithiocarbamate. The spectra of both complexes have been examined. The extraction constants and partition coefficients between chloroform and water have been determined, the former by the use of other strong complexing reagents as masking agents for palladium. The stability constants and the exchange constant for the two complexes have been calculated.

Spectrophotometric determination of osmium(IV), iridium(IV) and platinum(IV) and separation and determination of palladium(II) and ruthenium(III) in presence of other platinum metals, with oximidobenzotetronic acid as reagent: G. S. Manku, A. N. Bhat and B. D. Jain, *Talanta*, 1969, **16**, 1421. (Department of Chemistry, University of Delhi, Delhi-7, India.)

Summary—Oximidobenzotetronic acid is suggested as a reagent for the spectrophotometric determination of osmium(IV), iridium(III), iridium(IV), platinum(IV) and for separation and determination of palladium(II) and ruthenium(III) in the presence of other platinum metals. Iridium(III) and (IV) can be estimated when present together.

Rapid spectrophotometric determination of cobalt after extraction using oximidobenzotetronic acid: G. S. Manku, A. N. Bhat and B. D. Jain, *Talanta*, 1969, **16**, 1431. (Department of Chemistry, University of Delhi, Delhi-7, India.)

Summary—A spectrophotometric method based on the extraction of cobalt with benzene solutions of oximidobenzotetronic acid (OBTA) is proposed for the estimation of 0·2–3·0 ppm of cobalt. The 3:1 OBTA:Co complex containing cobalt(III) has its absorption maximum at 430 nm; its molar absorptivity in benzene is $1{\cdot}82 \times 10^3$ l. mole^{-1}. mm^{-1}. Since the blue iron(II) complex is not extracted into benzene, iron(II) and cobalt(II) can be separated and determined spectrophotometrically.

ИССЛЕДОВАНИЕ ДИЭТИЛДИТИОКАРБАМИНАТОВ ПАЛЛАДИЯ, ВКЛЮЧАЯ ОПРЕДЕЛЕНИЕ ИХ КОНСТАНТ УСТОЙЧИВОСТИ:

G. B. Briscoe and S. Humphries, *Talanta*, 1969, **16**, 1403.

Резюме—Изучена реакция палладия с диэтилдитиокарбаминатом меди и выделены два комплекса: диэтилдитиокарбаминат палладия и диэтилдитиокарбаминат хлорида палладия. Испытаны спектры обоих комплексов. Определены константы экстракции и коэффициенты распределения между хлороформом и водой, в случае констант экстракции с использованием других сильных комплексообразующих реагентов в качестве маскирующих агентов для палладия. Вычислены константы устойчивости и константа обмена для двух комплексов.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ОСМИЯ(IV), ИРИДИЯ(IV) И ПЛАТИНЫ(IV) И РАЗДЕЛЕНИЕ И ОПРЕДЕЛЕНИЕ ПАЛЛАДИЯ(II) И РУТЕНИЯ(III) В ПРИСУТСТВИИ ДРУГИХ ПЛАТИНОВЫХ МЕТАЛЛОВ С ИСПОЛЬЗОВАНИЕМ ОКСИМИДОБЕНЗОТЕТРОНОВОЙ КИСЛОТЫ В КАЧЕСТВЕ РЕАГЕНТА:

G. S. Manku, A. N. Bhat and B. D. Jain, *Talanta*, 1969, **16**, 1421.

Резюме—Оксимидобензотетроновая кислота предложена в качестве реагента для спектрофотометрического определения осмия(IV), иридия(IV), иридия(III), платины(IV) и для разделения и определения палладия(II) и рутения(III) в присутствии других платиновых металлов. Иридий(III) и (IV) можно определять один в присутствии другого.

БЫСТРОЕ СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КОБАЛЬТА ПОСЛЕ ИЗВЛЕЧЕНИЯ ОКСИМИДОБЕНЗОТЕТРОНОВОЙ КИСЛОТОЙ:

G. S. Manky, A. N. Bhat and B. D. Jain, *Talanta*, 1969, **16**, 1431.

Резюме—Предложен спектрофотометрический метод для определения 0,2–3,0 мг/л кобальта основанный на извлечении кобальта бензоловым раствором оксимидобензотетроновой кислоты (ОБТК). Комплекс 3:1 ОБТК : Co содержащий кобальт(III) имеет максимум светопоглщения при 430 нм; его молярное поглощение в бензоле равно $1,82 \times 10^3$ л.моль$^{-1}$.мм$^{-1}$. Голубой комплекс железа(II) не извлекается бензолом, потому железо(II) и кобальт(II) можно отделять и определять спектрофотометрическим методом.

