An International Journal of Analytical Chemistry

ταλαντα

talanta

The Title Section, Contents List, Author and Subject Indexes to Vol. 17, Nos. 1–6 are included in this issue

PERGAMON PRESS
OXFORD · LONDON · NEW YORK · PARIS
1970 VOLUME 17, NO. 6 JUNE

pergamon press

MICROANALYSIS BY THE RING OVEN TECHNIQUE
Second Edition
H. WEISZ

This second enlarged and revised edition deals with the ring oven technique which, although originally developed as a qualitative separation technique for extremely minute samples, has now found wide applications in different branches of analytical chemistry. Full details of apparatus, methods and their application and possibilities for future development are given.
172 pp 60s

PERIODATE OXIDATION OF DIOL AND OTHER FUNCTIONAL GROUPS: ANALYTICAL AND STRUCTURAL APPLICATIONS
G. DRYHURST

A summary of the chemistry of organic periodate oxidations. It covers the historical developments of the reaction since its discovery to the present state of knowledge and includes brief outlines of important preparations, physical properties and uses of periodates as well as a large number of well tried and recommended analytical methods.
194 pp 70s

THE DETERMINATION OF ORGANIC PEROXIDES
R. M. JOHNSON and I. W. SIDDIQI

This monograph brings together the analytical chemistry and the corresponding analytical methods for organic peroxide analysis. Chemical and instrumental methods are covered, including column, paper, thin-layer and gas chromatography.
132 pp 50s

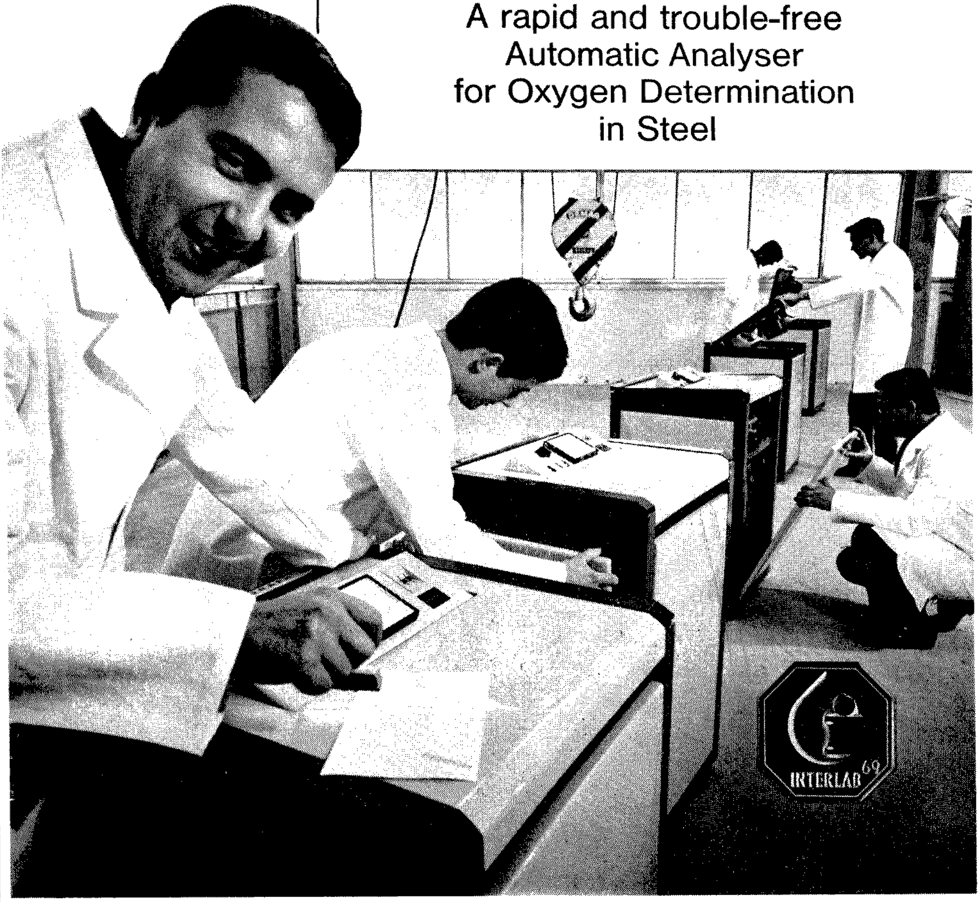
THE DETERMINATION OF CARBOXYLIC FUNCTIONAL GROUPS
R. D. TIWARI and J. P. SHARMA

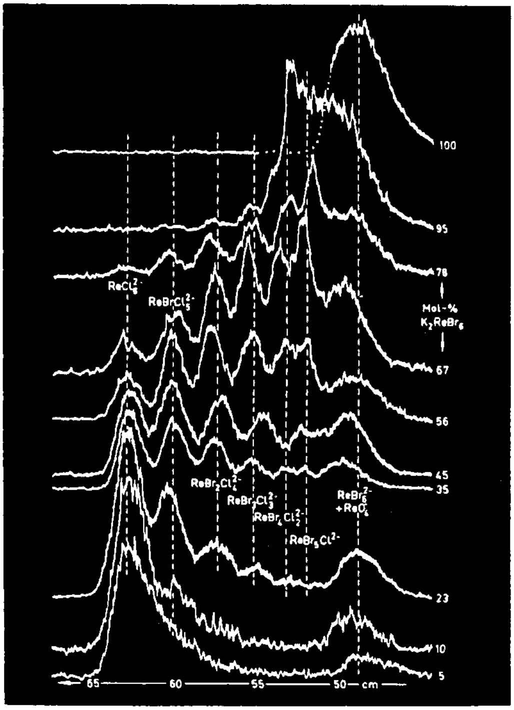
This book covers important methods, both chemical and physical, for the determination of carboxylic acids and their derivatives on macro, semimicro, micro and submicro scales. It includes methods which cover almost all types of compounds containing the carboxylic and other functions and emphasis has been laid on methods which will be useful in routine analytical work.
144 pp 60s

ANALYTICAL CHEMISTRY IN SPACE
RICHARD E. WAINERDI

Basic engineering considerations and analytical chemistry methodology related to performing meaningful measurements in the space environment are covered in this book. Such measurements include the analysis of interplanetary space and the surface analysis of the moon and other planetary bodies. A special aspect of this book includes the miniaturization of analytical experiments and their incorporation into space vehicles.
284 pp 140s

For further details of these or other books
from Pergamon Press, please write to:
College Department, Pergamon Press Ltd.,
Headington Hill Hall, Oxford.

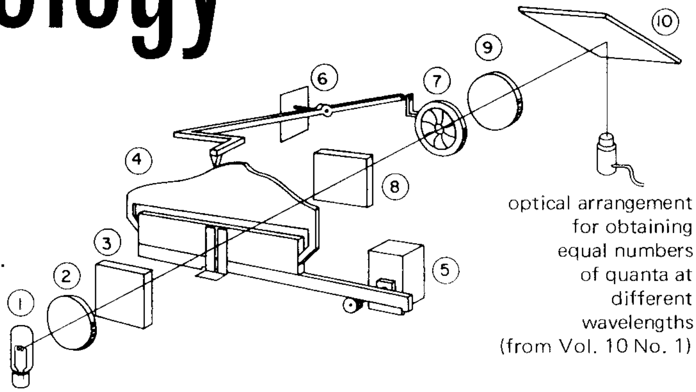

INTERLAB 69



$ReCl_6^{2-}$
$ReBrCl_5^{2-}$
$ReBr_2Cl_4^{2-}$
$ReBr_3Cl_3^{2-}$
$ReBr_4Cl_2^{2-}$
$ReBr_5Cl^{2-}$
$ReBr_6^{2-}$ + ReO_4^-
100
95
78
Mol-%
K_2ReBr_6
67
56
45
35
23
10
5
65
60
55
50 cm

Photochemistry and Photobiology

EXECUTIVE EDITOR
Kendric C. Smith
Department of Radiology
Stanford University
School of Medicine
Stanford, California, U.S.A.



optical arrangement
for obtaining
equal numbers
of quanta at
different
wavelengths
(from Vol. 10 No. 1)

This is an established journal concerned with every aspect of photochemistry and photobiology. Its especial interests lie in the fields of the photochemistry of biological materials and related substances, the action of infrared, visible and ultraviolet light biological systems, and particularly with the quantum aspects of these subjects.

Photochemistry and Photobiology is internationally alert and carries up-to-date information on research and conferences in these sciences. Occasionally the proceedings of international Symposia are published. These have covered such subjects as: Chlorophyll Metabolism, Molecular Mechanisms in Photobiology, Chemiluminescence, Photomorphogenesis and Photosensitization in Solids. Additional features of Photochemistry and Photobiology include a tabulation of papers published in other journals which are relevant to photobiology, especially photosynthesis, and descriptions and reviews of new books. Invited review articles on various areas of photochemistry and photobiology are also published from time to time.

Amongst the papers published in a recent issue are:

B.J. BARNHART and S. H. COX: Recovery of Haemophilus influenzae *from ultraviolet and X-ray damage.*

E. BEN-HUR and I. ROSENTHAL: Photosensitized splitting of pyrimidine dimers

V.A. BELYAKOV and R.F. VASSIL'EV: Chemiluminescence in hydrocarbon oxidation in solution. A quantitative study of the excitation and emission steps

Copies of the special conference issues and all back issues of Photochemistry and Photobiology are always available.

Published monthly (2 Volumes a year)

Write now for free inspection copy and full subscription rates

Pergamon Press
OXFORD · NEW YORK · TORONTO · SYDNEY · BRAUNSCHWEIG

1/70

Gas Chromatography

L. Szepesy CSc.

Editor, English translation:
E.D.Morgan BSc, MA, DPhil, FRIC.

An authoritative source of information on many special techniques and uses of gas chromatography. Fundamentals and theory are discussed where necessary for a working knowledge in the applications of the theoretical equations. Essential information on column types and packings, and column operation, as well as special techniques, covers the latest developments, giving useful suggestions and a great many references for practical application.

592 01238 7 372 pages 95 illustrations **100s**

Available from leading booksellers or:

The Butterworth Group
88 Kingsway London WC2B 6AB

chemistry

The 1970 sectional list is available.
Write to

Dept. ED.
Pergamon Press Ltd
Headington Hill Hall
Oxford OX3 0BW
England

THE PERGAMON TRANSLATION SERVICE offers:

translation of
scientific papers
industrial promotion literature
from and into any language
artwork ready for camera
typesetting
printing

for information please contact:

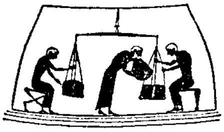
Pergamon Press Ltd
Translation Service
Mrs Shelley
Pergamon House
348-350 Gray's Inn Road
London WC1
Tel: 01-837 6484

or

Pergamon Press Incorporated
Fairview Park
Elmsford
New York 10523
USA

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

Annual Subscription Rates (including postage)

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

Publishing Offices

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

Copyright © 1970 Pergamon Press Ltd.

ห้องสมุด กรมวิทยาศาสตร์

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 importan 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 pap short communications and reviews are refereed in the normal manner. Preliminary communications a refereed urgently and accorded priority in publication. Correspondence of interest to analytical chemi 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 Spectroscop
Spectrochimica Acta, Part B: Atomic Spectroscopy
Tetrahedron
Tetrahedron Letters
Water Research

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

Talanta, 1970, Vol. 17, pp. 443 to 454. Pergamon Press. Printed in Northern Ireland

END-POINT EVALUATION IN INSTRUMENTAL TITRIMETRY—II

CONFIDENCE INTERVALS IN EXTRAPOLATION OF LINEAR TITRATION CURVES

PAVEL JANDERA
Department of Analytical Chemistry
STANISLAV KOLDA
Department of Mathematics
and
STANISLAV KOTRLÝ®
Department of Analytical Chemistry, College of Chemical Technology, Pardubice, Czechoslovakia

(*Received* 11 *August* 1969. *Accepted* 10 *December* 1969)

Summary—The random titration error has been evaluated by single linear regression analysis of both linear branches of titration curves. As a simplification the confidence interval of a titration is estimated by substituting divergent linear confidence limits for the curved confidence limits of both branches of the curve. The influence of the angle between both branches upon the confidence interval of a titration has also been evaluated. The procedure has been proved advantageous by applying it to several amperometric and photometric titrations of lead and by comparing the results with those obtained by the complementary approach of Liteanu and Cörmös, and by the usual statistical treatment of end-points obtained by graphical extrapolation. The method allows a critical consideration of the experimental conditions with regard to the desired level of precision.

THE WIDESPREAD development and application of linear titration curves *e.g.*, photometric, amperometric, *etc.*, has made it necessary to study the attainable precision and accuracy of end-point evaluation.

The usual graphical procedure of linear end-point extrapolation based on linear segments of titration curve has been considered by many to be inadequate. Boulad[1] has proposed a simple calculation of the end-point which is taken as the intersection point of two straight lines, each being defined by two points before and beyond the equivalance point, respectively. Another simplified end-point evaluation has been developed by Lydersen[2] for conductometric titrations. As the ratio of the slopes of two adjacent branches of the titration curve is constant for a given titration system, the first branch of the titration curve can be characterized by a single point and the other one is represented by a straight line calculated by the method of least squares. In a series of papers, Liteanu and his co-workers[3–7] have shown the advantage of using single linear regression analysis of both linear segments of the titration curve. The end-point is calculated as the intersection point of both regression lines,[3,4] and the slope difference is also useful for the purpose.[7] The elimination of points with a suspiciously large deviation has been also discussed.[5] To evaluate an end-point confidence interval of a single titration (*cf.*, ref. 6), parallel linear confidence limits are substituted for the curved borders of confidence belts along the regression lines. The importance of having a sufficient number of experimental points has also been

---

* Part I—*Talanta*, 1970, **17**, 151.

stressed and the influence of the angle between both linear branches upon the confidence interval of a titration has been demonstrated by three experimental titration curves.[6]

One drawback to these contributions lies in the evident lack of experimental data necessary to check the influence of various sources of random experimental error in instrumental titrimetry. It has been difficult, therefore, to judge the validity of the conclusions reached.

In this paper a new simplifying approach to the evaluation of the confidence interval of a single titration is given. The results of a detailed study of random errors in a series of amperometric and photometric titrations, which is the subject of the next paper of this series,[8] are partially presented here to allow comparison of various approaches to the analysis of titration error and to illustrate the influence of the angle between both branches of the titration curve.

DERIVATION OF EQUATIONS

List of symbols

A_0, A_0' A_1, A_1'	Coefficients of estimated regression lines
c	Analytical (molar) concentration
$K =$	$s_{A_1}t - s_{A_1}'t'$; auxiliary symbol, equation (19)
$K_{\bar{x}} =$	$s_{A_1}t\bar{x} - s_{A_1}'t'\bar{x}'$; auxiliary symbol, equation (19)
n, n'	Numbers of pairs of experimental values x_i, y_i and x_i', y_i' respectively
s_{A_1}, s_{A_1}'	Estimates of standard deviation of the slope values A_1 and A_1' respectively
s_{yx}, s_{yx}'	Estimates of standard deviation characterizing the distribution of y_i values either side of the estimated regression line
t, t'	Statistical *Student's* t-value taken from the Table for $n - 2$ or $(n' - 2)$ degrees of freedom and confidence level α
x, x'	Measured volumes of titrant
x_e	Consumption of titrant at end-point
Δx_e	Confidence interval of the end-point
x_i, x_i'	Experimental values of the measured volume of titrant
x_k	Chosen volume of the titration reagent
$\bar{x}, \bar{x}'$	Arithmetic means from the appropriate set of volume readings
x_{e_1}, x_{e_2}	Values limiting the confidence interval of the end-point
y, y'	Quantities of determinand
y_i, y_i'	Experimental values for the quantity of determinand
y_k	Actual value of the quantity of determinand corresponding to the value of x_k
$\tilde{y}_k$	Value of the quantity of determinand calculated for x_k, using the regression line
Δy_k	Confidence interval for y_k about the value of $\tilde{y}_k$
$\bar{y}, \bar{y}'$	Arithmetic means of all experimental values of y_i or y_i' respectively
α	Statistical confidence level
γ	Angle between linear branches of a titration curve

Note—The unprimed symbols refer to the branch before the equivalence point, the primed symbols refer to the branch of the curve beyond the equivalence point.

Statistical approaches to estimation of the confidence interval of a single titration

The random titration error is characterized by a confidence interval within which the end-point of a single titration can be found, at a certain probability level. The relation between the error in the measured values x_i, y_i, which are used for the end-point extrapolation, and the appropriate confidence interval, can be solved by single linear regression analysis on the assumption that for each of the fixed values x_i there is a distribution of the variates y_i which follows a normal Gaussian law. The variance of these distributions is constant and the average values of the distributions lie on the regression line.

For every actual value of x_k the corresponding confidence interval for y at a confidence level α is given by (*cf.* ref. 9)

$$\Delta y_k = 2ts_{yx}\sqrt{\frac{1}{n} + \frac{(x_k - \bar{x})^2}{\sum\limits_{i=1}^{n}(x_i - \bar{x})^2}}, \tag{1}$$

expressing the spread either side of the value $\tilde{y}_k$ calculated from the expression for the estimated regression straight line[9] $\tilde{y}_k = A_0 + A_1x_k$ before the equivalence point.

Similarly, the branch of the titration curve beyond the equivalence point can be characterized by the straight line $\tilde{y}_k = A_0' + A_1'x_k$ with the corresponding confidence interval

$$\Delta y_k = 2t's_{yx}'\sqrt{\frac{1}{n'} + \frac{(x_k - \bar{x}')^2}{\sum\limits_{i=1}^{n'}(x_i - \bar{x}')^2}}. \tag{2}$$

The values of *Student's t* are found in the statistical tables for a chosen probability, $(1 - \alpha)100\%$, and for the degrees of freedom $n - 2$, $n' - 2$, respectively.

The estimates of standard deviations corresponding to the distribution of the y-values either side of both regression lines are given by the expressions

$$s_{yx} = \sqrt{\frac{\sum\limits_{i=1}^{n}(A_0 + A_1x_i - y_i)^2}{n - 2}} \tag{3}$$

$$s_{yx}' = \sqrt{\frac{\sum\limits_{i=1}^{n'}(A_0' + A_1'x_i - y_i)^2}{n' - 2}}. \tag{4}$$

The confidence intervals form confidence belts with curved borders along both extrapolation straight lines (curves 1–4 in Fig 1). The geometrical interpretation of the confidence interval of a particular titration is also illustrated in Fig. 1. It would be possible to calculate its value as a difference between the outer intersects of the confidence limits, $x_{e_2} - x_{e_1}$. It is more convenient, however, to solve this problem by simplified models of confidence limits.

Liteanu and Cörmös have tried to find a suitable simplification by considering the confidence belts as limited by parallel straight lines at a distance of $\pm ts_{yx}$ or $\pm t's_{yx}'$ from both regression straight lines $\tilde{y} = A_0 + A_1x$, or $\tilde{y} = A_0' + A_1'x$, respectively, which is a rather subjective choice. The solution of the regression lines yields the expression for the end-point

$$x_e = \frac{A_0 - A_0'}{A_1' - A_1}. \tag{5}$$

The range of the confidence interval of the end-point, Δx_e, is limited by the confidence limits of x_{e_2} and x_{e_1},[6]

$$\Delta x_e = |x_{e_2} - x_{e_1}| = 2\frac{ts_{yx} + t's_{yx}'}{|A_1' - A_1|}. \tag{6}$$

A certain drawback to the method of parallel confidence limits consists in neglecting

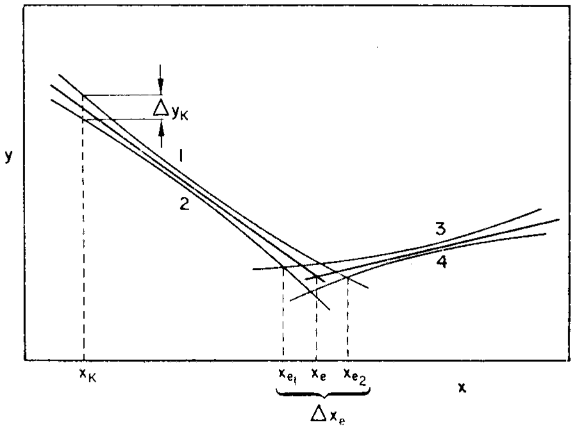


FIG. 1.—Theoretical shape of confidence belts along extrapolated branches of a titration curve.
Δy_k denotes the confidence interval for an actual value y_k either side of the calculated value $\tilde{y}_k$.

the curvatures of the theoretical confidence belts (*cf.* Fig. 1) which may be pronounced in the middle part of the branch and close to the equivalence point.

This problem can be solved by another simplifying approach which will be presented here. The two confidence limits of the confidence belts are also assumed to be linear, but they are drawn through the mean point on the regression line, defined by $\bar{x}$, $\bar{y}$, where

$$\bar{x} = \sum_{i=1}^{n} x_i/n \tag{7}$$

$$\bar{y} = \sum_{i=1}^{n} y_i/n. \tag{8}$$

If it is assumed that the values of the only random variable y are normally distributed for each x, the confidence intervals of the slope values are represented by

$$\langle A_1 - ts_{A_1};\ A_1 + ts_{A_1} \rangle \tag{9}$$

$$\langle A_1' - t's_{A_1}';\ A_1' + t's_{A_1}' \rangle \tag{10}$$

where A_1, A_1' are the estimates of regression coefficients, s_{A_1}, s_{A_1}' are the estimates of standard deviations of the slope values of both regression straight lines, and the *Student's* t, t' values are chosen at the desired confidence level.

The estimates of standard deviations of the slopes are defined as follows

$$s_{A_1} = \frac{s_{yx}}{\sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2}} \tag{11}$$

$$s_{A_1}' = \frac{s_{yx}'}{\sqrt{\sum_{i=1}^{n'} (x_i - \bar{x}')^2}}. \tag{12}$$

The inherent assumption of this model consists in defining borders of confidence

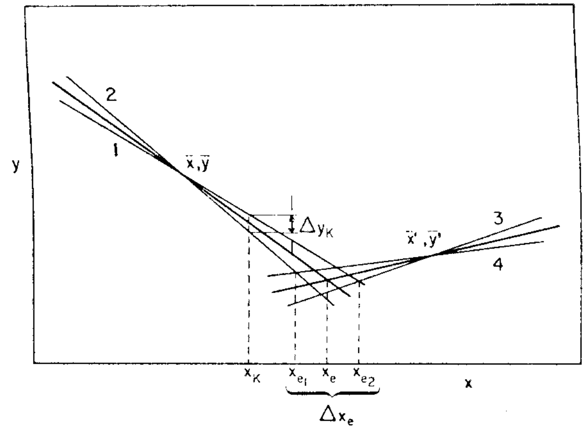


FIG. 2.—Model of divergent linear confidence limits along the extrapolated branches of a titration curve.
The linear confidence limits are given by: *1*—equation (13); *2*—equation (14); *3*—equation (15); *4*—equation (16).

belts as straight lines with slopes given by the confidence limits of the slopes of both regressions lines. It can easily be shown that these limits are identical with the asymptotes of the hyperbolically shaped borders of the confidence belts on both branches of the titration curves. Thus, the equations for the limits in Fig. 2 are obtained

$$y = A_0 - ts_{A_1}\bar{x} + x(A_1 + ts_{A_1}) \quad \text{(straight line No. 1)} \qquad (13)$$

$$y = A_0 + ts_{A_1}\bar{x} + x(A_1 - ts_{A_1}) \quad \text{(straight line No. 2)} \qquad (14)$$

$$y = A_0' - t's_{A_1}'\bar{x}' + x(A_1' + t's_{A_1}') \quad \text{(straight line No. 3)} \qquad (15)$$

$$y = A_0' + t's_{A_1}'\bar{x}' + x(A_1' - t's_{A_1}') \quad \text{(straight line No. 4)} \qquad (16)$$

The end-point of a titration to be evaluated can be calculated from equation (5) and is found within an interval defined by the intersect x_{e_2} of the straight line limits Nos. 1 and 3 and by the intersect x_{e_1} of the limits Nos. 2 and 4 (Fig. 2).

By solving the appropriate equations we obtain

$$x_{e_2} = \frac{A_0 - ts_{A_1}\bar{x} - A_0' + t's_{A_1}'\bar{x}'}{A_1' + t's_{A_1}' - A_1 - ts_{A_1}} \qquad (17)$$

$$x_{e_1} = \frac{A_0 + ts_{A_1}\bar{x} - A_0' - t's_{A_1}'\bar{x}'}{A_1' - t's_{A_1}' - A_1 + ts_{A_1}} \qquad (18)$$

Thus, the confidence interval of the titration is given by

$$\Delta x_e = |x_{e_2} - x_{e_1}| = 2\left|\frac{K(A_0 - A_0') + K_{\bar{x}}(A_1 - A_1')}{(A_1 - A_1')^2 - K^2}\right| \qquad (19)$$

where

$$K = s_{A_1}t - s_{A_1}'t'$$

and

$$K_{\bar{x}} = s_{A_1}t\bar{x} - s_{A_1}'t'\bar{x}'.$$

In most practical cases, the values of K^2 in the denominator can be neglected since the value of the other term is greater by at least two orders of magnitude. Equation (19) can be simplified to

$$\Delta x_e = 2\left|\frac{K_{\bar{x}}}{A_1 - A_1'} + \frac{K(A_0 - A_0')}{(A_1 - A_1')^2}\right|. \tag{20}$$

Substituting from equation (5), we obtain the final form of the expression for Δx_e:

$$\Delta x_e = 2\left|\frac{s_{A_1}t(x_e - \bar{x}) + s_{A_1}'t'(\bar{x}' - x_e)}{A_1' - A_1}\right|. \tag{21}$$

Factors influencing the confidence interval of a titration

Besides the uncertainty in the measurement of variables, *e.g.*, the readings of the titrant volume and the physicochemical quantity taken for indication of the end-point, other important factors determine the level of the titration error, *viz.* the angle between both linear branches of the titration curve, the number of experimental points and their distribution upon the titration curve.

The influence of the angle upon the confidence interval of the titration can be shown, if the slope value of the regression line before equivalence is calculated, using expressions for the tangent of γ.

In the case of parallel confidence limits we thus obtain

$$\Delta x_e = 2\,\frac{ts_{yx} + t's_{yx}'}{1 + (A_1')^2}\,|A_1' - \operatorname{cotan}\gamma|. \tag{22}$$

For the divergent linear limits the following expression can be written:

$$\Delta x_e = 2\left|\frac{[K(A_0 - A_0')(1 - A_1'\tan\gamma) + K_{\bar{x}}(1 + (A_1')^2)\tan\gamma](1 - A_1'\tan\gamma)}{[1 + (A_1')^2]^2\tan^2\gamma}\right|. \tag{23}$$

The symbols K and $K_{\bar{x}}$ were defined above [equation (19)].

TABLE I.—COMPARISON OF PRECISION IN SERIES OF AMPEROMETRIC TITRATIONS OF LEAD

Concentrations, M			Confidence intervals† Δx_e, μl		Statistical treatment of 10 end-points evaluated, by	
Lead	EDTA	$\lvert A_1' - A_1\rvert$*	Parallel limits	Divergent limits	graphical extrapolation Δx_e, μl	linear regression Δx_e, μl
$1{\cdot}50 \times 10^{-4}$	10^{-2}	0·747	19·2	18·7	8·7	11·7
$0{\cdot}75 \times 10^{-4}$	5×10^{-3}	0·407	24·6	28·9	27·8	30·2
$0{\cdot}60 \times 10^{-4}$	4×10^{-3}	0·332	26·7	27·5	31·0	29·9
$0{\cdot}30 \times 10^{-4}$	2×10^{-3}	0.181	35·6	34·8	39·6	50·5

* Expressed in galvanometer scale units per μl of titrant.
† Mean of 5 values calculated.

The dependence of the confidence interval of titration upon the angle γ is illustrated by the data in Tables I and II and in Figs. 3 and 4. If the slope of the branches beyond the equivalence point is low, an approximation $|A_1' - A_1| \approx -\tan\gamma$ can be accepted. The effect of the angle expressed as the slope difference $|A_1' - A_1|$ can be seen in Figs. 3 and 4, which also allow comparison of the ranges of confidence intervals obtained by various approaches. Further, the horizontal short lines denote

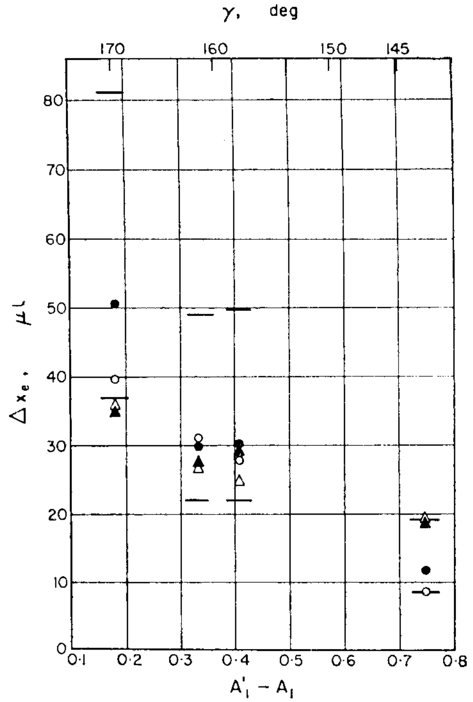


FIG. 3.—Comparison of confidence intervals of amperometric titrations of lead. The confidence intervals were evaluated from: ○, extrapolated end-points; ●, calculated end-points; △, mean value of 5 individual values obtained by the approach of parallel confidence limits; ▲, mean value of 5 individual values obtained by the approach of divergent confidence limits.

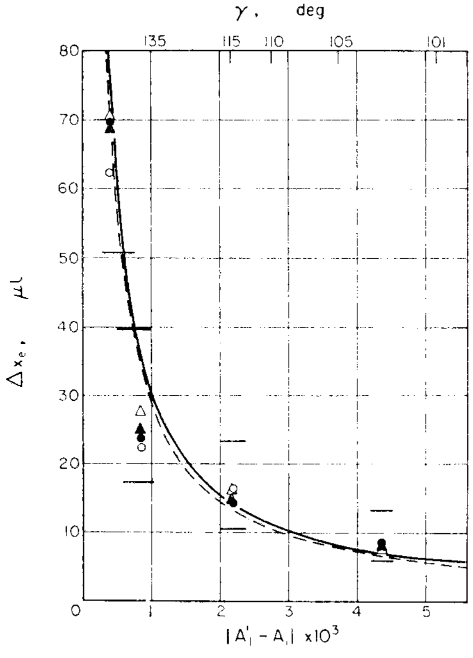


FIG. 4.—Comparison of confidence intervals of photometric titrations of lead. Full line represents the relationship according to equation (6), the dashed line according to equation (21). The legend for the points is the same as for Fig. 3.

TABLE II.—COMPARISON OF PRECISION IN SERIES OF PHOTOMETRIC TITRATIONS OF LEAD

Concentrations, M		$\lvert A_1' - A_1 \rvert$* $\times 10^3$	Confidence intervals† Δx_e, μl		Statistical treatment of 10 end-points evaluated, by	
Lead	EDTA		Parallel limits	Divergent limits	graphical extrapolation Δx_e, μl	linear regression Δx_e, μl
$1{\cdot}50 \times 10^{-5}$	10^{-3}	4·35	8·2	7·2	7·7	8·0
$0{\cdot}75 \times 10^{-5}$	5×10^{-4}	2·18	15·7	15·4	15·7	14·2
$0{\cdot}30 \times 10^{-5}$	2×10^{-4}	0·844	27·5	25·1	22·6	23·8
$0{\cdot}15 \times 10^{-5}$	10^{-4}	0·396	70·5	68·6	62·4	69·6

* Expressed in units of absorbance per μl of titrant.
† Mean of 5 calculated.

the limits where an actual value of confidence interval is found with a 90% probability. The calculation was based upon the $2ts$ estimates found by statistical treatment of the calculated end-points [equation (5)] of all titrations involved in one series. A double-sided confidence interval for the actual value of variance was taken into consideration. The χ-square distribution was employed and it was assumed that there is an equal probability in both directions of a deviation exceeding the calculated value of the confidence interval.

The values of the confidence intervals were calculated on the basis of data obtained by statistical treatment of a series of ten titrations which were evaluated either by graphical end-point extrapolation or by calculation using equation (5). The shift of estimates of Δx_e towards the lower limits can be attributed to the shape of the $(\chi)^2$ distribution. These confidence intervals can be compared with the average values of five intervals which were calculated for every single titration by both procedures indicated above. The individual confidence intervals which were obtained by all treatments studied are mostly found within the limits indicated, despite the perceptible differences especially at higher levels of experimental error. In Fig. 4, where the values of the confidence intervals of photometric titrations of lead are shown, a theoretical curve is traced showing the dependence of the confidence interval upon the difference in the slope values of both branches. The full line is for the approach with parallel confidence limits [equation (22)] and the dashed line is for the case of divergent linear limits [equation (23)]. For the evaluation of these functions the mean values of all four series of titrations were taken, *i.e.*, $s_{yx} = 3{\cdot}62 \times 10^{-3}$; $s_{yx}' = 2{\cdot}26 \times 10^{-3}$; $s_{A_1} = 2{\cdot}79 \times 10^{-5}$; $s_{A_1}' = 2{\cdot}68 \times 10^{-5}$. There is no appreciable difference between both theoretical curves, and the results of all the studied ways of treating experimental data are distributed close to these curves.

The range of the confidence interval depends also upon the number of experimental points employed for the computation of the regression lines. This factor can be seen from the general expressions for the confidence limits given by equations (1) and (2). The higher the numbers of experimental pairs n or n', the lower are the values of the discriminants, and the confidence belts become narrower. Consequently, the range of the confidence interval of titration is also narrower. This factor can also be illustrated by equation (21) for the divergent limits, since a greater number of variates accounts for lower values of the estimated standard deviation of the slopes, s_{A_1} and s_{A_1}'. The number of experimental pairs exerts an influence even upon the *Student's t* and t' values which are decreasing rapidly with increasing degrees of freedom.[9] To obtain a sufficient precision, it is usually necessary to take 6 or 8 pairs of readings at least for each of the extrapolation straight lines.[6] A greater number of experimental pairs does not lead to a more significant increase in precision.

Equation (21) for Δx_e in case of divergent confidence limits shows that the precision is increased for such an arrangement, when the set of experimental pairs being represented by the mean values of $\bar{x}$ or $\bar{x}'$, respectively, is situated sufficiently close to the equivalence point. This is counteracted by the requirement that the expressions $[\sum (x_i - \bar{x})^2]^{1/2}$ or $[\sum (x_i - \bar{x}')^2]^{1/2}$, respectively, should reach maximum values. An optimum arrangement satisfying both requirements is obtained for a case with gradually increasing density of experimental points on the linear part of the branch approaching the equivalence point.

EXPERIMENTAL

To study the random titration error lead was determined by two linear, instrumental methods, namely, photometric and amperometric titration with EDTA. Conditions were deliberately arranged so as to exaggerate the confidence intervals.

Apparatus

Polarograph. An LP55 model polarograph (Laboratory Instruments, Prague) was used in conjunction with a precise scale galvanometer.

Spectrophotometer. A Zeiss Spekol spectrophotometer was modified for spectrophotometric titrations.

Burette. A home-made syringe burette of 3–500 μl capacity was used. It was calibrated by weighing water delivered under medicinal paraffin. For 25 deliveries of 100 μl the standard deviation was 0·3 μl.

Procedures

Amperometric titrations. The mercury dropping electrode was used as indicating electrode in combination with a mercury pool as reference electrode. The applied potential difference was chosen so that the mean value of the limiting current was proportional to the unreacted lead ion concentration. The solution to be titrated (20 ml, ammonium tartrate buffer, pH = 8·5) was stirred and an inert atmosphere was maintained by passing a stream of nitrogen after each addition of titrant. The readings of the current oscillations were taken to evaluate the mean value (for details see ref. 8).

Photometric titrations. Xylenol Orange was used as indicator.[10] The titrations were carried out in a volume of 20 ml and the absorbance at 550 nm was measured. A titration curve with linear branches was obtained. The range of the linear segments of the curve depends upon the amount of indicator added and upon the pH value, pH = 5 being optimum.

In all titrations studied the experimental conditions were arranged so that the titration error was affected only by errors in the measured quantity and in measurement of the additions of the titrant. All other possible sources of error were carefully eliminated. All volumetric glassware was calibrated. The standard deviation for delivery from a 10-ml pipette was 0·002 ml, for example.

In all instrumental titrations 8–10 readings were taken on each branch of the titration curve, the sequence of the additions of titrant being even and identical within the series. In Fig. 5, one of the amperometric titration curves of $1{\cdot}5 \times 10^{-4}M$-lead chloride with $10^{-2}M$ EDTA is shown. The shape of the theoretical confidence belts can be compared with the simplified shapes of confidence belts obtained by both the treatments discussed. All details of our experiments and of the approaches used for an independent study of errors of all variables involved are given in Part III.[8]

The end-points of all these titrations were evaluated by graphical extrapolation and by the approach based upon single linear regression [equation (5)]. A programme for an electronic computer ODRA 1013 was developed to allow the rapid computation of the end-point and of its confidence interval by both procedures discussed.

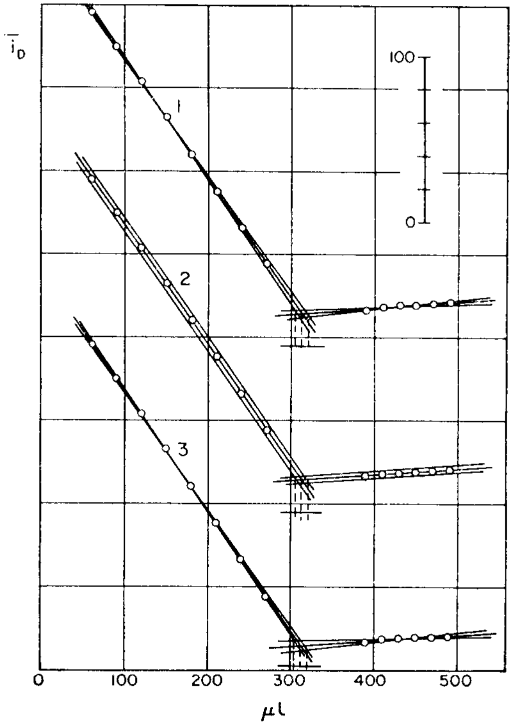


FIG. 5.—Evaluation of an amperometric titration of lead.
A 25-ml portion of $1{\cdot}5 \times 10^{-4}M$ $PbCl_2$ was titrated with $10^{-2}M$ EDTA. The confidence belts are limited by: *1*—theoretical borders resulting in single linear regression; *2*—parallel linear limits; *3*—divergent linear limits. The confidence intervals of the end-points are shown below each titration curve.

CONCLUSIONS

The analysis of the results obtained revealed that the end-point calculation based upon single linear regression leads to somewhat more accurate results than the common procedure of graphical end-point extrapolation.

The confidence intervals of tested instrumental titrations, calculated by both approaches, assuming either linear parallel confidence limits or linear divergent limits, are in good agreement with the results of the statistical treatment of the end-point data of each series. Under the experimental conditions studied both simplified approaches are capable of expressing the random spread of points on the linear branches of a titration curve. In these cases both linear simplifications of confidence belt borders sufficiently approached the hyperbolically curved theoretical limits near the equivalence point. Considering linear divergent limits, the greater the absolute values of the differences $|x - \bar{x}|$ and $|x - \bar{x}'|$, the better is the approach of the asymptotes to the curved limits. In our titrations, the y-values of the theoretical borders and of the asymptotes were approximately equal or deviated within 10% of the corresponding Δy_k value. As can be seen from the data summarized in Tables I and II, the divergent confidence limits approach can yield results which are in even closer accord with the data obtained by the statistical treatment of the end-point values.

From the practical point of view, both procedures for the evaluation of confidence intervals can be used to anticipate the level of random titration error from the experimental points of only one titration. In such a way, the optimum experimental conditions can be easily chosen to keep the titration error within desired limits.

The approaches studied also offer the possibility of a quantitative evaluation of some factors influencing the precision of instrumental titration. Besides the obvious requirement of a satisfactory level of precision in the measurements of both variables, there is an important effect of the value of the angle between both branches of the titration curve, or more explicitly, of the extent of the change in physical quantity per unit of the titration reagent added.

The study of the approach with divergent linear confidence limits pointed out the importance of the distribution of experimental points on the linear portions of both branches of the curve. For a higher precision to be obtained the density of readings should increase to a certain extent towards the equivalence point.

The use of computers for the analysis of titration error by the approaches discussed can eliminate the tedium of involved computations and offer further possibilities for a deeper study. Thus, a more reliable use of various methods of instrumental titrations could be achieved.

Zusammenfassung—Der zufällige Titrationsfehler wurde durch einmalige lineare Regressionsanalyse beider linearer Äste von Titrationskurven ermittelt. Zur Vereinfachung wird der Vertrauensbereich einer Titration durch Einsetzen divergenter linearer Vertrauensgrenzen beider Äste der Kurve abgeschätzt. Auch der Einfluß des Winkels zwischen beiden Ästen auf den Vertrauensbereich einer Titration wurde ermittelt. Die Vorteile des Verfahrens wurden durch Anwendung auf mehrere amperometrische und photometrische Titrationen von Blei nachgewiesen. Die Ergebnisse wurden mit solchen verglichen, die nach dem Komplementärverfahren von Liteanu und Cörmös sowie durch die übliche statistische Verarbeitung von graphisch extrapolierten Endpunkten gewonnen wurden. Das Verfahren erlaubt eine kritische Betrachtung der experimentellen Bedingungen im Hinblick auf die gewünschte Genauigkeit.

Résumé—On a évalué l'erreur de titrage fortuite par analyse de régression linéaire simple des deux branches des courbes de titrage. Dans un but de simplification, l'intervalle de confiance d'un titrage est estimé en substituant les limites de confiance linéaires divergentes aux limites de confiance incurvées des deux branches de la courbe. On a aussi évalué l'influence de l'angle entre les deux branches sur l'intervalle de confiance d'un titrage. On à démontré que la technique est avantageuse en l'appliquant à plusieurs titrages ampérométriques et photométriques du plomb et en comparant les résultats à ceux obtenus par l'approximation complémentaire de Liteanu et Cörmös, et par le traitement statistique usuel des points de fin de dosage obtenus par extrapolation graphique. La méthode permet une considération critique des conditions expérimentales par rapport au niveau de précision désiré.

REFERENCES

1. J. H. Boulad, *Bull. Soc. Chim. France*, 1936, 408.
2. P. L. Lydersen, *Z. Anal. Chem.*, 1966, **218**, 161.
3. C. Liteanu and D. Cörmös, *Talanta*, 1960, **7**, 18.
4. C. Liteanu and D. Cörmös, *Acta Chim. Acad. Sci. Hung.*, 1961, **27**, 9.
5. C. Liteanu, *Rev. Chim. Acad. Rep. Populaire Roumaine*, 1962, **7**, 291.
6. C. Liteanu and D. Cörmös, *Rev. Roumaine Chim.*, 1965, **10**, 361.
7. C. Liteanu and E. Hopirtean, *Studia Univ. Babes-Bolyai, Ser. Chem.*, 1966, **11**, 135; *Chem. Abstr.*, 1967, **66**, 25720*k*.

8. S. Kotrlý, P. Jandera and S. Kolda, *Sb. věd. prací, Vysoká škola chem.-technol., Pardubice,* 1970 **II, 23,** 3.
9. C. A. Bennett and N. L. Franklin, *Statistical Analysis in Chemistry and Chemical Industry,* p. 229. Wiley, New York, 1954.
10. S. Kotrlý and J. Vřešťál, *Collection Czech. Chem. Commun.*, 1960, **25**, 1148.