Precipitation of manganese ammonium phosphate from homogeneous solution: É. Buzágh-Gere and L. Erdey, *Talanta*, 1969, **16**, 1434. (Institute for General and Analytical Chemistry, Technical University, Budapest.)

Summary—Precipitation of manganese, zinc and cadmium ammonium phosphates from homogeneous solution by decomposition of metal EDTA complexes by boiling with hydrogen peroxide in presence of phosphate has been investigated. Precipitation of Cd is not quantitative, but of Mn is complete in 2 hr, and of Zn in 6 hr.

Determination of europium in minerals and rocks by neutron activation and γγ-coincidence spectrometry: O. B. Michelsen and E. Steinnes, *Talanta*, **16**, 1436 (Institutt for Atomenergi, Kjeller, Norway.)

Summary—Neutron activation followed by γγ-coincidence measurements of 9·3 hr ^{152}Eu is shown to be a convenient method for routine determination of europium in minerals and rocks. In the concentration range 10–150 ppm the method is free of interference from other elements, and neutron shielding effects do not interfere seriously in the analysis. The precison of the method is about 5%.

Voltammetric oxidation of anthraquinones in acetonitrile and nitromethane: M. Ashraf and J. B. Headridge, *Talanta*, 1969, **16**, 1439. (Department of Chemistry, The University, Sheffield, England).

Summary—The voltammetric oxidation of seven anthraquinones to the singly-charged radical cations has been investigated in acetonitrile and nitromethane. The voltammetric waves can be used for the quantitative determination of anthraquinones. Benzoquinones, naphthaquinones and phenanthraquinones are not oxidized in these solvents.

ОСАЖДЕНИЕ СМЕШАННОГО ФОСФАТА МАРГАНЦА И АММОНИЯ ИЗ ГОМОГЕННОГО РАСТВОРА:

É. Buzágh-Gere and L. Erdey, *Talanta*, 1969, **16**, 1434.

Резюме—Исследовано осаждение смешанных фосфатов марганца, цинка и кадмия с аммонием из гомогенного раствора путем разложения комплексов ЭДТА с металлами кипением с перекисью водорода в присутствии фосфата. Осаждение Cd не количествено, но осаждение Mn закончено после 2 ч., Zn после 6 ч.

ОПРЕДЕЛЕНИЕ ЕВРОПИЯ В МИНЕРАЛАХ И ГОРНЫХ ПОРОДАХ МЕТОДАМИ НЕЙТРОННОАКТИВАЦИОННОГО АНАЛИЗА И СПЕКТРОМЕТРИИ $\gamma\gamma$-СОВПАДЕНИЯ:

O. B. Michelsen and E. Steinnes, *Talanta*, 1969, **16**, 1436.

Резюме—Нейтронноактивационный анализ с последующим измерением $\gamma\gamma$-совпадения 9,3 ч ^{152}Eu оказался удачным методом для серийного определения европия в минералах и горных породах. В области концентраций 10–150 мкг г метод является свободным от мешающих других элементов, а эффекти защищания нейтронов не мешают анализу серьезно. Точность метода приблизительно 5%.

ВОЛЬТАМПЕРОМЕТРИЧЕСКОЕ ОКИСЛЕНИЕ АНТРАХИНОНОВ В АЦЕТОНИТРИЛЕ И НИТРОМЕТАНЕ:

M. Ashraf and J. B. Headridge, *Talanta*, 1969, **16**, 1439.

Резюме—Исследовано вольтамперометрическое окисление семь антрахинонов до однозаряженных катионов радикалов в ацетонитриле и нитрометане. Вольтамперометрические волны можно использовать для количественного определения антрахинонов. В этих растворителях бензохиноны, нафтохиноны и фенантрахиноны не окисляются.

Determination of fluoride in potable waters by ion-exchange and potentiometric titration: T. S. LIGHT, R. F. MANNION and K. S. FLETCHER III, *Talanta*, 1969, **16**, 1441. (Research Center, The Foxboro Company, Foxboro, Massachusetts, U.S.A.)

Summary—A procedure is described for the accurate titration of fluoride at the 1 mg/l. level in potable water. The procedure employs an ion-exchange step for concentration of fluoride and removal of interfering ions, and Th(IV) as titrant. Precision and relative error of the method are both 1 %.

An improved apparatus for continuous carrier-free ionophoresis: W. PREETZ and H. L. PFEIFER, *Talanta*, 1969, **16**, 1444. (Institut für Analytische Chemie und Radiochemie der Universität des Saarlandes, Saarbrücken, Germany.)