Talanta, 1970, Vol. 17, pp. 455 to 463. Pergamon Press. Printed in Northern Ireland

PREPARATIVE GAS CHROMATOGRAPHY OF VOLATILE METAL COMPOUNDS—I

SEPARATION OF ALUMINIUM, CHROMIUM AND IRON β-DIKETONATES

R. BELCHER, C. R. JENKINS, W. I. STEPHEN and P. C. UDEN
Department of Chemistry, The University of Birmingham, P.O. Box 363,
Birmingham, England

(*Received* 24 *April* 1969. *Revised* 15 *October* 1969. *Accepted* 10 *December* 1969)

Summary—The analytical gas chromatography of a range of fluorinated and unfluorinated β-diketonates of aluminium, chromium and iron has been studied in detail and conditions have been established for their complete separation; the complexes of trifluoroacetylpivaloylmethane show the best characteristics for this purpose. A range of liquid phases and column conditions have been considered and Apiezon substrates have been shown to give optimal resolution. The technique has been extended to a preparative scale with up to 0·1-g chelate samples, and the efficiency of the process demonstrated by the removal of 2% proportions of two metal complexes from a sample of the third. Implications of the technique for the purification of metals are discussed.

THE APPLICATION of preparative gas chromatography to the purification of metals as their volatile derivatives offers great possibilities, for this technique has a high separatory efficiency. However, developments in this field have been restricted both by the lack of volatility and by the high reactivity of many inorganic compounds. Analytical gas chromatographic separations of many β-diketonates are now well documented,[1] and although preparative separations have not yet been reported, the production of pure metal compounds by this method appears feasible. The β-diketonates are most attractive in this respect as many of them have both high volatility and thermal stability,[2] they are formed by a wide range of metals, often by quantitative extraction of the metal ion with the β-diketone,[3,4] and unlike many other metal compounds, they require no special handling techniques. We now report the first preparative gas chromatographic separation of metal complexes of this type.

Gas chromatographic separations of metal β-diketonates have usually been studied by injection of small samples onto short columns of low liquid phase loading. The aims of the work described in this paper were first to devise an optimal set of conditions for the complete resolution of a mixture of metal β-diketonates on the analytical scale, and secondly to increase sample size and adapt column parameters to a preparative scale with a view to purification of one complex by removal of others.

The aluminium, chromium and iron derivatives of a wide range of β-diketones were chosen for the initial examination. Several analytical separations of aluminium and chromium,[5,6] and aluminium and iron trifluoroacetylacetonates[7,8] have previously been achieved, but a complete separation of the chromium and iron complexes of the same β-diketone has not been reported. Sievers[9] claims a partial separation of the trifluoroacetylacetone derivatives of these metals on a polyethylene wax substrate, but the peaks are ill-defined and base-line return is incomplete. The separation of complexes with very similiar volatilities is often made more difficult by the existence of asymmetrical peaks and low column efficiencies, which are the result of undesirable column interactions.

In the work described in this paper, particularly good separations and minimization of undesirable column interactions were obtained with complexes of perfluoroalkanoylpivaloylmethanes. Previously published studies of these complexes have been mainly concerned with rare earth complexes,[10,11,12] and metal heptafluorobutanoylpivaloylmethanates.[13]

EXPERIMENTAL

General nomenclature

The following nomenclature is used for description of the β-diketonates. The abbreviations refer to the enolate ion used in the formation of the metal complex.

Pentane-2,4-dione (acetylacetone), AA
1,1,1-Trifluoropentane-2,4-dione (trifluoroacetylacetone), TFA
2,2,6,6-Tetramethylheptane-3,5-dione (dipivaloylmethane), DPM
1,1,1-Trifluoro-5,5-dimethylhexane-2,4-dione (trifluoroacetylpivaloylmethane), TPM
1,1,1,2,2-Pentafluoro-6,6-dimethylheptane-3,5-dione (pentafluoropropanoylpivaloylmethane), PPM
1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyloctane-4,6-dione (heptafluorobutanoylpivaloylmethane), HPM

Reagents

Acetylacetone was obtained commercially. Trifluoroacetylacetone was prepared by the Claisen condensation of ethyltrifluoroacetate and acetone with sodium methoxide; dipivaloylmethane and its fluorinated analogues by the condensation of the appropriate esters and ketones with sodium hydride.

The aluminium, chromium and iron complexes were synthesized by the addition of the stoichiometric quantity of the β-diketone dissolved in ethanol, to an aqueous solution of the metal ion. The resultant solution was either buffered with sodium acetate or its pH was adjusted to *ca.* 7 by the addition of $4M$ ammonia solution. The precipitated metal chelate was filtered off, dried, and purified by sublimation under reduced pressure. The TPM complexes appeared initially as oils but solidified after standing for a few days.

For the preparative gas chromatographic studies the complexes were prepared from "Specpure" chromium metal, iron sesquioxide and hydrated aluminium chloride (Johnson, Matthey and Co.). All possible precautions were taken to exclude the introduction of any foreign ions during these preparations.

Gas chromatography—analytical separations

The Varian Aerograph Autoprep 700 fitted with a katharometer detector was used as a conventional analytical gas chromatograph. The injection port and detector block temperatures were maintained from 10 to 20° higher than that of the column, and a mixture of hydrogen and nitrogen (1:3 v/v) was used as the carrier gas. Samples (0–50 μl of 5 or 10% w/v solutions of the chelates in chloroform) were introduced into the glass-lined injection port of the apparatus with a microsyringe. A Pye "series 104" chromatograph equipped with a flame ionization detector was also used, samples (0–10 μl of 1000 or 2000 ppm solutions of the chelates in chloroform) being introduced directly on to the column.

Phase Separations Ltd. supplied the column packing materials and the Pye 104 columns were obtained pre-coiled. Before coating the celite supports were treated successively with $4M$ hydrochloric acid, water, $2M$ sodium hydroxide, water and methanol, and were then silaned with hexamethyldisilazane in petroleum ether, and coated by standard methods. The only exceptions to this treatment were the Universal B supports which were used as obtained, already coated. The procedure for the coating of Teflon with a liquid phase was that given by Kirkland.[14]

The following columns were used to obtain the analytical results.

(1) 0·46 m × 0·6 cm Cu, 5% SE-30 on PhaseSep N (60–80 mesh) (Autoprep)
(2) 1·8 m × 0·6 cm Cu, 10% SE-30 on PhaseSep N (60–80 mesh) or Chromosorb G (60–80 mesh) (Autoprep)
(3) 1·5 m × 0·6 cm glass, 10% SE-30 on PhaseSep N (60–80 mesh) (Pye 104)
(4) 1·8 m × 0·6 cm Cu, 10% SE-30 on Teflon (Autoprep)
(5) 1·8 m × 0·6 cm Cu, 10% Apiezon M on PhaseSep N (60–80 mesh) (Autoprep)

(6) 3·05 m × 0·6 cm Cu, 10% Apiezon L on Universal B (60–80 mesh) (Autoprep)
(7) 1·8 m × 0·6 cm Cu, 10% Diethylene glycol adipate (DEGA) on Chromosorb G (60–80 mesh) (Autoprep)

Gas chromatography—preparative separations

The Varian Aerograph Autoprep 700 was used as a preparative chromatograph combining automatic injection and collection systems, so that a single separation was continually repeated. The eluates were collected in liquid-air-cooled bottles supplied for the instrument. The column used was a 6·1 m × 9·5 mm aluminium tube packed with 15% Apiezon L on Universal B (44–60 mesh), supplied by Jones Chromatography and Co.

Universal B is a support material manufactured by Phase Separations Ltd., which has characteristics similar to a flux-calcined diatomite but is extremely inert, showing almost complete suppression of the adsorptive effect. This support proved greatly superior to white supports such as Chromosorb W or PhaseSep N (Phase Separations Ltd.) and also the alkaline surface support Chromosorb G. Universal B as purchased was found to have characteristics superior to PhaseSep N and Chromosorb G and W even after these had been subjected to successive acid and alkaline washes and hexamethyldisilazane treatment. It is largely to the use of this support that may be attributed the considerable improvement in resolution on both analytical and preparative columns. Pre-treatment of Universal B before coating did not produce better results than those obtained by using the ready-coated support as purchased.

TABLE I.—MAJOR FEATURES OF THE MASS SPECTRA OF THE ALUMINIUM, CHROMIUM AND IRON TRIFLUOROACETYLPIVALOYLMETHANATES

m/e	Ion	
612	$[Al(TPM)_3]^{+\cdot}$	$(M)^{+\cdot}$
555	$[Al(TPM)_3 - C(CH_3)_3]^+$	$(M - 57)^+$
543	$[Al(TPM)_3 - CF_3]^+$	$(M - 69)^+$
417	$[Al(TPM)_2]^+$	$(M - 195)^+$
367	$[Al(TPM)_2 - CF_2]^+$	$(M - 245)^+$
241	$(TPM\text{-}Al\text{-}F)^+$	$(M - 371)^+$
191	$[(TPM\text{-}Al\text{-}F) - CF_2]^+$	$(M - 421)^+$
637	$[Cr(TPM)_3]^{+\cdot}$	$(M)^{+\cdot}$
580	$[Cr(TPM)_3 - C(CH_3)_3]^{+\cdot}$	$(M - 57)^+$
442	$[Cr(TPM)_2]^+$	$(M - 195)^+$
385	$[Cr(TPM)_2 - C(CH_3)_3]^+$	$(M - 252)^+$
247	$[Cr(TPM)]^+$	$(M - 390)^+$
641	$[Fe(TPM)_3]^{+\cdot}$	$(M)^{+\cdot}$
584	$[Fe(TPM)_3 - C(CH_3)_3]^+$	$(M - 57)^+$
446	$[Fe(TPM)_2]^+$	$(M - 195)^+$
389	$[Fe(TPM)_2 - C(CH_3)_3]^+$	$(M - 252)^+$
377	$[Fe(TPM)_2 - CF_3]^+$	$(M - 264)^+$
251	$[Fe(TPM)]^+$	$(M - 390)^+$

The sample solution for the preparative separation of equal quantities of the metal TPM complexes was prepared by dissolving 0·4 g each of $Al(TPM)_3$, $Cr(TPM)_3$ and $Fe(TPM)_3$ in 6 ml of chloroform.

The sample solution for the separation of $Cr(TPM)_3$ from 2% $Al(TPM)_3$ and 2% $Fe(TPM)_3$ was prepared by dissolving $Cr(TPM)_3$ (2·88 g), $Al(TPM)_3$ (0·06 g) and $Fe(TPM)_3$ (0·06 g) in 15 ml of chloroform.

The gas chromatographic conditions used for each preparative separation were as follows:

sample: 0·5-ml injection
column temperature: 160–162°
injection temperature: 170°
detector temperature: 170–175°
collector temperature: 175–180°
filament current: 145 mA
attenuation: ×2
hydrogen/nitrogen flow-rate: 133 ml/min (30 psig).

Mass spectrometry

An A.E.I. M.S.9 double focusing mass spectrometer with direct injection probe was used in the characterization of eluates by means of the metal–$(TPM)_3^+$ and metal–$(TPM)_2^+$ ions. The major features of the mass spectra are given in Table I.

Emission spectrographic analysis

A Hilger-Watts large quartz spectrograph, with a high frequency plasma torch as the emission source,[15] was used to analyse the eluates from the preparative column. Chloroform solutions of the chelates were aspirated directly into the plasma.

RESULTS AND DISCUSSION

Analytical separations

The gas chromatographic behaviour of the aluminium, chromium and iron complexes of some fluorinated and unfluorinated β-diketones was studied on the analytical scale for two main reasons; to discover which complexes were potentially suitable for preparative scale elution by virtue of volatility and stability, and to find the conditions for quantitative separation of all three metals (which necessitated investigation of the interactions that occurred between the complexes and the chromatographic column). In general large samples of the complexes were injected into columns containing fairly high liquid phase loadings in order to approximate to preparative gas chromatographic conditions.

Unfluorinated β-diketonates. The major limitation in the gas chromatography of unfluorinated β-diketonates is their low volatility. Thus even if adequate separations could be obtained, the high column temperatures would certainly lead to decomposition on preparative columns. This prediction was confirmed for a mixture of the aluminium, chromium and iron acetylacetonates. All were eluted unchanged at 160° from column (1), but at the temperature of *ca.* 200° needed for their elution from column (2) breakdown of both the aluminium and iron complexes was indicated.

Almost complete separation was obtained for a mixture of the three metal dipivaloylmethanates from column (1) at 170° but retention times were similar to those of the acetylacetonates and no elution of discrete peaks could be obtained on longer columns.

Trifluoroacetylacetonates. The considerable increase in volatility afforded by fluorinated β-diketonates shows greater promise for preparative separations provided that adequate resolution can be achieved. Thus aluminium, chromium and iron trifluoroacetylacetonates were eluted individually from column (2) at 150° with retention times of 5½, 10 and 10½ min respectively.

However, despite variation of chromatographic parameters, complete resolution of the chromium and iron peaks was not achieved. This failure was attributed in part to adsorption effects which have been discussed by Veening and Huber[16] and by Uden and Jenkins.[17] These adverse characteristics appeared particularly severe for the trifluoroacetylacetonates but were greatly reduced for the perfluoroalkanoylpivaloylmethanates.

Trifluoroacetylpivaloylmethanates, pentafluoropropanoylpivaloylmethanates and heptafluorobutanoylpivaloylmethanates. The chromatography of chelates of these ligands with aluminium, chromium and iron was evaluated in the hope that they would show a combination of the favourable characteristics of the chelates containing tertiary butyl groups and of the enhanced volatility of the fluorinated β-diketonates.

Results obtained with silicone gum columns showed this hope to be partially realized. Improved separation was found between chromium and iron TPM complexes when compared with the trifluoroacetylacetonates but complete return to baseline could not be obtained. The use of PTFE support material [column (4)] reduced column efficiency to such an extent that no separation at all was observed.

It seemed possible that the PPM and HPM complexes might have shorter retention times and permit use of lower column temperatures, [Fe(TPM)$_3$ and Cr(TPM)$_3$ sublime at 58–62°/0·6 mbar; Fe(PPM)$_3$, Cr(PPM)$_3$, Fe(HPM)$_3$ and Cr(HPM)$_3$ sublime at 40–45°/0·6 mbar], but no reduction in retention time was found and resolution of the chromium and iron chelates was poorer. The elution pattern remained constant with variation of liquid phase loading, column and injection temperatures and increased sample size. Retention data are given in Table II and show the decrease in separation with increasing fluoroalkyl chain length.

TABLE II.—RETENTION TIMES OF THE ALUMINIUM, CHROMIUM AND IRON β-DIKETONATES ON SILICONE GUM RUBBER SE-30 [COLUMN (3) AT 160°C]

Sample	Ret. time, *min*	Sample	Ret. time, *min*	Sample	Ret. time, *min*
Al(TFA)$_3$	$3\frac{1}{2}$	Cr(TFA)$_3$	$6\frac{1}{2}$	Fe(TFA)$_3$	8
Al(TPM)$_3$	$11\frac{2}{3}$	Cr(TPM)$_3$	$16\frac{3}{4}$	Fe(TPM)$_3$	22
Al(PPM)$_3$	13	Cr(PPM)$_3$	$16\frac{3}{4}$	Fe(PPM)$_3$	19
Al(HPM)$_3$	$16\frac{1}{2}$	Cr(HPM)$_3$	21	Fe(HPM)$_3$	23

TABLE III.—RETENTION TIMES OF THE ALUMINIUM, CHROMIUM AND IRON β-DIKETONATES ON APIEZON M [COLUMN (5) AT 159°C]

Sample	Ret. time, *min*	Sample	Ret. time, *min*	Sample	Ret. time, *min*
Al(TFA)$_3$	$3\frac{1}{2}$	Cr(TFA)$_3$	$6\frac{3}{4}$	Fe(TFA)$_3$	$7\frac{1}{2}$
Al(TPM)$_3$	9	Cr(TPM)$_3$	$14\frac{1}{4}$	Fe(TPM)$_3$	$20\frac{1}{2}$
Al(PPM)$_3$	8	Cr(PPM)$_3$	$10\frac{1}{2}$	Fe(PPM)$_3$	$12\frac{3}{4}$
Al(HPM)$_3$	8	Cr(HPM)$_3$	$9\frac{3}{4}$	Fe(HPM)$_3$	$11\frac{1}{2}$

A considerable change was noted with Apiezon columns. It appeared that interaction with the chelates was much smaller than for the silicone gum rubber columns.[13] Table III gives the retention data for an Apiezon column.

The order of elution on the Apiezon column corresponded to ease of sublimation, and retention times were shorter than on the silicone gum column. The decrease in interaction with the liquid phase led to a marked improvement in the resolution of the chromium and iron peaks although the separation again deteriorated with increasing length of the fluorocarbon chain. Completely resolved peaks were obtained for the chromium and iron TPM complexes and it was found that further improvement in peak shape and reduction in retention time were attained by using a column of Apiezon L coated on Universal B support [column (6)].

It was concluded that preparative separations could best be performed with the TPM complexes on a column with a high loading of Apiezon L on Universal B.

Preparative separations

The effect of increasing the column dimensions and sample size was first investigated. An increase in peak resolution was obtained when an analytical scale injection was made into the preparative column (6·1 m × 9·5 mm aluminium, 15% Apiezon L on Universal B); $3\frac{1}{2}$ min now separated the peaks instead of the 2 min on the 3·05-m column (6). The complexes could be eluted with reasonable retention times from the 6·1-m column at temperatures as low as 160°. Figure 1 shows that separation was still good when larger samples were injected (0·5 ml), containing equal weights (33 mg) of each complex.

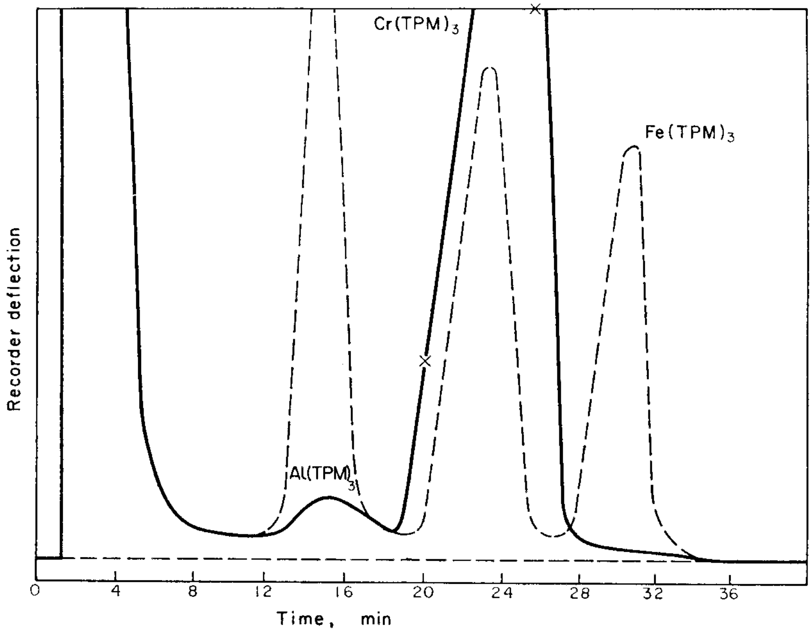


FIG. 1.—Chromatogram of the preparative separation of Cr(TPM)$_3$ from 2% Al(TPM)$_3$ and 2% Fe(TPM)$_3$. [– – – – – – – chromatogram of the separation of equal amounts (33 mg) of each chelate]

Sample: 0·1 g of total chelate injected. Column: 6·1 m × 9·5 mm Al, 15% Apiezon L on Universal B (44–60 mesh). Column temp. 162°C. Hydrogen/nitrogen flow-rate: 133 ml/min.

An attempt was then made to separate the chromium TPM complex from 2% w/w each of the aluminium and iron TPM complexes. A total of 0·1 g of mixed complexes was injected automatically in 0·5-ml portions with a syringe operated by an air piston. A small peak corresponding to the aluminium complex was observed in addition to the main chromium–TPM peak (Fig. 1) but the katharometer did not detect any iron complex. On comparing the chromatogram with that obtained in the earlier separation, it was assumed that either the iron had been eluted after the chromium peak but not detected, or it had been retained or decomposed on the column. Since the analysis of the collected chromium chelate showed very low levels of iron impurity, the assumption that the iron chelate was not emerging from the column in any considerable quantity during the collection period seems justified. Furthermore these low levels suggest that any iron possibly present as an impurity in the support material was not being leached out to any measurable extent.

No detectable quantity of iron complex could be trapped out between the end of the predicted position of the iron peak and the beginning of the next collection period. Nevertheless, as a general rule, a time lapse of some 5 min was allowed between the end of the chromium peaks and the reactivation of the injection cycle, thus giving a total time lapse of about 25 min between chromium collection periods.

By successive automatic injection 1 g of chromium trifluoroacetylpivaloylmethanate was collected in a bottle cooled in liquid air; this collection took place during the time between the crosses marked on the peak in Fig. 1. The aluminium, chromium and iron TPM complexes have melting points (60–80°) which are much lower than those of the corresponding complexes of most other β-diketones. These complexes, once molten, can be extensively supercooled and resolidify very slowly.

During the first few collection cycles the chromium complex was trapped out relatively poorly in the liquid-air cooled trap, remaining there as oil, recovery over the first five injections being about 45 %. Subsequently as solidification of the complex began, collection efficiency improved markedly, rising to over 80 % after 25 injections. Overall recovery for 1 g of collected complex was about 65 %. Improved trapping techniques, perhaps employing initial seeding of the trap with crystals of the complex or using an absorbing medium, should improve overall efficiency considerably. There was no indication that more than a very small proportion of the chromium complex was lost by adsorption or decomposition on the column.

Purity of the eluates. Chromium TPM complex which had been passed alone through the preparative column, and the chromium complex which had been separated from the aluminium and iron impurities, were analysed by plasma torch emission spectrography. The $Cr(TPM)_3$ passed alone through the column contained 0·055 % $Al(TPM)_3$ and $Fe(TPM)_3$ 0·028 %. The $Cr(TPM)_3$ separated from 2 % $Al(TPM)_3$ and 2 % $Fe(TPM)_3$ contained 0·091 % $Al(TPM)_3$ and 0·027 % $Fe(TPM)_3$. The impurity levels in the original sample of chromium trifluoroacetylpivaloylmethanate were also of this order.

The separation of the chromium complex from the aluminium and iron complexes appears most successful, the added impurity levels being reduced to about those in the original sample. A similar separation of the aluminium TPM complex from 2 % of impurities was attempted with the same preparative column, after the chromium TPM separations. The analysis of the aluminium complex showed that the iron had been effectively removed [less than 0·028 % $Fe(TPM)_3$ remaining] and that most of the chromium had been eliminated [0·28 % $Cr(TPM)_3$]. However, the level of the chromium impurity was higher than would have been expected from the well separated peaks on the chromatogram. As the column was purged in this case for 36 hr before purification of the aluminium complex, the probable explanation for the higher chromium level in the eluate is that a portion of the chromium chelate remained adsorbed or had otherwise interacted with the column material during the chromium purification experiment and was not removed by purging. Passage of the aluminium complex through the column then produced a displacement of the adsorbed chromium species which was then eluted with the aluminium complex. We have commented on this type of behaviour previously[17] for smaller samples where it is more pronounced for iron and aluminium chelates than for chromium chelates. However the much larger quantities of the chromium complex to which the column had been previously exposed in this experiment clearly made this behaviour more pronounced. A further separation, that of the iron trifluoroacetylpivaloylmethanate from 2 % each of the aluminium and chromium complexes was then attempted on the same column after a further lengthy period of purging. The results in this case showed that higher levels of the impurity chelates remained after separation even though resolution appeared good on the chromatogram. The further deterioration could be attributed once again to a build-up of both aluminium and chromium on the column. Better results could certainly be obtained in the latter experiments if fresh columns were used for the purification of each specific chelate. Considerable study must be made of this aspect of the technique in order to maintain high purities for the products.

CONCLUSIONS

The results demonstrate the feasibility of preparative scale separations of metal β-diketonates, even for a pair of metals such as chromium and iron, having complexes with very similar volatilities. The choice of ligand is of major importance to ensure maximal resolution and adequate volatility, while all chromatographic parameters must be fully explored and optimized during preliminary analytical investigations. Adsorption of chelates, a problem which is unlikely to be completely eliminated, suggests that eluates of the highest purity may best be obtained from a column which is used only for the purification of that particular metal complex.

The good purity levels obtained for the chromium complex suggest possibilities for the production of ultrapure metals by preparative gas chromatography. To produce significant amounts of pure metals however, considerable quantities of the complexes must be chromatographed as the proportion of metal in the complexes is low. It seems doubtful whether a batch process such as described here could be scaled up to separate sufficient quantities of complexes in a reasonable time, but studies now proceeding in the use of continuous gas chromatographic techniques may make commercial scale separations possible.

Work has been done by Van Hemert *et al.*[18] and Moshier *et al.*[19] which shows that pure metals may readily be regenerated from fluorinated metal β-diketonates by reduction with hydrogen gas at an elevated temperature.

Born–Haber calculations might be used to predict the relative stabilities of the metal-fluorine bonds formation of which could affect recovery of metals in other preparative applications.

Acknowledgements—The analyses of the eluates by the high-frequency plasma torch method were carried out in conjunction with Mr. S. Greenfield and the staff of the Analytical Research Department, Albright and Wilson Ltd., to whom the authors are indebted. The authors wish to thank Dr. J. R. Majer for his advice on mass spectrometry. One of us (C. R. J.) gratefully acknowledges the receipt of a maintenance grant from the United Kingdom Atomic Energy Authority, Aldermaston.

Zusammenfassung—Die analytische Gaschromatographie einer Anzahl fluorierter und nicht fluorierter β-Diketonate von Aluminium, Chrom und Eisen wurde in ihren Einzelheiten untersucht und die Bedingungen ermittelt, unter denen man vollständige Trennung erreicht. Die Komplexe von Trifluoracetylpivaloylmethan haben in dieser Hinsicht die besten Eigenschaften. Verschiedene flüssige Phasen und Säulenbedingungen wurden in Betracht gezogen; die beste Auflosung ergaben Apiezon-Träger. Das Verfahren wurde auf den präparativen Maßstab mit Chelatproben bis zu 0,1 g ausgedehnt. Die Wirksamkeit dieses Trennprozesses wurde durch Entfernung von 2 prozent-Anteilen zweier Metall-komplexe aus einer Probe des dritten demonstriert. Es werden Folgerungen für die Reinigung von Metallen diskutiert, die sich aus dem Verfahren ergeben.

Résumé—On a étudié en détail la chromatographie en phase gazeuse analytique d'une gamme de β-dicétonates fluorés et non fluorés de l'aluminium, du chrome et du fer et on a établi les conditions de leur séparation complète; les complexes du trifluoracétylpivaloylméthane montrent les meilleures caractéristiques dans ce but. On a considéré gamme de phases liquides et de conditions de colonne et l'on a montré que les substrats à l'Apiezon donnent la résolution optimale. On a étendu la technique à l'échelle préparative avec des échantillons de chélates jusqu'à 0,1 g et l'efficacité de la technique a été démontrée par l'élimination de deux complexes métalliques dans la proportion de 2% d'un échantillon du troisième. On discute des incidences de la technique sur la purification de métaux.

REFERENCES

1. R. W. Moshier and R. E. Sievers, *Gas Chromatography of Metal Chelates*, Pergamon, Oxford, 1965.
2. R. E. Sievers, B. W. Ponder, M. L. Morris and R. W. Moshier, *Inorg. Chem.*, 1963, **2**, 693.
3. G. P. Morie and T. R. Sweet, *Anal. Chem.*, 1965, **37**, 1552.
4. W. D. Ross and R. E. Sievers, *Talanta*, 1968, **15**, 87.
5. R. D. Hill and H. Gesser, *J. Gas Chromatog.*, 1963, **1**, 11.
6. D. K. Albert, *Anal. Chem.*, 1964, **36**, 2034.
7. W. G. Scribner, W. J. Treat, J. D. Weiss and R. W. Moshier, *ibid.*, 1965, **37**, 1136.
8. R. W. Moshier and J. E. Schwarberg, *Talanta*, 1966, **13**, 445.
9. R. W. Moshier and R. E. Sievers, *Gas Chromatography of Metal Chelates*, p. 81. Pergamon, Oxford, 1965.
10. K. J. Eisentraut and R. E. Sievers, *J. Am. Chem. Soc.*, 1965, **87**, 5254.
11. C. S. Springer, Jr., D. W. Meek and R. E. Sievers, *Inorg. Chem.*, 1967, **6**, 1105.
12. K. J. Eisentraut and R. E. Sievers, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1931.
13. R. E. Sievers, J. W. Connolly and W. D. Ross, *J. Gas Chromatog.*, 1967, **5**, 241.
14. J. J. Kirkland, *Anal. Chem.*, 1963, **35**, 2003.
15. S. Greenfield, I. L. Jones and C. T. Berry, *Analyst*, 1964, **89**, 713.
16. H. Veening and J. F. K. Huber, *J. Gas. Chromatog.*, 1968, **6**, 326.
17. P. C. Uden and C. R. Jenkins, *Talanta*, 1969, **16**, 893.
18. R. L. Van Hemert, L. B. Spendlove and R. E. Sievers, *J. Electrochem. Soc.*, 1965, **112**, 1123.
19. R. W. Moshier, R. E. Sievers and L. B. Spendlove, *U.S. Patent* 3,356,527, 1967.

Talanta, 1970, Vol. 17, pp 465 to 473. Pergamon Press. Printed in Northern Ireland

SPECTROPHOTOMETRIC STUDY AND ANALYTICAL APPLICATION OF RARE EARTH TIRON COMPLEXES—I

DETERMINATION OF NEODYMIUM, HOLMIUM AND ERBIUM

TOMITSUGU TAKETATSU and NOBUYO TORIUMI
College of General Education, Kyushu University, Fukuoka, Japan

(*Received* 6 *October* 1969. *Accepted* 22 *December* 1969)

Summary—The absorption spectra of neodymium, holmium and erbium Tiron complexes in aqueous solution have been measured from 340 to 650 nm. The absorbance at the wavelength of maximum absorption band of an aqueous medium containing neodymium (pH 4·5), neodymium (pH 12·0), holmium (pH 5·0) and erbium (pH 5·0) Tiron complexes was about 4 (at 578 nm), 9 (at 571 nm), 9 (at 450 nm) and 5 (at 376 nm) times greater, respectively, than for the same quantities of the corresponding chlorides. The spectrophotometric determination of these elements has been investigated. Combining ratios of Tiron to rare earth have been found to be 3:2 and 2:1.

IN GENERAL, absorption spectra of tervalent rare earth ions in solution are complex and composed of sharp lines which arise from pure electronic transitions within the $4f$ subshell, which is shielded by the $5s$ and $5p$ outer shells from interaction with an ionic field. If the strength of the ionic field surrounding the rare earth ions is sufficient to penetrate the shielding, some absorption bands may be shifted in wavelength and enhanced in sensitivity. Such effects have been observed in the case of formation of chelate compounds.[1–3] Moreover, *O,O*-type ligands seem to be more effective for the enhancement of the sensitivity than *O, N*- and *N,N*-type ligands. Since Yoe first introduced Tiron (disodium 1,2-dihydroxybenzene-3,5-disulphonate), which is one of the *O,O*-type ligands, for the colorimetric determination of titanium and iron,[4] the reagent has been applied to the spectrophotometric determination of cerium,[5] molybdenum,[6] niobium,[7] uranium[8] and scandium.[9]

We have found that a few of the absorption bands of neodymium, holmium and erbium are enhanced remarkably when Tiron is reacted with these metal ions in weakly acidic and alkaline media. In the present paper, we describe the formulae and analytical application of these Tiron complexes.

EXPERIMENTAL

Reagents

Metal ion solutions. Standard solutions of neodymium, holmium and erbium chlorides were obtained by dissolving the 99·9% pure oxides in warm dilute hydrochloric acid and then removing the excess of acid by evaporation. The concentrations of these elements were determined by titration with EDTA, Xylenol Orange being used as the indicator.

Tiron. Tiron obtained from the Dojindo Co. Ltd. Research Laboratories was at least 95% pure and was used without further purification.

All other chemicals used were of analytical-reagent grade.

Procedure

A hydrochloric acid solution containing less than about 20 mg of the metal ions was transferred into a beaker and evaporated to near dryness on a water-bath. The residue was dissolved by adding 2 ml of 0·5*M* Tiron. Then for neodymium, holmium and erbium, 2 ml of 1·0% hexamine solution were added to the solution and the pH of the solution was adjusted to 4·5–5·0 with dilute hydrochloric acid

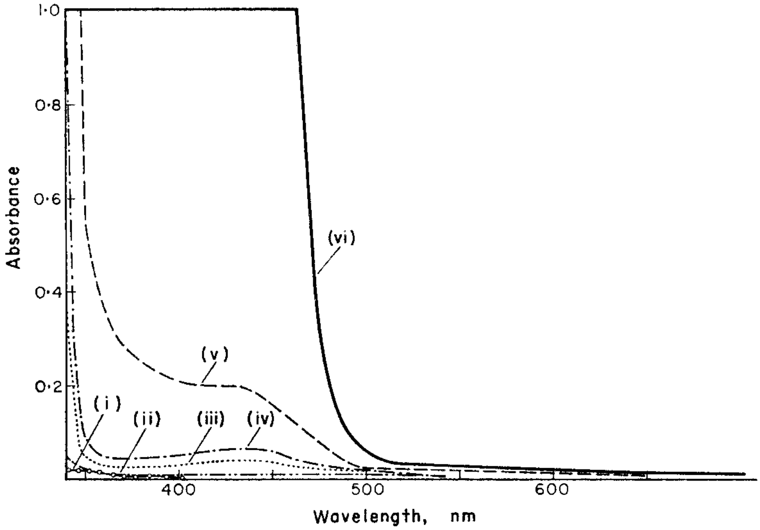


FIG. 1.—Absorption spectra of 0·1M Tiron solutions at various pH values. pH—(*i*) 4·9; (*ii*) 6·2; (*iii*) 7·1; (*iv*) 8·3; (*v*) 10·2; (*vi*) 12·2.

and sodium hydroxide solutions, or for neodymium, the pH was adjusted to 12·0 ± 0·5 with 0·1M sodium hydroxide. Then the solution was transferred to a 10-ml volumetric flask and made up to volume with water. The absorbance for neodymium, holmium and erbium at pH 4·5–5 and for neodymium at pH 12 was measured at 578, 450, 376 and 571 nm respectively. The concentration of the metal ions was obtained graphically from Beer's law plots. Water was used as a reference unless otherwise. All the experiments were carried out at 20–25°.

RESULTS AND DISCUSSION

Absorption spectra of 0·1M Tiron solutions at differing pH were measured between 340 and 650 nm (Fig. 1). With increase of pH, a broad absorption band gradually appears which gives a maximum at about 430 nm. In alkaline medium of pH 12, there is a strong absorption band at wavelengths below about 500 nm. Absorption spectra of aqueous solutions containing neodymium, holmium or erbium and an excess of Tiron were recorded from 340 to 650 nm as a function of pH (Figs. 2–4). The absorbances at the absorption maxima for neodymium Tiron complexes are 4·1 (at 578 nm), 4·0 (at 579 nm) and 8·6 (at 571 nm) times greater than that of the chloride and for holmium and erbium Tiron complexes at pH 5 the absorbances are about 9 (at 450 nm) and 5 (at 376 nm) times greater than those of the corresponding chlorides. Holmium and erbium Tiron complexes in alkaline media were not examined, because the main absorption bands occurred below 500 nm.

Figure 5 shows the variation of absorbance at the maxima of absorption bands for these metal complexes, as a function of pH. The absorption spectra for the neodymium complexes give almost identical patterns in the pH ranges 4·0–5·0 (α-type), 6·0–7·0 (β-type) and 11·5–12·5 (γ-type). The absorbances for holmium and erbium Tiron complexes are almost constant over the pH range 4·5–5·0.

Mole-ratio plots for the reaction at pH 4·5–5·0 gave the ratio of Tiron to lanthanide as 3:2. At pH 7 the same ratio (3:2) was found for Tiron:Nd, but in more alkaline media (pH 12) constant absorbance at 571 nm is not obtained until the mole-ratio of Tiron to neodymium is about 5. The absorption spectrum of the neodymium complex

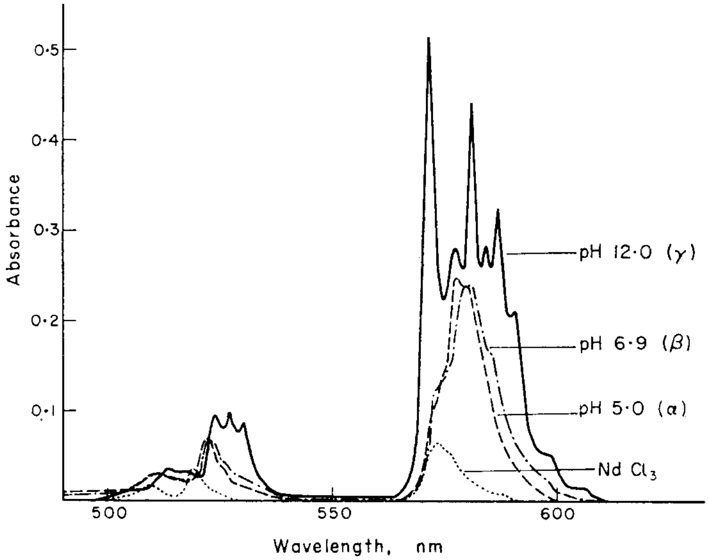


FIG. 2.—Absorption spectra of neodymium Tiron complexes at various pH values. Nd 0·00936M; Tiron 0·1M; measured *vs.* reagent blank.

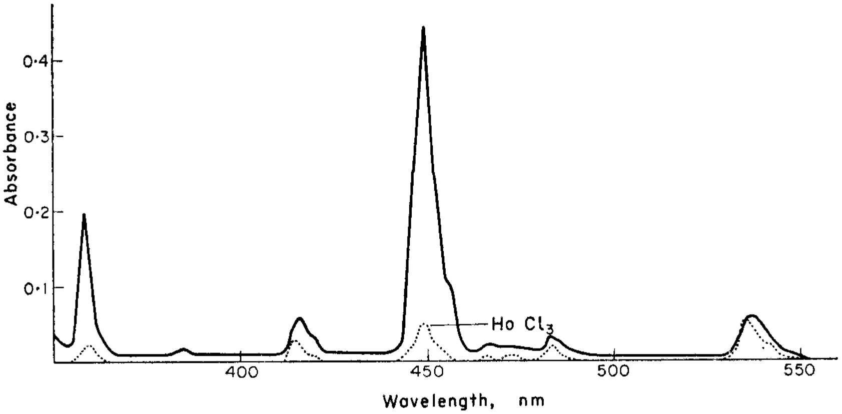


FIG. 3.—Absorption spectrum of holmium Tiron complex at pH 5·0. Ho 0·0125M; Tiron 0·1M.

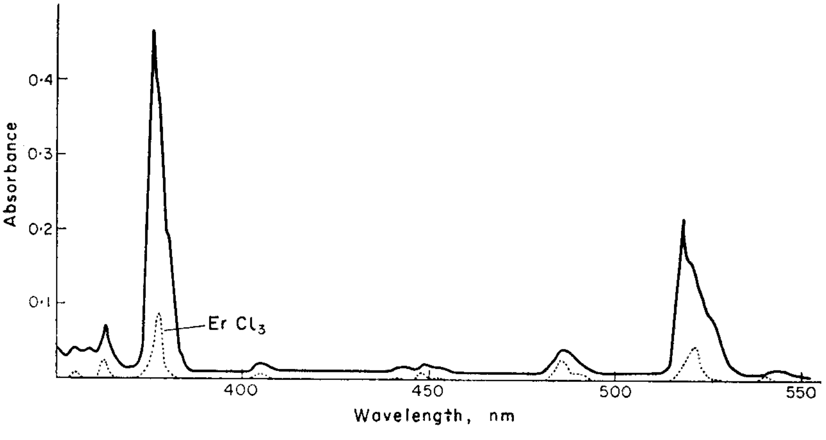


FIG. 4.—Absorption spectrum of erbium Tiron complex at pH 5·0. Er 0·0145M; Tiron 0·1M.

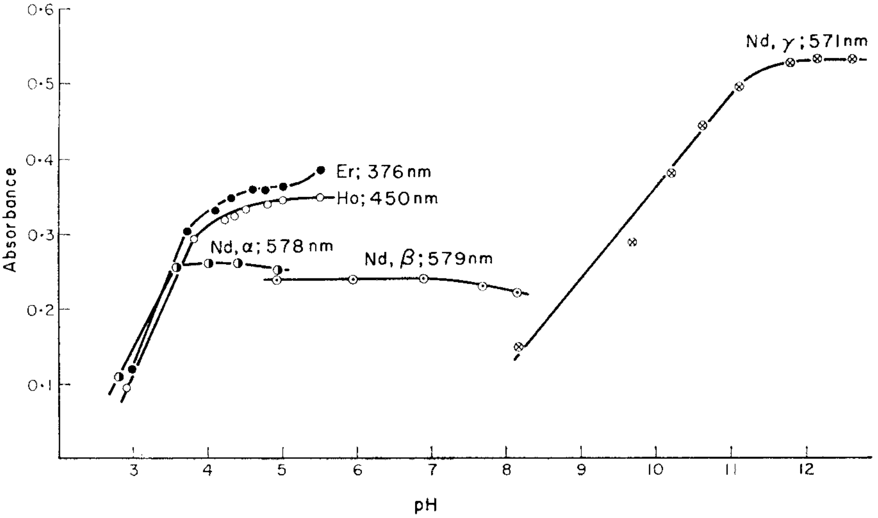


FIG. 5.—Variation of absorbance at the maxima of absorption bands, as a function of pH.

at pH 12 changes in a complicated manner as a function of the mole-ratio of Tiron to neodymium. Even in alkaline media, no hydrolysis of the metal is observed when the mole-ratio Tiron:Nd = 0·5. The spectrum at the mole-ratio Tiron:Nd = 3:2 almost corresponds to that of the β-type shown in Fig. 2. For determination of these metal ions, a tenfold excess of Tiron was taken as the minimum requirement.

The absorption spectra of these Tiron complexes are stable with time, especially in acidic medium. Even in alkaline medium (pH 12) the absorption bands of the neodymium Tiron complex remained constant for 24 hr, though the absorbance slightly increased because of a change in the absorption band of the reagent.

The systems follow Beer's law up to 4 mg/ml (Nd, pH 4·5, 578 nm), 2·5 mg/ml (Nd, pH 12, 571 nm), 4 mg/ml (Ho, pH 4·8, 450 nm), 5 mg/ml (Er, pH 4·8, 376 nm).

Effects of diverse ions

The effects of other rare earth ions on the determination of neodymium, holmium and erbium were investigated. The results are shown in Table I. Cerium ions do not interfere in acidic medium when the procedure is carried out with ascorbic acid added. Europium ions give an interference for holmium and erbium because the Tiron complexes have a broad absorption band below 550 nm. Ytterbium Tiron complexes (which have an absorption band below 430 nm) also give an interference for erbium.