Summary—An apparatus is described which achieves constant transverse flow of electrolyte by means of hydrostatic regulation of the flow-rate from selected capillaries. The absence of pumps and mechanical control devices reduces both the expense and the possibility of failure. The apparatus is particularly suitable for the separation of temperature-sensitive compounds.

Selective complexometric determination of mercury, using thiourea as masking agent: RAJINDER PAL SINGH, *Talanta*, 1969, **16**, 1447. (Department of Chemistry, Punjabi University, Patiala-4, India.)

Summary—A method is described for selective complexometric determination of mercury, thiourea being used as masking agent. An excess of EDTA is added and the surplus EDTA is back-titrated with lead nitrate, with Xylenol Orange or Methylthymol Blue as indicator (pH 5–6). Thiourea is then added to decompose the mercury–EDTA complex and the liberated EDTA is again back-titrated with lead nitrate. The interference of various cations has been studied.

ОПРЕДЕЛЕНИЕ ФТОРИДА В ПИТЬЕВОЙ ВОДЕ МЕТОДОМ ИОННОГО ОБМЕНА И ПОТЕНЦИОМЕТРИЧЕСКОГО ТИТРОВАНИЯ:

T. S. Light, R. F. Mannion and K. S. Fletcher III, *Talanta*, 1969, **16**, 1441.

Резюме—Описана процедура для точного титрования фторида при концентрации I мг/л в питьевой воде. Процедура основана на концентрировании фторида и удалении мешающих ионов с использованием ионного обмена и титровании с Th(IV). Точность метода и относительная ошибка равны 1%.

УСОВЕРШЕНСТВОВАННЫЙ ПРИБОР ДЛЯ НЕПРЕРЫВНОГО ИОНОФОРЕЗА БЕЗ НОСИТЕЛЯ:

W. Preetz and H. L. Pfeifer, *Talanta*, 1969, **16**, 1444.

Резюме—Описан прибор которым можно получать непрерывный поперечный поток электролита путем гидростатическойо регуляции скорости потока из отбранных капилляров. Отсутствие насосов и механических регуляторов снижает расходы и возможность появления недостатков. Прибор является особенно пригодным для разделения термосенсибильных веществ.

СЕЛЕКТИВНОЕ КОМПЛЕКСОНОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ РТУТИ С ИСПОЛЬЗОВАНИЕМ ТИОМОЧЕВИНЫ В КАЧЕСТВЕ МАСКИРУЮЩЕГО АГЕНТА:

Rajinder Pal Singh, *Talanta*, **16**, 1447.

Резюме—Описан метод селективного комплексонометрического определения ртути с использованием тиомочевины в качестве маскирующего агента. Раствору добавляют избыток ЭДТА который оттитрируют нитратом свинца, с ксиленолоранжевым или метилтимоловым синим в качестве индикатора (pH 5–6). Затем добавляют тиомочевину для разрушения комплекса ртути с ЭДТА и выделенный ЭДТА снова оттитруют с нитратом свинца. Изучено влияние разных катионов.

Journal of Inorganic and Nuclear Chemistry

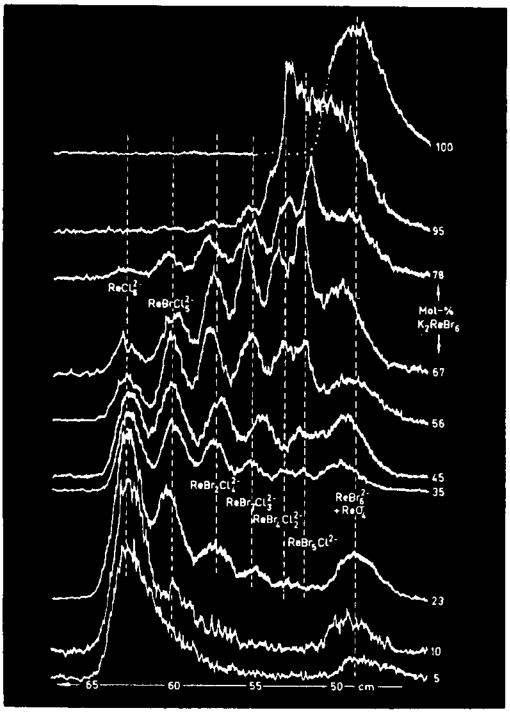
Editors

J. J. Katz *Argonne National Laboratory Illinois USA*
A. G. Maddock *University Chemical Laboratory Cambridge England*
C. B. Amphlett *Atomic Energy Research Establishment Didcot England*
J. H. van Santen *Philips Research Laboratories Eindhoven The Netherlands*

Published Monthly

The Journal of Inorganic and Nuclear Chemistry provides an international medium for communication in the broad areas of inorganic and nuclear chemistry, including synthetic and structural inorganic chemistry, co-ordination chemistry, kinetics and mechanisms of inorganic reactions, nuclear properties and reactions.