Composition of the chelates

The continuous variation method was used to investigate the ratio in which Tiron combines with rare earths. The total concentration of neodymium and Tiron was maintained at $9{\cdot}5 \times 10^{-3}M$. The continuous variation plots at pH 4·5 (at 578 nm), 7·0 (at 579 nm) and 12·0 (at 579 nm) are illustrated in Figs. 6–8. The peaks at mole-fractions [Nd]/([Nd] + [Tiron]) of 0·40 and 0·33, indicate, combining ratios of 1·5 and 2 Tiron molecules per neodymium ion. For holmium and erbium at pH 4·8 the

TABLE I.—DETERMINATION OF NEODYMIUM, HOLMIUM AND ERBIUM IN SYNTHETIC SAMPLES CONTAINING DIVERSE METAL IONS

Metal ions added, *mg*		Nd (pH 4·5, 578 nm)* Found, *mg*	Metal ions added, *mg*		Nd (pH 12·0, 571 nm)† Found, *mg*
La	18·96	$13{\cdot}7_0$	La	7·58	$6{\cdot}5_8$
Ce	9·12	$13{\cdot}6_0$	Ce	4·57	Interference
Pr	18·16	$13{\cdot}8_5$	Pr	9·03	$6{\cdot}5_8$
Sm	13·71	$13{\cdot}7_0$	Sm	6·86	$6{\cdot}5_0$
Eu	13·81	$13{\cdot}9_0$	Eu	4·60	$6{\cdot}6_0$
Gd	15·74	$13{\cdot}8_5$	Gd	6·29	$6{\cdot}5_5$
Tb	16·05	$13{\cdot}9_0$	Tb	6·42	$6{\cdot}6_0$
Dy	7·94	$13{\cdot}7_5$	Dy	3·19	$6{\cdot}5_5$
Ho	3·29	$13{\cdot}6_0$	Ho	8·12	$6{\cdot}5_0$
Er	19·85	$13{\cdot}6_0$	Er	9·72	$6{\cdot}5_8$
Tm	8·46	$13{\cdot}8_5$	Tm	3·40	$6{\cdot}6_2$
Yb	18·81	$13{\cdot}7_0$	Yb	7·53	$6{\cdot}5_0$
Lu	13·42	$13{\cdot}7_5$	Lu	13·42	$6{\cdot}7_3$
Y	8·03	$13{\cdot}6_0$	Y	4·02	$6{\cdot}5_8$
		Ho (pH 5·0, 450 nm)§ Found, *mg*			Er (pH 5·0, 376 mμ)‡ Found, *mg*
La	18·96	$16{\cdot}3_4$	La	18·96	$19{\cdot}4_0$
Ce	4·57	$16{\cdot}2_5$	Ce	4·57	$19{\cdot}4_0$
Pr	22·59	Interference	Pr	22·59	$19{\cdot}5_5$
Nd	13·50	$16{\cdot}0_0$	Nd	13·50	$19{\cdot}7_5$
Sm	13·71	$19{\cdot}9_0$	Sm	13·71	$19{\cdot}2_4$
Eu	9·20	Interference	Eu	9·20	Interference
Gd	15·74	$16{\cdot}2_5$	Gd	15·74	$19{\cdot}3_5$
Tb	16·05	$16{\cdot}2_0$	Tb	16·05	$19{\cdot}3_5$
Dy	7·97	$16{\cdot}5_5$	Dy	7·97	$19{\cdot}3_0$
Er	19·85	$16{\cdot}5_5$	Ho	16·44	$19{\cdot}3_5$
Tm	8·38	$16{\cdot}6_0$	Tm	8·38	$19{\cdot}5_0$
Yb	7·53	$16{\cdot}6_0$	Yb	7·53	Interference
Lu	13·42	$16{\cdot}7_0$	Lu	13·42	$19{\cdot}4_5$
Y	8·03	$16{\cdot}6_0$	Y	8·03	$19{\cdot}5_5$

* Taken—13·75 mg.
† Taken—6·75 mg.
‡ Taken—19·45 mg.
§ Taken—16·44 mg.

combining ratio is also 1·5:1. These Tiron complexes probably exist as binuclear complexes, Ln_2 (Tiron)$_3$.

However, the results of the continuous variation plots for neodymium, especially in alkaline media, are not always accurate because the spectra vary with concentration of Tiron. Therefore, the method of continuous variation was used again with lower concentrations of neodymium and Tiron. The ultraviolet absorption spectra as a function of pH are given in Fig. 9. Although the absorption bands are not observed if the pH is below 5·0, the bands having a maximum in a range 310–325 nm appear with increasing pH. The total concentration of neodymium and Tiron was $3{\cdot}03 \times 10^{-5}M$ and the absorbance was measured at 310 (pH 7·0) and 325 nm (pH 12·0), respectively. As shown in Figs. 7 and 8, the results correspond with those for the visible region.

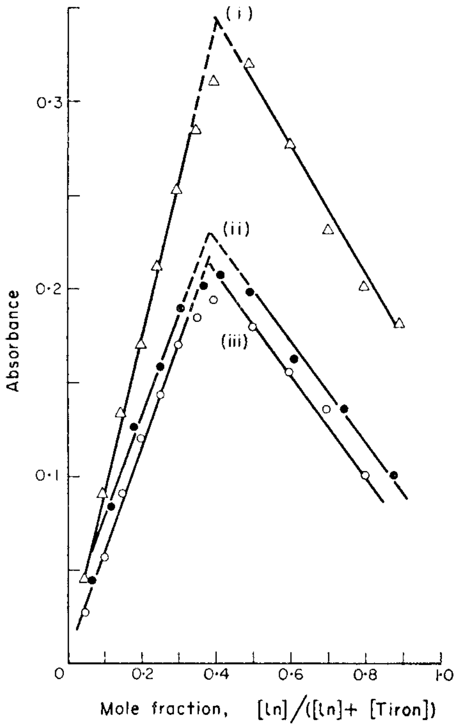


FIG. 6.—Continuous variation plots for neodymium, holmium and erbium in weakly acidic media.
(*i*) [Er] + [Tiron], 1·06 × $10^{-2}M$; pH 4·8; 376 nm
(*ii*) [Ho] + [Tiron], 9·96 × $10^{-3}M$; pH 4·8; 450 nm
(*iii*) [Nd] + [Tiron], 9·53 × $10^{-3}M$; pH 4·5; 578 nm.

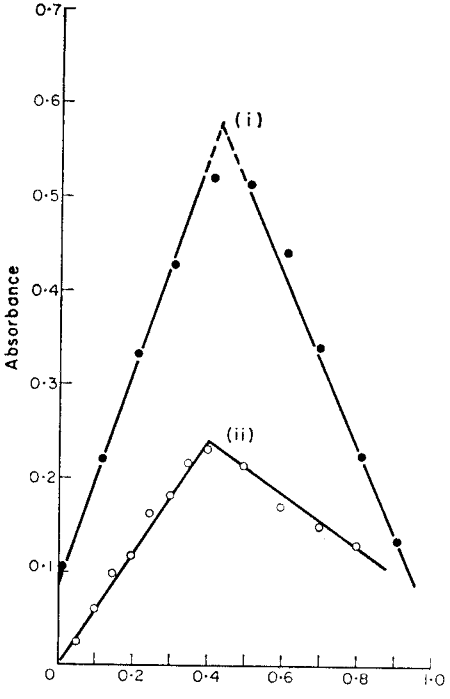


FIG. 7.—Continuous variation plots for neodymium in neutral media.
(*i*) [Nd] + [Tiron], 3·03 × $10^{-5}M$; pH, 7·0; 310 nm
(*ii*) [Nd] + [Tiron], 9·53 × $10^{-3}M$; pH, 7·0; 579 nm.

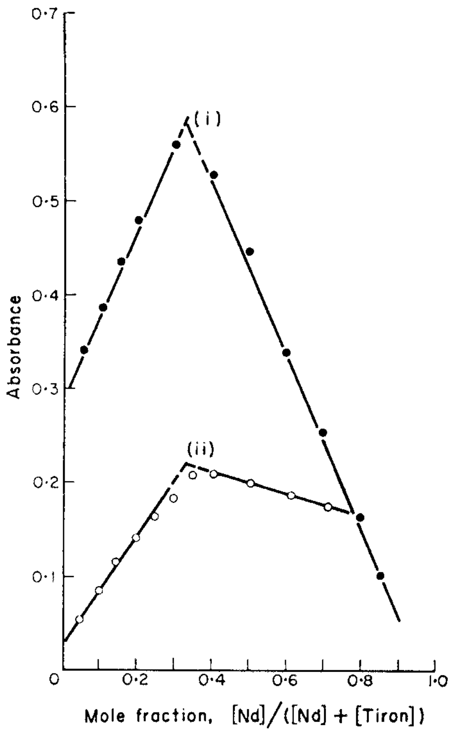


FIG. 8.—Continuous variation plots for neodymium in alkaline media.
(*i*) [Nd] + [Tiron], 3·03 × $10^{-5}M$; pH, 12·0; 325 nm
(*ii*) [Nd] + [Tiron], 9·53 × $10^{-3}M$; pH, 12·0; 579 nm.

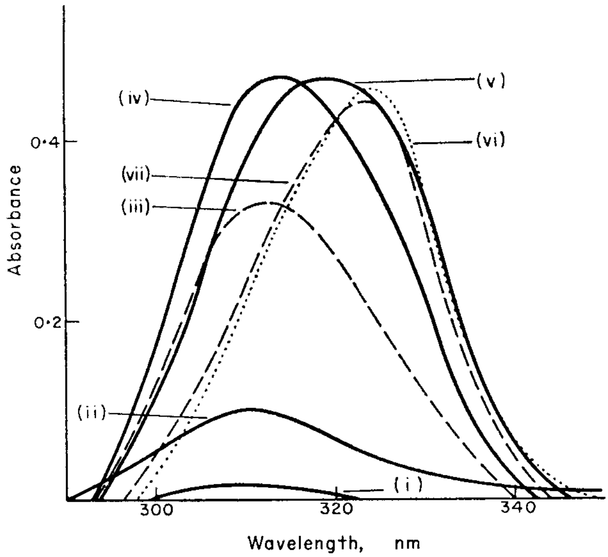


FIG. 9.—Variation of absorption spectra of neodymium complexes in ultraviolet region as a function of pH.
Nd, 6·06 × $10^{-5}M$; Tiron, 1·2 × $10^{-4}M$; reference, reagent. pH: (*i*), 5·0; (*ii*), 5·5; (*iii*), 6·0; (*iv*), 6·6; (*v*), 8·0; (*vi*), 10·0; (*vii*), 12·0.

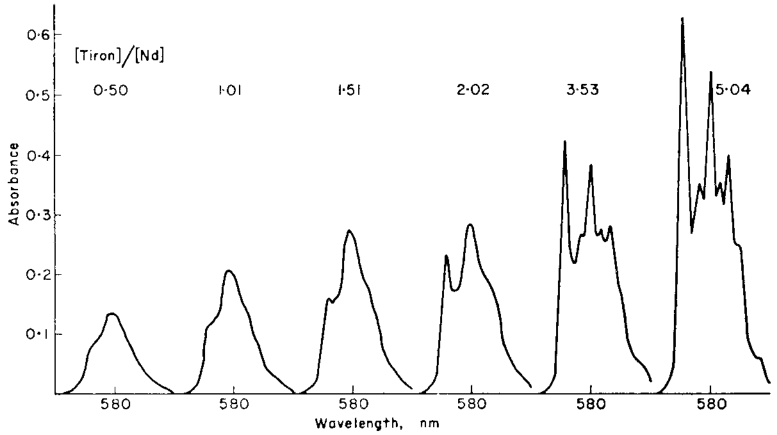


Fig. 10.—Variation of absorption spectra of neodymium Tiron complexes at pH 12 as a function of mole ratio of Tiron to neodymium. Nd, 1·24 × $10^{-2}M$.

All the results from the continuous variation and mole-ratio plots at pH 4·5 and 7 show the combining ratio of 3:2 Tiron: Ln. At pH 12, there is a discrepancy between the continuous variation and mole-ratio plots; the continuous variation method may not be suitable here because the spectrum of the neodymium complex at pH 12 is remarkably dependent upon the concentration of the reagent, as shown in Fig. 10. The complexity and enhancement of the γ-type neodymium complex spectra may be explained by formation of higher order complexes, *e.g.*, Tiron:Nd = 5, which may be deduced from the results of the mole-ratio method and from the fact that the coordination number of rare earths may be as high as nine or ten.

Zusammenfassung—Die Absorptionsspektren der Tironkomplexe von Neodym, Holmium und Erbium in wäßriger Lösung wurden von 340 bis 650 nm gemessen. Die Extinktionen bei der Wellenlänge der stärksten Absorptionsbande eines wäßrigen Mediums mit den Tironkomplexen von Neodym (pH 4,5), Neodym (pH 12,0), Holmium (pH 5,0) und Erbium (pH 5,0) waren um die Faktoren 4 (bei 578 nm), 9 (bei 571 nm), 9 (bei 450 nm) und 5 (bei 376 nm) größer als mit den entsprechenden Mengen der betreffenden Chloride. Die spektrophotometrische Bestimmung dieser Elemente wurde untersucht. Als Verbindungsverhältnisse Tiron: seltene Erde wurden 3:2 und 2:1 gefunden.

Résumé—On a mesuré les spectres d'absorption des complexes Tiron des néodyme, holmium et erbium en solution aqueuse de 340 à 650 nm. L'absorption, à la longueur d'onde de la bande d'absorption maximale, d'un milieu aqueux contenant les complexes Tiron de néodyme (pH 4,5), néodyme (pH 12,0), holmium (pH 5,0) et erbium (pH 5,0) est environ 4 (à 578 nm), 9 (à 571 nm), 9 (à 450 nm) et 5 (à 376 nm) fois plus élevée, respectivement, que pour les mêmes quantités des chlorures correspondants. On a étudié le dosage spectrophotométrique de ces éléments. On a trouvé que les rapports de combinaison du Tiron à la terre rare sont de 3:2 et 2:1.

REFERENCES

1. R. C. Vickery, *J. Chem. Soc.* 1954, 385.
2. T. Moeller and D. E. Jackson, *Anal. Chem.* 1950, **22,** 1393.
3. T. Taketatsu and C. V. Banks, *ibid.*, 1966, **38,** 1524.
4. J. H. Yoe and A. R. Armstrong, *Ind. Eng. Chem., Anal. Ed.*, 1947, **19,** 100.
5. B. Sarma, *J. Sci. Ind. Res.* (*India*), 1956, **15B,** 696; *Chem. Abstr.*, 1947, **51,** 17572.
6. F. Willi III and J. H. Yoe, *Anal. Chim. Acta*, 1953, **8,** 546.
7. H. Flaschka and E. Lassner, *Michrochim. Acta*, 1956, 778.
8. B. Sarma and C. P. Savariar, *J. Sci. Ind. Res.* (*India*), 1957, **16B,** 80; *Chem. Abstr.*, 1957, **51,** 11168.
9. H. Hamaguchi, N. Onuma, R. Kuroda and R. Sugisita, *Talanta*, 1962, **9,** 563.

Talanta, 1970, Vol. 17, pp. 475 to 482. Pergamon Press. Printed in Northern Ireland

APPLICATION OF THE UNTERZAUCHER METHOD TO THE DETERMINATION OF OXYGEN IN COKE

B. P. Kirk and H. C. Wilkinson
The British Coke Research Association, Chesterfield, Derbyshire, U.K.

(*Received* 14 *August* 1969. *Accepted* 26 *October* 1969)

Summary—The Unterzaucher method, used for the determination of oxygen in organic compounds and coal, has been adapted to the determination of oxygen in coke. Modifications were made to the conventional apparatus in order to eliminate any contribution made by the coke moisture to the determined oxygen content. The carbon dioxide produced from the combustion of the oxygen in the coke was estimated by a sensitive conductimetric method. Evidence is presented which indicates that additional liberation of oxygen from the coke mineral matter does not make a significant contribution to the total oxygen determined under the prescribed experimental conditions. The error of the determination is approximately 0·1%. A comparison is made between results obtained for a series of cokes and chars by the direct method and by an independent determination, based on neutron activation.

THE OXYGEN content of coal is related to certain coal properties such as coking power, liability to spontaneous combustion and oxidation. It is also an indication of coal rank. Because of its importance, many attempts have been made to derive a suitable experimental technique for the determination of oxygen in coal. The methods proposed fall generally within two groups, based on oxidation[1–3] or reduction[4–6] of the carbonaceous material. Within recent years the well known Schütze-Unterzaucher[7,8] method used for the determination of oxygen in organic compounds has been further developed[9,10] and methods based on this approach, *i.e.*, the reduction of the volatile oxygen compounds by carbon either with or without the addition of a catalyst, have been used. A survey of the field is given by Crawford, Glover and Wood[11] who determined oxygen in coal by a procedure and apparatus similar to that described by Oita and Conway.[10] This technique was further adapted for our purposes.

The principal difficulty associated with the application of such methods to the determination of oxygen in coal is that relating to the breakdown of the coal mineral matter at the temperature of pyrolysis and the inability of the method to assess the contribution to the total oxygen content made by the oxygen present in the mineral matter.

In an attempt to surmount these difficulties, methods have been suggested which incorporate a process of demineralization,[12] but such techniques are generally tedious and may introduce further sources of error into the determination, by causing retention of halogens or water.

The oxygen content of high-temperature cokes used in foundry and blast-furnace practice generally lies within the range 0·2–1·0%. It bears a superficial relation to the oxygen content of the parent coal but is more closely associated with the conditions of carbonization, particularly the temperature.

Some oxygen remains in the coke mineral matter after carbonization, but from generally available information it is considered that the contribution made by the coke mineral matter to the determined oxygen content is probably considerably smaller than that made by the mineral matter of coal to its oxygen content. This was investigated during the course of the work described in this paper.

EXPERIMENTAL

The elimination of moisture and adsorbed gases from the sample

The results of previous work[13] has shown that complete release of moisture from the analysis sample was not attained until temperatures of the order of 350° were reached in the drying of the coke. In order to remove moisture and adsorbed gases, including oxygen, from the sample and at the same time to prevent their re-adsorption, a method was devised to permit their removal without withdrawal of the sample from the apparatus.

For this purpose, the pyrolysis tube of the conventional apparatus (*E*, Fig. 1) was extended to include a wide-bore tap *D* and an evacuation section *F* which would be heated to a temperature of approximately 350° by an electric heating tape. Provision was also made to apply vacuum and simultaneous heating to section *F* to remove adsorbed gases from the sample. After this pretreatment the sample was moved by means of a pusher and external magnet through tap *D* into the pyrolysis tube *E*.

The effect of mineral matter upon the determined oxygen content

The principal constituents of the mineral matter of coke are silicates, aluminates and ferruginous substances. The former substances are generally found in combination with alkalis or alkaline earths, and the iron is largely present as sulphide. It is possible that some of these substances could release oxygen on pyrolysis at high temperatures, but it is considered that the extent of such decomposition would be small at a pyrolysis temperature of 1050°, since the principal components of the mineral matter are dissociated to only a small extent at this temperature. Experiments were undertaken to confirm these observations.

Laboratory cokes 1–3 were prepared by the carbonization of various proportions of float-and-sink fractions of one coal. Cokes 4 and 5 incorporated additional shale in the blend, and cokes 21–24 were prepared from a further coal or coal/shale blend. Samples 1–5, 21 and 22 were carbonized to a maximum temperature of 950° and cokes 23 and 24 were heated to 1100°. Approximately 100 g were taken for each test.

The oxygen content of these cokes was determined, with a pyrolysis temperature of 1050°, and the results are presented in Table I. There was evidence that the amount of oxygen found increased as the mineral-matter content increased but such increases were not systematic (*cf.* the oxygen and mineral-matter contents of cokes 1 and 2, 4 and 5 and 23 and 24).

It is important to bear in mind the inherent variability of coal samples in assessing the significance of the differences in the determined oxygen contents of the various cokes. Furthermore, small differences in carbonizing conditions result in the production of cokes which may be considered to be homogeneous for practical purposes, but by comparison with chemical compounds display a considerable degree of heterogeneity. It is therefore to be expected that there will be a greater inherent variation in results in the work considered in this paper than would be the case when substances of uniform quality are used.

Further tests were undertaken in which some samples of the same cokes were demineralized by treatment with hydrofluoric and hydrochloric acids, washed free from halogens as completely as possible and dried. The oxygen contents of the demineralized samples were determined, with the results shown in Table II.

The oxygen content of four of the demineralized samples was found to be higher, by a mean value of 0·08% oxygen, than that of the corresponding samples containing mineral matter. The oxygen content of sample 3 was 0·14% lower than that of the corresponding mineral-containing sample. Further experiments were made using a thermobalance to establish the loss in weight of coke ash, of the shale used in the preparation of some of the samples, and of mixtures of graphite and shale where the reducing action of the carbon on the mineral matter could be studied. The average loss in weight between 830 and 1100° from four different samples of ash was 0·2%, and from mixtures of 90% graphite and 10% shale was 0·6%. The implication of these results is that a 100 mg sample of coke, having an ash content of 10% (a reasonable value for the ash content of a high temperature coke), could lose approximately 0·06% by weight by breakdown of mineral matter. This weight loss would not necessarily be entirely due to loss of oxygen. No measurable weight loss was observed when shale was heated under the same conditions.

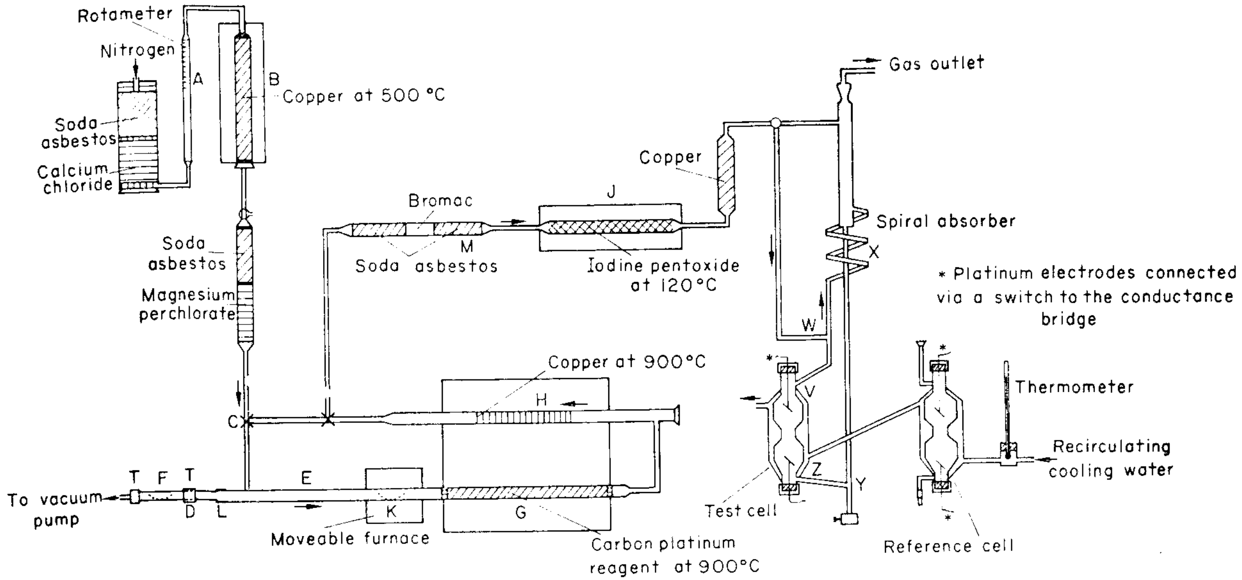


FIG. 1.—Apparatus for the direct determination of oxygen.

TABLE I.—THE RELATION BETWEEN DETERMINED OXYGEN CONTENT AND MINERAL MATTER FOR LABORATORY COKES

Sample	Blend composition	Oxygen %			Mineral matter % d.b.†
		1	2	Mean	
1	Coal A (Floats)	0·79	0·75	0·77	1·23
2	Coal A (Floats and sinks)	0·85	0·84	0·84	1·49
3	Coal A (Floats and sinks)	0·92	0·90	0·91	3·69
4	Coal A (Floats, sinks and shale)	1·01	1·08	1·04	6·00
5	Coal A (Floats, sinks and shale)	1·25	1·20	1·22	10·71
21	Coal B	0·22	0·20	0·21	3·55
22	Coal B and shale	0·30	0·28	0·29	13·77
23	Coal B*	0·08	0·10	0·09	3·38
24	Coal B and shale*	0·16	0·16	0·16	14·61

* Carbonized at 1100°.
† Dry basis.

TABLE II.—THE EFFECT OF DEMINERALIZATION ON COKE OXYGEN CONTENT

Sample	Mean oxygen % d.m.m.f.† Before demineralization Mean	Mean oxygen % d.m.m.f.† After demineralization Mean	Ash %*
1	0·78	0·93	0·08
2	0·86	0·94	—
3	0·94	0·80	—
4	1·10	1·18	—
5	1·36	1·39	0·24

* *cf.* Table I.
† Dry, mineral-matter-free basis.

The general conclusions forthcoming from these experimental results strongly indicated that there was little breakdown of mineral matter under the experimental pyrolysis conditions. Any small release of oxygen attributable to this cause was less than the overall error claimed for the determination.

The dependence of the determined oxygen content upon pyrolysis temperature

To establish whether complete release of oxygen from the carbon took place at or below 1050°, tests were carried out in which the sample was heated to this temperature without removal from the apparatus and the release of oxygen was measured at specific temperatures between 500 and 1000°. At each temperature the experiment was allowed to proceed (usually for about 20 min) until the amount of oxygen released was less than or equal to the blank value. The pyrolysis temperature was then increased, within 1–2 min, to the next highest level.

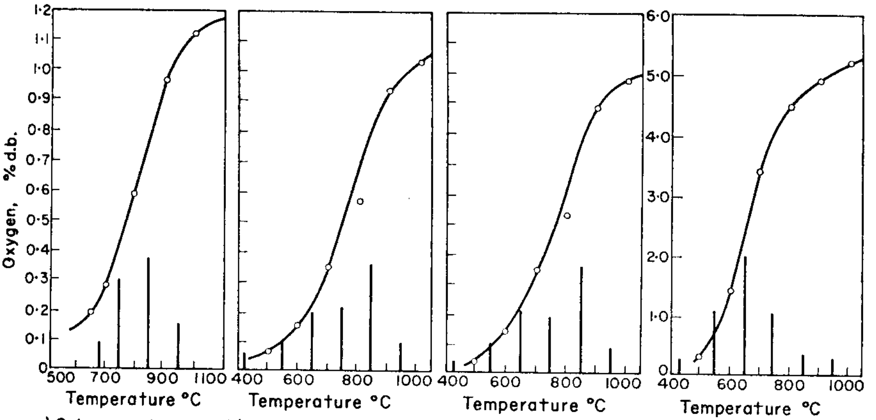
The results of these tests indicated that whilst the release of oxygen was not entirely complete at 1000°, the quantity liberated between 900 and 1000° and between 1000° and 1050° was quite small. The data are summarized in Fig. 2.

Higher pyrolysis temperatures were not considered to be feasible, because of the construction of the apparatus and the increased possibility of decomposition of the mineral matter.

A comparison of direct and indirect oxygen determination on cokes and chars

On the basis of the results of the preliminary experimental work the following technique was used to determine the oxygen content of several chars, laboratory cokes and commercial cokes, and the results were compared with corresponding values obtained by a neutron-activation method and with indirect estimates. Figure 1 shows the apparatus used.

Up to 150 mg of sample, crushed to pass a 0·06-mm mesh test-sieve, were weighed into a small platinum boat and introduced *via* the joint *L* into the evacuation side *F* of the pyrolysis tube. Oxygen-free nitrogen entered the apparatus *via* a rotameter *A* and purification train *B* containing copper wire at a temperature of 500° to remove the last traces of oxygen from the gas. The amount of residual oxygen in the cylinder gas appeared to be variable, and it was essential to carry out a periodic reduction



a) Coke sample 4–demineralised b) Coke sample 7(i)–demineralised c) Coke sample 7(ii)–demineralised d) 600 °C cellulose char

FIG. 2.—Dependence of oxygen release on pyrolysis temperature. The vertical lines represent difference values and hence rates of release.

of the resulting copper oxide by passing hydrogen through *B*, the frequency of this operation being indicated by the analytical precision. By manipulation of taps *C* and *D* the oxygen-free nitrogen was passed over the sample for 30 min at a rate of 25 ml/min. The nitrogen flow was then isolated from the sample and the temperature of *F* raised to about 350° by the surrounding heating tape; at the same time *F* was gradually evacuated to approximately 10 µbar. After 30 min the system was isolated from the vacuum, the heating tape removed and nitrogen allowed to leak into *F*. When the pressure was stable throughout the system the sample was moved by means of a pusher and magnet through the wide-bore tap *D* to a position just ahead of the furnace *G* containing the carbon-platinum catalyst at 900 ± 5°.

The conductance cells were now brought into a stable condition,[14] the pyrolysis furnace was moved over the sample in *E* and the temperature raised rapidly at approximately 150°/min to a final temperature of 1050°.

The volatile products of pyrolysis were carried by the nitrogen stream through the reaction tube *G* where at a temperature of 900° the carbon-platinum reagent converted the oxygenated gases into carbon monoxide. Sulphur compounds were removed from the gas stream by copper gauze at 900° in furnace *H*. The sulphur-free gases then passed successively through soda-asbestos to remove acidic gases, Bromac (bromine absorbed on activated charcoal) to remove any unsaturated hydrocarbons and a further soda-asbestos absorber (*M*) which removed any liberated bromine.

Carbon monoxide was finally oxidized to carbon dioxide by passage over iodine pentoxide at 118–120° (furnace *J*) and the iodine released in this reaction was removed by copper gauze before the conductimetric estimation of carbon dioxide was made. The basis of the conductimetric method is described by Strouts *et al.*[14]

The results of the first series of tests are presented in Table III, together with the results of oxygen determinations carried out on our behalf by the A.E.R.E., using neutron-activation analysis. These results included oxygen present as mineral oxygen and an approximate allowance for this oxygen was made by deducting 50% of the ash content from the total oxygen content. The adjusted results are shown in columns 6, 7 and 8 of Table III. For five of the samples, this adjustment amounted to 0·08% or less. Where available,values of oxygen content estimated by difference are included for comparison with the determined values.

The results for the two chars were about 0·5% higher by the activation method than by the chemical method, presumably because of partial retention of oxygen by these materials.[15]

There was better agreement between the values obtained for the five demineralized coke samples, the mean algebraic difference being 0·11% of oxygen with no indication of bias for either method.

In Table IV the results are given of further determinations which were carried out on samples of laboratory and commercial cokes. These samples were not demineralized. The experimental results expressed on the dry basis are compared with calculated values for oxygen.

The discrepancy between the determined and "difference" values of the oxygen content of the cokes varied between 0·89% (Sample 12) and 0·08% (Sample 17). The mean difference for samples 11, 13, 14, 16, 17 and 20 was 0·14%, four of the determined values being higher and two lower than the

TABLE III.—COMPARISON OF THE OXYGEN CONTENTS OF CHARS AND DEMINERALIZED COKES DETERMINED BY TWO METHODS AND BY CALCULATION

Sample	Direct determination, % A	B	Mean	Oxygen by difference, % d.b.	Neutron activation, % A	B	Mean	Ash %
Cellulose Char A	5·76	5·59	5·68	6·03	6·50	5·99	6·24	0·97
PVDC Char B	1·49	1·48	1·48	1·77	1·93	1·87	1·90	0·04
Coke 6	1·11	1·19	1·15	—	1·04	1·05	1·04	0·08
Coke 7	1·02	1·03	1·02	—	1·26	1·24	1·25	0·16
Coke 8	1·18	1·18	1·18	1·37	1·18	1·14	1·16	0·11
Coke 9	1·27	1·28	1·28	—	1·34	1·29	1·32	0·36
Coke 10	1·42	1·52	1·47	—	1·34	1·32	1·33	0·12

TABLE IV.—COMPARISON OF THE MEASURED AND CALCULATED OXYGEN CONTENTS OF COKES

Sample	Moisture %	% Dry basis: Ash	C	H	N	S	Cl	Mineral matter*	Oxygen by difference	Oxygen determined A	B	Mean
11	2·80	6·01	89·13	0·68	1·54	1·25	0·08	6·84	1·73	1·74	1·88	1·81
12	3·70	8·72	84·39	0·83	1·59	1·86	0·03	9·96	3·20	2·30	2·32	2·31
13	1·65	6·08	89·38	0·83	1·26	1·43	0·00	7·03	1·50	1·49	1·35	1·42
14	0·98	3·66	92·94	0·58	1·46	0·73	0·01	4·15	0·86	0·71	0·74	0·72
15	0·36	10·37	87·59	0·31	0·95	0·69	0·03	10·91	0·21	0·60	0·54	0·57
16	0·90	11·79	85·84	0·23	0·78	1·18	0·05	12·58	0·52	0·75	0·67	0·71
17	0·55	11·42	86·41	0·28	0·70	1·46	0·02	12·39	0·20	0·26	0·30	0·28
18	1·16	10·70	86·88	0·40	1·11	1·21	0·02	11·51	0·08	0·51	0·55	0·53
19	0·40	11·76	86·21	0·26	1·02	1·53	0·04	12·78	−0·31	0·38	0·39	0·38
20	1·40	12·56	84·71	0·81	0·83	0·97	0·00	13·21	0·44	0·67	0·74	0·70

* Mineral matter (d.b.) = Ash + 2S/3.

"difference" values. The causes for greater divergence between the derived and determined results for samples 12, 15, 18 and 19 are not apparent.

The values of the "oxygen by difference" were obtained by subtracting the sum of the percentages of carbon, hydrogen, nitrogen, chlorine and mineral matter from 100. The total analytical error associated with all these determinations is approximately 0·5%, and the calculated oxygen may be in error by this amount. Whilst an error of this magnitude may not be too serious with respect to the calculated oxygen content of coal (which is frequently reported as oxygen plus errors) it is of the same order of magnitude as the oxygen content of many high-temperature cokes. Correction of the calculated results to a mineral matter free basis would not be expected to produce a significantly more accurate value for the calculated oxygen content of coke.

DISCUSSION

An examination of the relationship between the determined hydrogen, oxygen and moisture contents (Table IV) indicates that both hydrogen and oxygen contents tended in general to increase with the moisture content of the coke. Although experience suggests that a fraction of the moisture was not eliminated by heating at 350°, nevertheless the atomic ratio of hydrogen to oxygen was considerably greater than the stoichiometric ratio for water, suggesting that some of the hydrogen was originally in combination with the coke.

It is interesting that the amount of oxygen released from coke appears to be a function of pyrolysis temperature between 500 and 1000° (Figs. 2*a*, 2*b*, 2*c*). There appeared to be a pronounced maximum rate of release of oxygen at 850°. For the cellulose char (Fig. 2*d*) the maximum release occurred at a temperature of 650°. Apart from this maximum, there was a steady release of oxygen at temperatures between 650 and 850°, but a lower rate between 500 and 650° and above 850°. These observations could be of interest in relation to the nature of the carbon–oxygen bonding in cokes and carbons and may be worthy of further study.

The reduction in the amount of oxygen released above temperatures of 850–900° suggests that loss of oxygen from the coke substance was virtually complete at 1000–1050°.

The presence of mineral matter appeared in certain cases to make a small contribution to oxygen release, possibly due to the presence of carbonates, reformed by the action of moisture and carbon dioxide upon alkali or alkaline-earth oxides present in the mineral matter. On the other hand, the small amounts of additional oxygen detected in the presence of mineral matter may be accounted for on the basis of constituents of the mineral matter promoting catalytic liberation of oxygen from the coke.

As already stated, it is considered that the quantity of additional oxygen liberated in the presence of mineral matter is not significant by comparison with the overall error of the determination and the advantages in accuracy to be gained by demineralization of the coke are questionable.

The standard deviation of the analyses by the direct method described was slightly less than 0·05% (10 variates). The determined oxygen content was found to be related to the determined carbon content by the relationship

$$O = 43{\cdot}58 - 0{\cdot}44C\ (\%\ \text{d.m.m.f.})$$

the use of which results in a better value for the oxygen content than the "difference value" which is quoted in our Tables.

It does not appear to be essential with coke, as with coal, to remove the mineral matter from the sample prior to the determination of oxygen, but the coke must be crushed to pass a 0·06-mm mesh sieve.

It was found to be essential to calibrate and service the apparatus periodically. After approximately twenty determinations the oxygen content of a reference sample, *e.g.*, acetanilide, was determined, or a known amount of carbon dioxide was passed through the apparatus. With these precautions the precision of the determination can be maintained at better than 0·05%.

Acknowledgements—This work formed part of the programme of research of The British Coke Research Association. We are indebted to The Director for permission to publish this paper.

Zusammenfassung—Das zur Bestimmung von Sauerstoff in organischen Verbindungen und Kohle verwendete Verfahren nach Unterzaucher wurde der Sauerstoffbestimmung in Koks angepaßt. Die übliche Apparatur wurde abgeändert, um einen Beitrag der Feuchtigkeit des Kokses zum ermittelten Sauerstoffgehalt zu verhindern. Das durch die Verbrennung des Sauerstoffs im Koks entstandene Kohlendioxid wurde durch eine empfindliche konduktometrische Methode bestimmt. Es wird gezeigt, daß zusätzliche Freisetzung von Sauerstoff aus den Mineralbestandteilen des Kokses keinen wesentlichen Beitrag zum unter den Bedingungen der Vorschrift ermittelten Gesamt-Sauerstoffgehalt liefert. Der Fehler der Bestimmung beträgt etwa 0,1 prozent. Die an einer Anzahl von Koksen und Kohlen mit der direkten Methode erhaltenen Ergebnisse werden verglichen mit denen einer auf Neutronenaktivierung beruhenden indirekten Methode.

Résumé—La méthode d'Unterzaucher, utilisée pour le dosage de l'oxygène dans les composés organiques et la houille, a été adaptée au dosage de l'oxygène dans le coke. Des modifications ont été effectuées sur l'appareil ordinaire afin d'éliminer toute contribution apportée par l'humidité du coke à la teneur en oxygène dosée. Le gaz carbonique produit par la combustion de l'oxygène dans le coke a été dosé par une méthode conductimétrique sensible. On apporte des preuves indiquant que la libération supplémentaire d'oxygène de la matière minérale du coke ne contribue pas de manière significative à l'oxygène total déterminé selon les conditions expérimentales prescrites. L'erreur du dosage est d'approximativement 0,1%. On effectue une comparaison entre les résultats obtenus pour une série de cokes et de produits de carbonisation par la méthode directe et par une détermination indépendante, basée sur l'activation de neutrons.

REFERENCES

1. M. Dolch and H. Will, *Brennstoff-Chem.*, 1931, **12**, 141, 166.
2. W. R. Kirner, *Anal. Chem.*, 1936, **8**, 57.
3. J. W. Whittaker, R. N. Chakrovorty and A. K. Ghosh, *J. Sci. Ind. Res. India*, 1956, **15B**, 72.
4. H. Ter Meulen, *Rec. Trav. Chim.*, 1924, **43**, 899; 1934, **53**, 116.
5. H. Guerin and P. Marcel, *Bull. Soc. Chim. France*, 1952, 310.
6. C. E. Spooner, *Fuel*, 1947, **26**, 15.
7. M. Schütze, *Z. Anal. Chem.*, 1939, **118**, 145.
8. J. Unterzaucher, *Chem. Ber.*, 1940, **73B**, 391.
9. *Idem*, *Analyst*, 1952, **77**, 584.
10. I. J. Oita and H. S. Conway, *Anal. Chem.*, 1954, **26**, 600.
11. A. Crawford, M. Glover and J. H. Wood, *Microchim. Acta*, 1961, 46.
12. W. Radmacher and A. Hoverath, *Brennstoff-Chem.*, 1959, **40**, 97.
13. H. C. Wilkinson, *Fuel*, 1965, **44**, 191.
14. C. R. N. Strouts, H. M. Wilson and R. T. Parry-Jones, (Eds.), *Chemical Analysis*, Vol. III, pp. 85–96. Oxford University Press, Oxford, 1962.
15. H. E. Blayden and D. T. Westcott, *Proc. Conf. Carbon, 5th, 1961*. Vol. 2, pp. 97–112. Pergamon, Oxford, 1963.

Talanta, 1970, Vol. 17, pp 483 to 489. Pergamon Press. Printed in Northern Ireland

MACRORETICULAR CHELATING ION-EXCHANGERS

R. F. Hirsch,® E. Gancher* and F. R. Russo†
Department of Chemistry, Seton Hall University,
South Orange, New Jersey 07079, U.S.A.

(*Received* 29 *December* 1969. *Accepted* 25 *January* 1970)

Summary—Two macroreticular chelating ion-exchangers have been prepared and characterized. One contains the iminodiacetate group and the second contains the arsonate group as the ion-exchanging site. The macroreticular resins show selectivities among metal ions similar to those of the commercially available microreticular chelating resins. Chromatographic separations on the new resins are rapid and sharp.

In recent years there has been an increasing interest in highly selective ion-exchangers.[1,2] The goal has been to achieve sharp separations of metal ions without the addition of complexing reagents to the eluent and to concentrate traces of metals from large volumes of very dilute solutions.

The inherent lack of selectivity of the conventional strong acid cation-exchanger, with a sulphonate ion-exchanging group, makes it unsatisfactory for the separation of many mixtures of metals. Even metal ions which are otherwise quite different from each other in their chemical behaviour are often unresolved by the sulphonate resin. For example, the equilibrium constant, K_{Li}^{M}, for the ion-exchange reaction

$$\tfrac{1}{2}\text{M}^{2+} + \overline{\text{Li}^+} = \tfrac{1}{2}\overline{\text{M}^{2+}} + \text{Li}^+$$

(the bars indicate the species in the resin) is 3·29 for Mg^{2+}, 3·47 for Zn^{2+}, 3·85 for Cu^{2+}, 3·93 for Ni^{2+} and 5·16 for Ca^{2+} on Dowex 50W-X8.[3] Separation of these metals on this resin must therefore rely on chemical reagents which bind some of the metals as rapidly eluted neutral or anionic complexes, while the others are not bound and remain on the resin.[4]

If the ion-exchanging group on the resin is able to form covalent complexes with metals—which the sulphonate group cannot—then the resin will exhibit a greater selectivity among them, due to variations in the strengths of the complexes. One such group is the iminodiacetate ion, $\text{—N(CH}_2\text{COO}^-)_2$. The commercial resin Dowex A-1 (Chelex 100) contains this exchange group. The selectivity constants for this resin, relative to calcium [K_{Ca}^{M}] are 4·9 for Mn^{2+}, 15·2 for Co^{2+}, 19·8 for Zn^{2+}, 52 for Ni^{2+}, and 500 for Cu^{2+}.[5] A second selective group is the phosphonate ion, $-PO_3^{2-}$, which is the ion-exchanging group in Duolite C-63. Selectivities of this resin relative to nickel [K_{Ni}^{M}] are 1·3 for Co^{2+}, 2·9 for Mn^{2+}, 20·5 for Zn^{2+}, and 53 for Cu^{2+}.[6] Both types of resin are weak acids, which is to say that the ionic group has a strong preference for hydrogen ion. Thus in both cases control of the pH of the eluent is all that is necessary for sharp separations of many metals from each other.

Many other chelating ion-exchangers have been studied.[1] The main limitation of these materials is that they are based on a gel or microreticular copolymer matrix.

---

* Present address: Olivetti-Underwood, Englewood Cliffs, New Jersey.
† Present address: Engelhard Industries, East Newark, New Jersey.

This means that the resin undergoes large changes in volume on conversion from one ionic form to another.[7] Such volume changes can disrupt the uniform packing of the resin in a column. In addition, with low degrees of swelling the rate of ion-exchange reactions becomes slow, which is undesirable in chromatography.

Over the past decade a new type of copolymer has been developed for use in ion-exchangers. It is called macroreticular, since it has a permanent macroscopic structure regardless of the ionic form.[8,9,10] In particular, there is an extensive network of large pores, up to 50 nm in diameter or even larger, throughout the interior of the resin beads.[11] This pore structure allows exchange reactions to proceed rapidly in any ionic form of the resin, even if the resin is placed in a non-polar solvent, such as hexane, which does not swell it. Several macroreticular strong acid cation-exchangers and strong and weak base anion-exchangers have become commercially available[12] and have found use in diverse analytical procedures.[13,14,15]

The results that have been published regarding the properties of chelating ion-exchangers, combined with the data on the macroreticular resins, suggested that the highly porous copolymer could serve as the basis of selective ion-exchangers with more satisfactory properties than the microporous materials. In this paper we report on some newly-prepared selective macroreticular cation-exchangers containing the iminodiacetate and the arsonate[16] groups. Synthetic procedures, properties, and chromatographic behaviour are discussed.