This monthly journal publishes original research papers, both experimental and theoretical in the inorganic field. Emphasis is primarily on such topics as new compounds and reactions, structures, solution complexes, reaction mechanisms, preparation and application of stable and radioactive isotopes, including the fission products and the actinide elements.



Manuscripts are accepted in English, French or German. Short communications are published on the basis of originality, interest and timeliness. All papers should be directed to a chemical audience, and chemical aspects and principles should be emphasised.

A companion to this journal is Inorganic and Nuclear Chemistry Letters, with Joseph J. Katz as the editor-in-chief. This journal provides a medium for the very prompt communication of papers in the same areas of inorganic and nuclear chemistry.

A selection of papers from Volume 31 Issue 8

A. C. RUTENBERG and J. S. DRURY Chemical fractionation of uranium isotopes
V. V. SAVANT and C. C. PATEL Diphenyl sulphoxide complexes of some oxocations
E. E. FLAGG and D. L. SCHMIDT Some fluoroalanes and related intermediates
JUDITH KITCHENS and J. L. BEAR A study of some rhodium (II) acetate adducts
K. H. KHOO and J. D. MURRAY Saturated salt solutions–II. Ion pair formation between thallium (I) and nitrate in the presence of bromate and alkali metal ions

Please write for free inspection copies of these two journals together with a cumulative index

Pergamon Press

OXFORD · NEW YORK · LONDON · PARIS · SYDNEY

7/69

Volume 16, No. 10 October 1969

Contents

Presentation of Belcher Honour Issue and Fifth Talanta Medal I

The Louis Gordon Memorial Award VII

T.N.Dobbelstein and H.Diehl: A membrane electrode for nitrate and other univalent anions 1341

G.Knapp und H.Spitzy: Untersuchungen zur Optimierung der Reaktionsbedingungen für die katalytische Jodwirkung auf das System Ce(IV)-arsenige Säure (Eine modifizierte Sandell-Kolthoff-Reaktion) 1351

G.Knapp und H.Spitzy: Eine Apparatur zur automatischen Jodbestimmung im Nanogrammbereich 1361

Y.Dutt, R.P.Singh and M.Katyal: Metal complexes with tropolones 1369

W.Ibrahim Awad and S.S.M.Hassan: Microdetermination of nitrates and nitramines—I. Titrimetric methods based on the reduction with iron(II), titanium(III), and a mixture of both . . 1383

W.Ibrahim Awad and S.S.M.Hassan: Microdetermination of nitrates and nitramines—II. Gasometric methods based on reduction with mercury, iron(II), titanium(III) and hydroquinone . . 1393

G.B.Briscoe and S.Humphries: An investigation of the diethyldithiocarbamates of palladium, including the determination of their stability constants 1403

G.S.Manku, A.N.Bhat and B.D.Jain: Spectrophotometric determination of osmium(IV), iridium(IV) and platinum(IV) and separation and determination of palladium(II) and ruthenium(III) in the presence of other platinum metals, with oximidobenzotetronic acid as reagent 1421

Short Communications

G.S.Manku, A.N.Bhat and B.D.Jain: Rapid spectrophotometric determination of cobalt after extraction using oximidobenzotetronic acid 1431

É.Buzágh-Gere and L.Erdey: Precipitation of manganese ammonium phosphate from homogeneous solution 1434

O.B.Michelsen and E.Steinnes: Determination of europium in minerals and rocks by neutron activation and $\gamma\gamma$-coincidence spectrometry 1436

M.Ashraf and J.B.Headridge: Voltammetric oxidation of anthraquinones in acetonitrile and nitromethane 1439

T.S.Light, R.F.Mannion and K.S.Fletcher, III: Determination of fluoride in potable waters by ion-exchange and potentiometric titration 1441

W.Preetz and H.L.Pfeiffer: Eine verbesserte Apparatur zur kontinuierlichen trägerfreien Durchflussionophorese 1444

Rajinder Pal Singh: Selective complexometric determination of mercury, using thiourea as masking agent 1447

Papers Received i

Publications Received iii

Summaries for Card Indexes . . . .

Talanta Annual Subscription Rates (including postage)

$10 (£3.10.)—*Bona fide* students

$90 (£36)—Multiple-reader institutions

Private individuals whose departmental libraries subscribe, may obtain this Journal for their personal use at a reduced rate of $15 (£5.5.) per annum.

Printed in Northern Ireland at The Universities Press, Belfast