EXPERIMENTAL

Starting materials and reagents

XAD-1 macroreticular styrene–divinylbenzene copolymer was obtained from the Rohm and Haas Company, Philadelphia, Penn. The beads were washed with $2M$ hydrochloric acid, methanol and acetone, screened to 20–50 mesh, and dried under vacuum before use. All other chemicals were of the highest available purity, usually reagent grade.

*Synthetic procedures**

Iminodiacetate resin. The XAD-1 was chloromethylated with chloromethyl methyl ether in the presence of anhydrous tin(IV) chloride.[17] After washing and drying under vacuum, the chloromethylated copolymer was refluxed with $1M$ sodium iodide in acetone to convert it into the iodomethylated form.[18] The latter was heated for 10 days at 75° with diethyl iminodiacetate in acetonitrile, producing the diethyl iminodiacetate derivative of the copolymer. This was hydrolysed by heating with ethanolic sodium hydroxide to give the iminodiacetate resin.[19]

Arsonic acid resin. The XAD-1 was nitrated by heating with nitric–sulphuric acid mixture (40:60) for 2 hr at 60°. After washing and drying, the nitrated resin was reduced by refluxing with tin(II) chloride in hydrochloric acid for 2 hr, washed, and diazotized with nitrous acid at 0°. The beads were then washed with cold aqueous sodium carbonate solution and mixed with $0{\cdot}5M$ aqueous sodium arsenite at 25° for 1 hr and at 60° for an additional hour to obtain the arsonic acid copolymer.[20]

Characterization of products

Infrared spectra were obtained on a Beckman Model IR-10 Spectrophotometer; there were no noticable differences when the mineral oil mull and KBr pellet methods of sample preparation were used.

Relative volumes in the different ionic forms were determined by packing a column with resin in the sodium form, converting it into the other forms, and observing the volume of the resin bed in each case.

Hydrogen ion capacity was determined by the standard technique.[21]

Metal ion capacities were determined by equilibrating weighed samples (fully converted into the sodium form) with a measured amount of standard metal ion solution [copper(II), zinc or calcium]. An aliquot of the supernatant liquid was titrated with standard EDTA under appropriate conditions.[22] The results were checked by washing the sample free from the metal solution with demineralized water,

---

* These are available in fuller detail from the senior author.

and treating the resin with $1M$ hydrochloric acid to displace the absorbed metal ions, which were then titrated with EDTA.

All capacities refer to the dry resin weight on a hydrogen-form basis.

Chromatography

A resin sample was equilibrated with buffer and packed into a chromatographic column, forming a bed about 100 mm long and 10 mm in diameter. Two ml of a mixture of metals ($0{\cdot}01M$ in each) in this buffer were added to the column. Elution was carried out with buffer solutions of various pH values at a flow-rate of 2 ml/min. Fractions were collected and analysed for relative metal ion concentrations with a Perkin–Elmer Model 290 Atomic Absorption Spectrophotometer under standard conditions for each metal.[23]

RESULTS AND DISCUSSION

Syntheses

The procedures described above are the optimum ones found in this work. Several other routes were studied in each case and were less satisfactory. The iminodiacetate resin could not be obtained from chloromethylated copolymer in as high capacity by reaction with disodium iminodiacetate, iminodiacetonitrile, or diethanolamine (procedures suggested in the literature for gel resins[1]). The procedure chosen, using diethyliminodiacetate as the aminating reagent, gave somewhat better results with iodomethylated XAD-1 (95% amination based on product nitrogen content) than with chloromethylated copolymer (70–80% amination).

The arsonic acid resin could not be obtained by reaction of chloro-iodomethylated copolymer with potassium arsenite or by refluxing XAD-1 with arsenic trichloride in the presence of aluminium trichloride catalyst, followed by hydrolysis (which was found to be a satisfactory procedure for preparation of a phosphonic acid resin, using phosphorus trichloride and aluminium trichloride[16]). It is possible that under milder conditions arsenic trichloride would be a satisfactory reagent for introducing arsenic into the copolymer.

Several other new macroreticular resins were prepared, but were not thoroughly characterized. Among the ion-exchanging groups attached to the copolymer were triphenylbenzylphosphonium and triphenylbenzylarsonium anion-exchangers and phosphonate cation-exchanger, all with exchange capacities greater than 1 mequiv per g of dry resin.

Properties of the resins

The iminodiacetate resin had a hydrogen ion capacity of 3·2 mmole/g and a copper capacity of 1·6 mmole/g. These values are similar to the respective capacities 2·9 and 1·5, published for Dowex A-1 or Chelex 100 gel-type iminodiacetate resins.[24] The high capacity is desirable for efficient operation in chromatography and other applications. The absence of ester in the resin was indicated by the lack of infrared absorption at 5·7 μm, absorption that was present prior to saponification of the diethyl iminodiacetate resin.

The volume was measured of the iminodiacetate resin in various ionic forms. There was no change in volume on interconversion between the Na^+, H^+, Cu^{2+}, and K^+ forms. Likewise, no volume change was observed when toluene or methanol was substituted for water in contact with the hydrogen or sodium forms. Dowex A-1, on the other hand, shows relative volumes of 0·45 for H^+, 0·55 for Zn^{2+}, 1·00 for Na^+ and 1·06 for K^+ forms in water, and 1·00 in water, 0·70 in methanol, and 0·47 in acetone for the sodium form.[7] These results suggest that the macroreticular chelating resin will be useful under a wider variety of conditions than the microreticular gel Dowex A-1.

The arsonate resin had a hydrogen capacity of 3·0 mmole/g. The metal ion capactities were 1·3 mmole Cu^{2+}/g, 1·4 mmole Zn^{2+}/g, and 1·1 mmole Ca^{2+}/g at pH 11, and 0·8 mmole Cu^{2+}/g at pH 3·5. Elemental analysis showed 6·4% nitrogen and (by difference) 16% oxygen in the final product. These results suggest the presence of other exchange groups in addition to the arsonate. A possible distribution of groups is 1·3 mmole arsonate/g, 1·0 mmole phenolate and 0·5 mmole azo/g (due to side-reactions of the diazonium intermediate), 3·3 mmole nitro/g (due to incomplete reduction), and 0·2 mmole carboxylate/g (due to oxidation of the copolymer during nitration). While the various side-products do affect the ion-exchange capacity of the arsonate resin, they would not interfere (with the possible exception of the carboxylate, which is only a small fraction of the total capacity) with the determination of the metal ion selectivity of the arsonate group.

The arsonate resin showed little volume change on conversion from one ionic form into another. Its exchange capacity is sufficient to allow use in various analytical

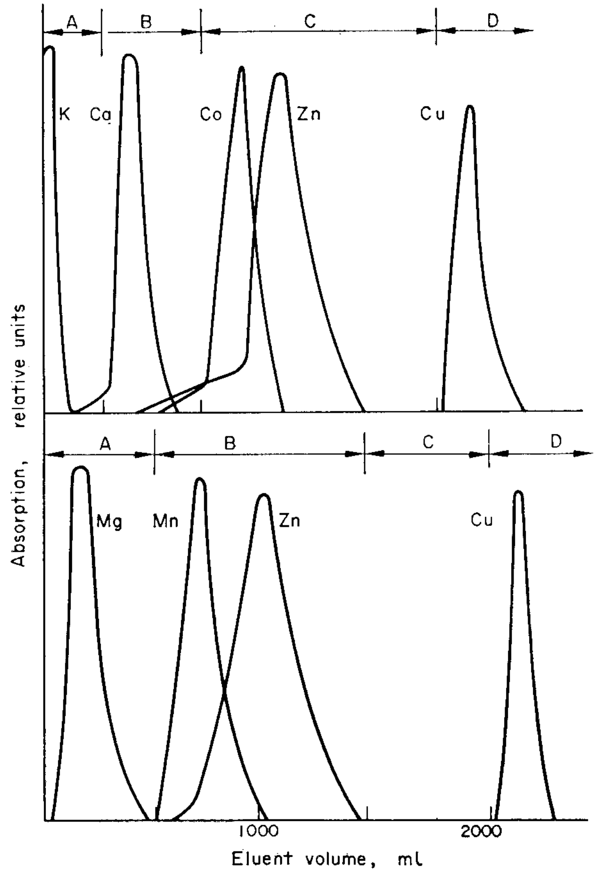


FIG. 1.—Chromatographic separations with the macroreticular iminodiacetate ion-exchange resin.
Buffer solutions: *A*—pH 4·3, *B*—pH 3·1, *C*—pH 2·0, *D*—pH 1·2.

applications, as the chromatographic results given below suggest. Unlike the iminodiacetate resin, which was gray, the arsonate resin was brick red in colour. It is likely that further synthetic studies would produce an arsonate resin with higher exchange capacity, fewer impurities, and a lighter colour.

Chromatography

Several mixtures of representative metal ions were used to test the selectivity of the two new macroreticular resins. Typical chromatograms are shown in Figs. 1 and 2.

The selectivity order for the macroreticular iminodiacetate resin is $K^+ < Mg^{2+} < Ca^{2+} < Mn^{2+} < Ni^{2+} < Co^{2+} < Zn^{2+} \leqslant Cu^{2+}$. Hering[1] determined the following order for a gel type iminodiacetate resin: $Na^+ < Mg^{2+} < Ca^{2+} < Co^{2+} < Zn^{2+} < Ni^{2+} \leqslant Cu^{2+}$, while Rosset[5] determined the selectivity of Dowex A-1 as $Mg^{2+} < Mn^{2+} < Co^{2+} < Zn^{2+} < Ni^{2+} \leqslant Cu^{2+}$. The elution order with the macroreticular chelating resin is therefore similar to that previously observed with the microreticular chelating resins.

The arsonate resin showed the selectivity order $Mg^{2+} < Ca^{2+} < Mn^{2+} < Co^{2+} < Ni^{2+} < Zn^{2+} \leqslant Cu^{2+}$. Persoz and Rosset[6] reported the following order of affinity for

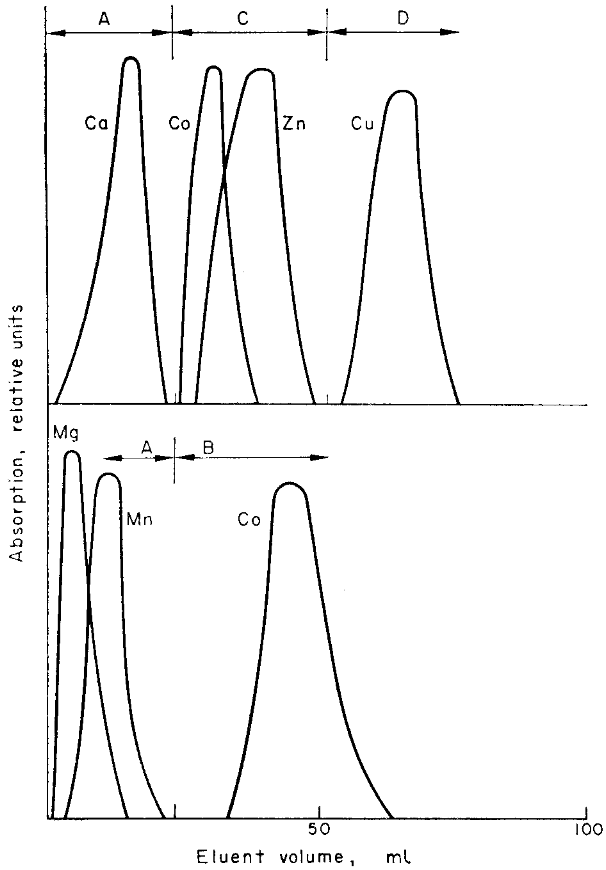


FIG. 2.—Chromatographic separations with the macroreticular arsonate ion-exchange resin.
Buffer solutions: *A*—pH 4·6, *B*—pH 3·5, *C*—pH 2·5, *D*—pH 1·5.

Duolite C-63, the phosphonate resin: $Mg^{2+} < Ca^{2+} < Ni^{2+} < Co^{2+} < Mn^{2+} < Zn^{2+} < Cu^{2+}$. The shift in position of the nickel and manganese is most likely due to the difference in co-ordinating properties between the arsonate and phosphonate groups.

The sharpness of the column separations would be improved if the ion-exchanger beads had been smaller and more uniformly sized. It is apparent, however, that sharp group separations can be carried out quickly with a short resin column and with suitable adjustments in the pH of the eluent. The eluent need not contain complexing agents, as is necessary with the strong acid cation-exchangers. The macroreticular resins should be useful under conditions in which the microreticular resins show unsatisfactory exchange rates and swelling behaviour.

Acknowledgement—The authors gratefully acknowledge the assistance of the Ion Exchange Division, Rohm and Haas Company, which supplied the starting materials.

Zusammenfassung—Zwei grob vernetzte chelatbildene Ionenaustauscher wurden dargestellt und charakterisiert. Einer enthält die Iminodiacetatgruppe, der andere die Arsenatgruppe als ionenaus tauschaktive Funktion. Die grob vernetzten Harze zeigen ähnliche Auswahleigenschaften unter Metallionen wie die handelsüblichen fein vernetzten chelatbildenden Harze. Chromatographische Trennungen an den neuen Harzen sind schnell und scharf.

Résumé—On a préparé et caractérisé deux échangeurs d'ions chélatants macroréticulaires. Le premier contient le groupe iminodiacétate et le second contient le groupe arsonate comme point actif pour l'échange d'ions. Les résines macroréticulaires montrent des sélectivités parmi les ions métalliques similaires à celles des résines chélatantes microréticulaires commercialement accessibles. Les séparations chromatographiques sur les nouvelles résines sont rapides et nettes.

REFERENCES

1. R. Hering, *Chelatbildende Ionenaustauscher*, Akademie-Verlag, Berlin, 1967.
2. G. Schmuckler, *Talanta*, 1965, **12**, 281.
3. O. D. Bonner and L. L. Smith, *J. Phys. Chem.*, 1957, **61**, 326.
4. O. Samuelson, *Ion Exchange Separations in Analytical Chemistry*, pp. 221–227, 306–310. Wiley, New York, 1963.
5. R. Rosset, *Bull. Soc. Chim. France*, 1966, 59.
6. J. Persoz and R. Rosset, *ibid.*, 1964, 2197.
7. The Dow Chemical Company, Midland, Michigan, *Bulletin* 164–80, 1959.
8. R. Kunin, E. Meitzner and N. Bortnick, *J. Am. Chem. Soc.*, 1962, **84**, 305.
9. J. R. Millar, *J. Chem. Soc.*, 1963, 218, 2779; 1964, 2740; 1965, 304.
10. E. Ergozhin, *Tr. Inst. Khim. Nauk, Akad. Nauk Kaz. SSR*, 1969, **23**, 53; *Chem. Abstr.*, 1969, **71**, 62013.
11. K. A. Kun and R. Kunin, *J. Polymer Sci., C*, 1967, **16**, 1457.
12. Y. Barbier and R. Rosset, *Bull. Soc. Chim. France*, 1966, 1388.
13. P. V. Webster, J. N. Wilson and M. C. Franks, *Anal. Chim. Acta*, 1967, **38**, 193.
14. D. J. Pietrzyk, *Talanta*, 1966, **13**, 209, 225.
15. J. S. Fritz and M. L. Gillette, *ibid.*, 1968, **15**, 287.
16. M. Marhol, *Chem. Listy*, 1964, **58**, 713.
17. K. W. Pepper, H. M. Paisley and M. A. Young, *J. Chem. Soc.*, 1953, 4097.
18. V. V. Korshak, S. V. Rogozhin and V. A. Davankov, *Vysokomol. Soyed.*, 1966, **8**, 1686; *Polymer Sci. USSR*, 1966, **8**, 1860.
19. R. Hering, *J. Prakt. Chem.*, 1966, **31**, 320.

20. J. R. Parrish, *Chem. Ind.* (*London*), 1956, 137.
21. R. Kunin, *Ion Exchange Resins*, 2nd Ed., p. 338 ff. Wiley, New York, 1958.
22. A. I. Vogel, *Quantitative Inorganic Analysis*, 3rd Ed., Chapter IV. Wiley, New York, 1961.
23. Perkin–Elmer Corporation, *Analytical Methods for Atomic Absorption Spectrophotometry*, Norwalk, Conn., U.S.A., 1968.
24. Bio-Rad Laboratories, *Catalog. U.*, Richmond, Calif., U.S.A., 1969.

Talanta, 1970, Vol. 17, pp. 491 to 498. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF SOME METHYLCARBAMATE INSECTICIDES BY A.C. POLAROGRAPHY AND CYCLIC VOLTAMMETRY

M. D. BOOTH and B. FLEET
Chemistry Department, Imperial College, London, S.W.7.

(*Received* 3 *December* 1969. *Accepted* 23 *January* 1970)

Summary—The study of adsorption–desorption phenomena represents an important extension to the range of organic compounds that can be determined by electrochemical methods. The present work has utilized this approach for the determination of a range of methylcarbamate insecticides. The tensammetric behaviour of this class of compound at the mercury electrode has been investigated by a.c. polarography and the optimum experimental conditions for their analytical determination have been derived. Cyclic voltammetry has also been used to study the electrode process and by using the peak obtained on the cathodic sweep it was possible to extend the limit of detection to the ppm level.

A VARIETY of methylcarbamates are used in agriculture as insecticides. Among the most common are Carbaryl (1-naphthyl methylcarbamate), Aldecarb (formerly temik) (2-methyl-2-methylthiopropionaldehyde *O*-methylcarbamoyl oxime) and Butacarb (3,5-di-t-butylphenyl *N*-methylcarbamate), of which Carbaryl has been the most extensively studied.

The analytical methods available for the determination of this class of compound are numerous. Carbaryl has been determined both by classical methods[1,2] and a variety of spectrophotometric methods.[3-6] A number of thin-layer chromatography (TLC) methods[7-11] have also been developed of which the method of Benson and Finocchiaro[7,9] appears to be the most widely used for the determination of Carbaryl in vegetable matter. Kovacs[12] introduced an infrared method the merits of which were later compared with an ultraviolet and an alkaline distillation method.[13] Gas chromatographic (GLC)[14-19] methods are also in evidence, based mainly on the conversion of the carbamate into the corresponding phenol.

Substantially less work has been done on the determination of Aldecarb and Butacarb. Existing methods are confined to colorimetric,[20] GLC[21] and radiotracer[22] methods for Aldecarb, and a TLC/radiotracer determination[23] for Butacarb. No analytical method appears in the literature for the fourth methylcarbamate studied, Methiocarb (3,5-dimethyl-4-thiomethylphenyl *N*-methylcarbamate).

Very little investigation has been made into the electrochemical behaviour of methylcarbamates. Only Carbaryl has been determined by electrochemical techniques.[24,26] One method[24,25] is based on nitrosation of Carbaryl followed by oscillopolarography, while the other[26] involves the polarographic determination of the products resulting from nitration of the aromatic nucleus.

The present work describes a method for the direct determination of methyl carbamates, based on their adsorption–desorption phenomena. Both a.c. polarographic and cyclic voltammetric techniques have been used.

EXPERIMENTAL

Reagents

Methylcarbamates were obtained from the Ministry of Technology, Laboratory of the Government Chemist. The purity of each compound was checked by melting point determination, and where necessary they were purified by crystallization from methanol.

A $10^{-2}M$ stock solution of each compound was prepared. The solutions of Aldecarb and Carbaryl contained only 20% methanol, but because of low solubility those of Butacarb and Methiocarb were made with 100% methanol. Buffer solutions were prepared from analytical grade reagents.

Apparatus

Direct current polarograms were recorded on a Metrimpex polarograph type OH-102. A Kalousek cell with a separated saturated calomel electrode (SCE) was used. Capillary characteristics, measured at 0·0 V *vs.* SCE in $0{\cdot}1M$ potassium chloride were $t = 4{\cdot}41$ sec, $m = 1{\cdot}88$ mg/sec at $h = 0{\cdot}75$ m.

The a.c. peaks were measured with a Cambridge Univector and general-purpose polarograph with the Metrimpex polarograph as the current-output recorder. A Heyrovský cell was used with a mercury pool as the anode.

Cyclic voltammograms were obtained on a Chemtrix polarograph Model SSP-2 in the three-electrode mode. The working electrode was a hanging mercury drop electrode, Metrohm type E410. A silver wire and an SCE were used as counter and reference electrodes respectively.

Procedure

A sample containing from 0·05 to 10 μmole of the insecticide is added to 1 ml of buffer solution ($0{\cdot}5M$ boric acid/$0{\cdot}5M$ sodium hydroxide) in a 10-ml volumetric flask and diluted to volume with water/methanol so that the final solution contains 2% v/v methanol. As the methanol has an effect on the shape of the peak it is important that the methanol content in the final solution should not exceed this value. In the case of Butacarb, however, where solubility problems arise, it was found that 10% methanol could be tolerated without serious interference, assuming that 4 ml of buffer solution were used.

For the analysis of insecticide residues it is suggested that the volume of the methanol extract after clean-up should be reduced to 1–2 ml in a Kuderna evaporator.[27] The 10-ml collection flask is removed and the residue evaporated to dryness in a stream of nitrogen gas. Then 1 ml of methanol is added to the residue and an aliquot or the whole of this solution is used for analysis.

In the a.c. polarographic method the solution for analysis is transferred to a Heyrovský cell, deoxygenated with nitrogen for 3 min, and the a.c. peak is measured from 0 V *vs.* the mercury pool anode. For cyclic voltammetry, peaks were recorded over the potential range from 0 to −2·0 V *vs.* SCE, a mercury drop size of 25·2 mm² being used.

RESULTS AND DISCUSSION

None of the compounds studied shows conventional d.c. polarographic waves. However, on a.c. polarography all compounds showed current peaks at potentials in the region from −1·0 to −1·5 V. That these peaks were tensammetric in character was elucidated by the depression of the base line of the supporting electrolyte (Fig. 1), and the absence of a d.c. polarographic wave. The electrocapillary curves (Fig. 2) for these compounds showed that they were adsorbed over a voltage region either side of the electrocapillary maximum where maximum adsorption occurred. At high negative potentials the capacitive current coincides with that of the supporting electrolyte since at these potentials the surfactant is not present at the mercury-solution interface. These sharp capacitive peaks would therefore appear to be due to a desorption process, and as such reflect periodic changes in the capacity of the double layer. Contributory evidence of the tensammetric character of these peaks is the rectilinear dependence of the peak potential on the log of the concentration of insecticide. It is also worthy of note that small steps are observed in the d.c. curve for these compounds at potentials where tensammetric peaks occur. These adsorption steps are characteristically much smaller than conventional d.c. polarographic waves.

The pH dependence of the tensammetric peaks for Aldecarb, Butacarb and

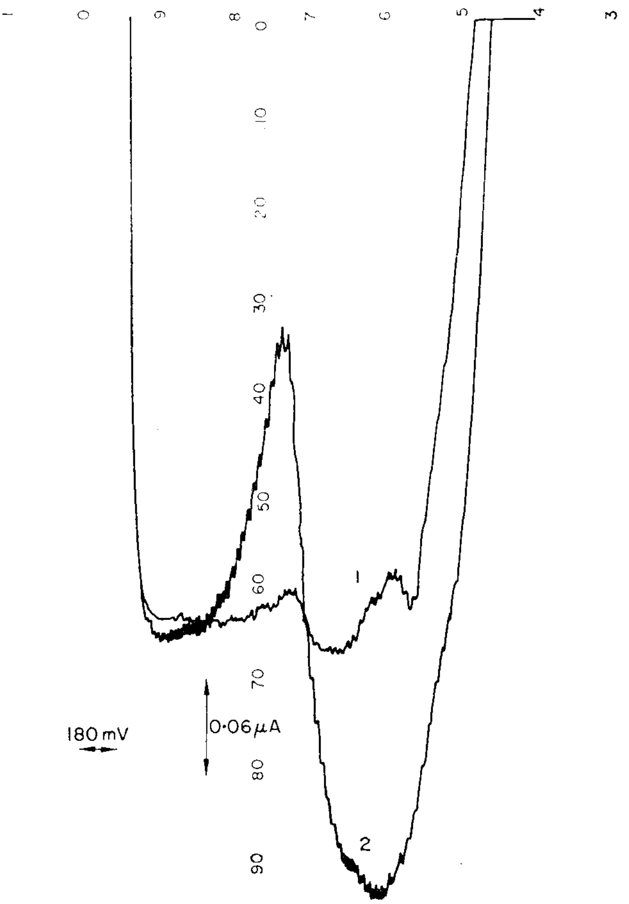


FIG. 1.—A.c. polarograms for: (1), 0; (2), 5 × $10^{-5}M$ Butacarb in 10% methanol at pH 8·98 (0·2M boric acid/0·2M sodium hydroxide); sensitivity 0·6 μA f.s.d.

Carbaryl are shown in Fig. 3. The optimum pH was found to be 8·4 (aqueous 0·5M sodium dihydrogen phosphate/0·5M sodium hydroxide buffer). The effect of variation of buffer concentration indicated that maximum peak height for Aldecarb, Methiocarb and Carbaryl was obtained in 0·05M buffer. Owing to the surface-active properties of the alcohols a maximum of 10% methanol could be tolerated. A 1–2% methanol solution was desirable. Because of the solubility of Butacarb, 10% methanol solutions 0·2M in buffer were necessary. A rectilinear dependence of peak current *vs.* concentration was obtained for all compounds and the results are summarized in Table I. The limit of detection for Aldecarb is $10^{-4}M$ as opposed to $10^{-5}M$ for the other compounds. This can be attributed to the solubility, molecular size and aliphatic nature of the compound.

The relationship between base-line depression and concentration of the surface-active carbamate is shown in Fig. 4 for Carbaryl and Aldecarb. A rectilinear relationship occurs over a limited concentration range, above which the form of a Langmuir isotherm is followed. This would appear to signify that the mercury surface is now completely covered with the adsorbed species.

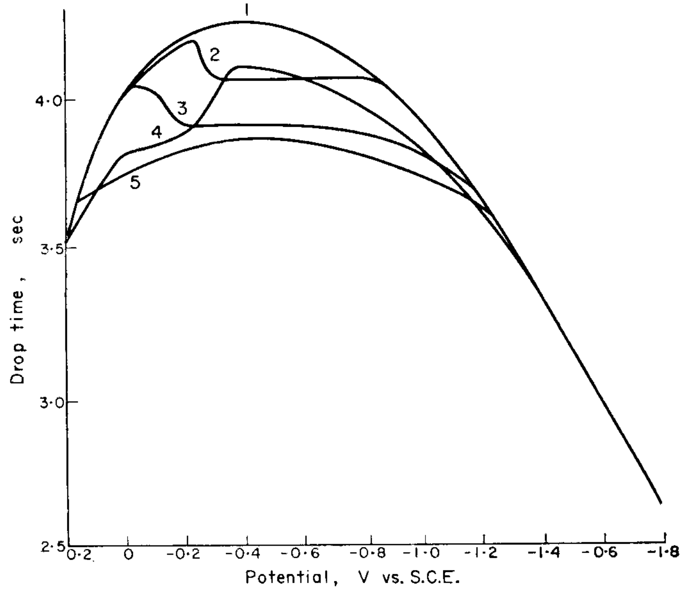


Fig. 2.—Electrocapillary curves for: (1), 0·05M boric acid/0·05M sodium hydroxide buffer in 2% methanol; (2), $5 \times 10^{-4}M$ Aldecarb in 0·05M buffer/2% methanol; (3), $10^{-4}M$ Methiocarb in 0·05M buffer/2% methanol; (4), $5 \times 10^{-5}M$ Butacarb in 0·2M buffer/10% methanol; (5), $2 \times 10^{-4}M$ Carbaryl in 0·05M buffer/2% methanol.

The effect of various cations (0·1M as chlorides) and various anions (0·1M as sodium salt) on the tensammetric peaks was investigated. In the case of cations the desorption potentials are increasingly negative in the sequence $La^{3+} < Mg^{2+} < Li^{+}$. The observed effect will to some effect depend on the displacement capability of the cation and the solubility of the species in solution. In the case of the anions NO_2^-, NO_3^-, ClO_4^-, CO_3^{2-}, CN^-, SO_4^{2-}, the effect on peak height and peak potential

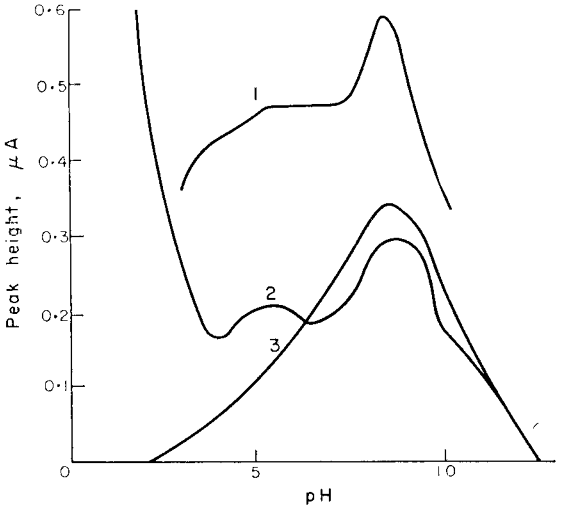


Fig. 3.—pH dependence of (1), $2 \times 10^{-4}M$ Carbaryl, and (2), $5 \times 10^{-4}M$ Aldecarb in 0·05M buffer/2% methanol; (3), $5 \times 10^{-5}M$ Butacarb in 0·2M buffer/10% methanol.

TABLE I.—CONCENTRATION DEPENDENCES FOR METHYLCARBAMATES

Concentration of methylcarbamate M	Current, μA							
	a.c. polarography				cyclic voltammetry			
	B	C	M	A	B	C	M	A
2×10^{-6}	—	—	—	—	—	—	—	—
4×10^{-6}	—	—	—	—	0·40	—	0·40	—
6×10^{-6}	—	—	—	—	0·60	0·45	0·60	—
8×10^{-6}	—	—	—	—	0·87	0·60	0·75	
1×10^{-5}	0·05	—	0·05	—	1·10	0·70	1·00	—
2×10^{-5}	0·07	0·05	0·09	—	2·00	1·30	2·40	—
4×10^{-5}	0·17	0·09	0·22	—	4·40	2·40	4·70	
6×10^{-5}	0·28	0·14	0·29	—	6·60	3·20	7·60	0·30
8×10^{-5}	0·37	0·18	0·41	—	9·00	4·40	9·20	0·40
1×10^{-4}	0·49	0·24	0·52	0·06	11·00	4·80	11·40	0·50
2×10^{-4}	L.S.	0·50	L·S.	0·12	—	—	—	0·95
4×10^{-4}	—	1·00	—	0·28	—	—	—	1·70
6×10^{-4}	—	1·41	—	0·43	—	—	—	2·80
8×10^{-4}	—	1·73	—	0·59	—	—	—	3·75
1×10^{-3}	—	2·07	—	0·71	—	—	—	4·40

B—Butacarb; C—Carbaryl; M—Methiocarb; A—Aldecarb. L.S.—Limited by solubility.

follows no specific pattern. This is primarily because at negative potentials it is the cation that determines the capacity and structure of the double layer. However, an interesting observation is that the shifts in the desorption potentials caused by changing the nature of the halide ion follow the same sequence as the salting-out coefficient for benzene in aqueous solution[28] (Fig. 5). This phenomenon was first noticed by Gierst and Pecasse[29] in a study of the effect of anions on the adsorption–desorption of pyridine at the dropping mercury electrode. Only the effect of fluoride on the desorption potential for Butacarb is anomalous.

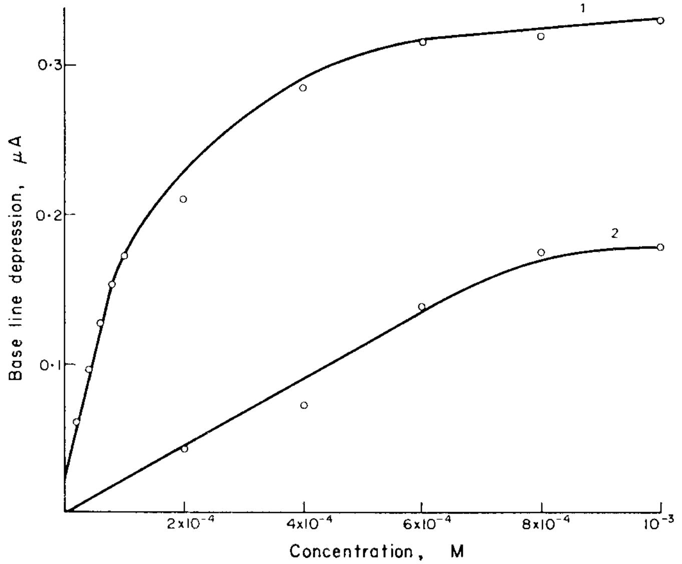


FIG. 4.—Base-line depression *vs.* concentration for (1), Carbaryl and (2), Aldecarb in 0·05M boric acid, 0·05M sodium hydroxide buffer (pH 8·4), 2% methanol.

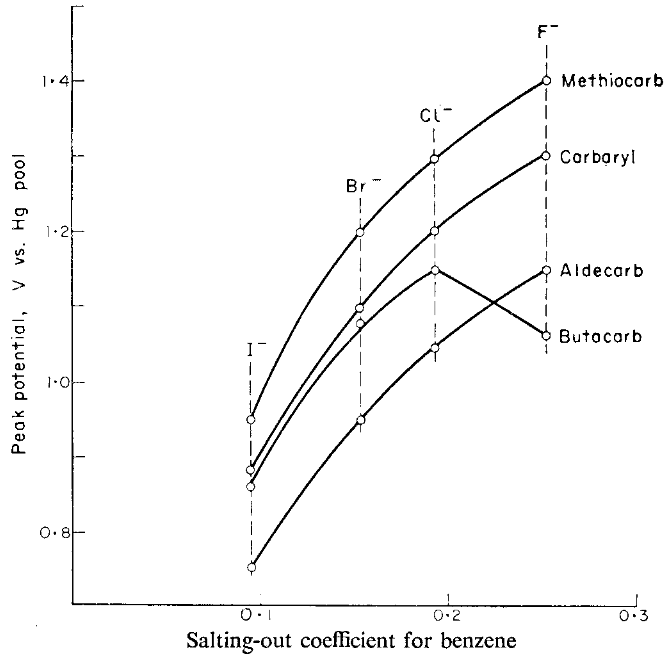


Fig. 5.—Relation between desorption potential of methylcarbamates on mercury, and salting-out coefficient for benzene; solutions as used for measurement of electrocapillary curves; halide concentration, 0·1*M*.

The extent of adsorption of the organic molecule is therefore not entirely governed by its own solubility. The solubility of the supporting electrolyte and any extraneous ions in solution must also be considered. This is an inherent drawback in the analytical utility of capacitive (tensammetric) peaks. The conditions under which the experiment is to be conducted must be clearly defined and closely adhered to.

Cyclic voltammetry

The cyclic voltammogram for Butacarb is shown in Fig. 6. A single cathodic–anodic peak is observed at the sweep rates used. The cathodic peak corresponds to

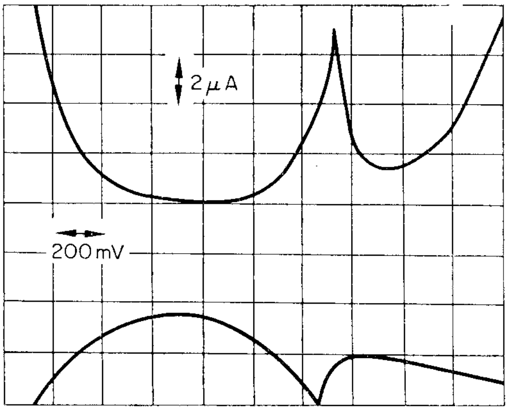


Fig. 6.—Cyclic voltammogram of 5 × $10^{-5}M$ Butacarb in 0·2*M* boric acid/0·2*M* sodium hydroxide buffer, 10% methanol. Scan rate, 4 V/sec.

the tensammetric peak described earlier caused by the desorption of the surface-active carbamate compound. This peak was utilized for analytical purposes. The anodic peak observed on the reverse scan is due to adsorption of the carbamate onto the electrode surface, replacing the cations of the supporting electrolyte. Methiocarb and Carbaryl show similar behaviour. Aldecarb shows in addition the capacitive peaks corresponding to adsorption of the surfactant on the cathodic scan, and desorption on the reverse scan.

A rectilinear dependence of peak current against concentration was observed for all compounds (Table I). Concentrations of the order of $5 \times 10^{-6}M$ (1 ppm) for Butacarb, Carbaryl and Methiocarb must be taken as the lower limit attainable with the apparatus used. The limit for Aldecarb is $5 \times 10^{-5}M$.

Acknowledgements—We wish to thank the Agricultural Research Council for the provision of a research assistantship for one of us (M. D. B.).

Zusammenfassung—Die Untersuchung von Adsorptions- und Desorptionserscheinungen stellt eine wichtige Erweiterung der Auswahl von organischen Verbindungen dar, die mit elektrochemischen Methoden bestimmt werden konnen. Die vorliegende Arbeit benutzte dieses Verfahren zur Bestimmung verschiedener Methylcarbamat-Insektizide. Das tensametrische Verhalten dieser Verbindungsklasse an der Quecksilberelektrode wurde mit Hilfe der Wechselstrompolarographie untersucht und die optimalen Versuchsbedingungen für die analytische Bestimmung solcher Substanzen ermittelt. Zur Untersuchung des Elektrodenprozesses wurde auch die cyclische Voltammetrie eingesetzt; mit Hilfe des Peaks, den man beim kathodischen Durchlauf erhält, ließ sich die Nachweisgrenze bis zum ppm-Bereich herabdrücken.

Résumé—L'étude des phénomènes d'adsorption–désorption représente une extension importante au domaine des composés organiques que l'on peut déterminer par des méthodes électrochimiques. Le présent travail a utilisé cette approache pour la détermination d'une série d'insecticides méthylcarbamatés. Le comportement tensammétrique de cette classe de composés à l'électrode de mercure a été étudié par polarographie en courant alternatif et l'on en a déduit les conditions expérimentales optimales pour leur détermination analytique. On a aussi utilisé la voltamétrie cyclique pour étudier le processus à l'électrode et en utilisant le pic obtenu sur le balayage cathodique il a été possible d'étendre la limite de détection au niveau de la *ppm*.

REFERENCES

1. M. A. Zugravescu and P. Gh. Zugravescu, *Rev. Chim.* (*Bucharest*), 1967, **18**, 430.
2. Yu. V. Lyande and A. A. Cherkasskii, *Zavodsk. Lab.* 1965, **31**, 799.
3. E. Nesemann, R. Schroeder and F. Sechofer, *Beitr. Tabakforsch.* 1968, **4**, 197.
4. M. A. Klisenko, *Zh. Analit. Khim.*, 1965, **20**, 634.
5. G. G. Guilbault and M. H. Sadar, *Anal. Chem.*, 1969, **41**, 366.
6. K. Wilhelm, J. Matkoviĉ and K. Weber, arch. Toxicol., 1968, **23**, 197.
7. J. M. Finocchiaro and W. R. Benson, *J. Assoc. Offic. Anal. Chem.*, 1965, **48**, 736.
8. R. Engst and D. Spranger, *Nahrung*, 1964, **8**, 653.
9. J. M. Finocchiaro and W. R. Benson, *J. Assoc. Offic. Anal. Chem.*, 1967, **50**, 888.
10. L. J. Faucheux Jr., *ibid.*, 1968, **51**, 676.
11. P. J. Wales, H. A. McLeod and W. P. McKinley, *ibid.*, 1968, **51**, 1239.
12. M. F. Kovacs Jr., *ibid.*, 1967, **50**, 566.
13. E. J. Broderick, R. M. Sherman and G. L. Mack, *ibid.*, 1968, **51**, 379.
14. L. Fishbein and W. L. Zielinski Jr., *J. Chromatog.*, 1965, **20**, 9.
15. *Idem, J. Gas Chromatog.*, 1965, **3**, 331.
16. J. W. Ralls and A. Cartes, *ibid.*, 1964, **2**, 132.

17. C. H. Van Middelem, T. L. Norwood and R. E. Waites, *ibid.*, 1965, **3**, 310.
18. L. I. Bulter and L. M. McDonough, *J. Agr. Food Chem.*, 1968, **16**, 403.
19. E. R. Holden, W. M. Jones and M. Beroza, *ibid.*, 1969, **17**, 56.
20. W. R. Meagher, R. Hendrickson and D. G. Shively, *J. Assoc. Offic. Anal. Chim.*, 1967, **50**, 1242.
21. J. C. Maitlen, L. M. McDonough and M. Beroza, *ibid.*, 1969, **52**, 786.
22. J. B. Knaak, M. J, Pallant, F. J. Kozbelt and L. J. Sullivan *J. Agr. Food Chem.*, 1968, **16**, 465.
23. M. W. Baker, E. L. Crampton, R. Harrison and T. I. Watkins, *ibid.*, 1967, **18**, 392.
24. R. J. Gajan, W. R. Benson and J. M. Finocchiaro, *J. Assoc. Offic. Agric. Chem.*, 1965, **48**, 958.
25. W. R. Benson and R. J. Gajan *J. Org. Chem.*, 1966, **31**, 2498.
26. R. Engst, W. Schnaak and H. Woggon, *Z. Anal. Chem.*, 1965, **207**, 30.
27. M. D. Booth and B. Fleet, *Anal. Chem.*, in press.
28. F. A. Long and W. F. McDevit, *Chem. Rev.*, 1952, **51**, 119.
29. L. Gierst and C. Pecasse, *Polarography* 1964, *Proc. 3rd. Intern. Conf. Southampton*, p. 305.

Talanta, 1970, Vol. 17, pp. 499 to 513. Pergamon Press. Printed in Northern Ireland

CATALYTIC REACTIONS—I

MECHANISMS

P. R. BONTCHEV
Department of Analytical Chemistry, University of Sofia, 1 Anton Ivanov Str., Sofia 26, Bulgaria

(*Received* 6 *August* 1969. *Accepted* 19 *January* 1970)

Summary—The mechanisms of some reactions used in catalytic analysis are discussed. The knowledge of the mechanism of a catalytic reaction can help in the development of new catalytic reactions and the choice of optimal conditions, and to show the possibilities for further increases in sensitivity.

THE RECENT intensive development of catalytic methods of analysis is a result of their high sensitivity combined with relatively simple procedures. More than 250 procedures are known for the determination of about 45 elements. Some monographs have been published[1–6] as well as the biennial reviews in *Analytical Chemistry*.

Many different types of catalytic reaction have been used for analytical purposes. In the present paper an attempt is made to generalize the results of investigations on the mechanisms of catalytic reactions in the hope that it will help in the development of new, *improved*, analytical procedures.

The homogeneous reactions used for the catalytic determinations of ions can be classified according to whether the catalytic ions change their oxidation state or not.

REACTIONS CATALYSED BY IONS THAT CHANGE THEIR OXIDATION STATE DURING THE REACTION

Most of the useful catalytic methods are based on reactions in this group, which includes the most sensitive reactions (sensitivity is usually 0·1–10^{-4} ppm, sometimes as low as 1 ppb) and hence those most frequently used.

A catalytic cycle frequently observed is:

$$\text{Red} + \text{M}^{(n+1)+} \rightarrow \text{P} + \text{M}^{n+} \tag{1}$$

$$\text{M}^{n+} + \text{Ox} \rightarrow \text{M}^{(n+1)+} + \text{Q} \tag{2}$$

where Red and Ox are the reagents of the redox reaction, and P and Q are the reaction products. The role of the oxidant Ox is simply to return the catalyst, the actual oxidant of Red, to its lower oxidation state, equation (2). Typical examples are transition metal ions in different oxidation states, such as vanadium, manganese, iron, copper, osmium, rhenium, or non-metal ions such as iodide and bromide.

A reaction of this type should be suitable for analytical purposes if the following two conditions are also satisfied:

(*a*) the oxidation potential E_{M} of the couple $\text{M}^{(n+1)+}/\text{M}^{n+}$ under the reaction conditions is higher than the potential E_{Red} of the couple P/Red and lower than the oxidation potential E_{Ox} of the couple Ox/Q, *i.e.*,

$$E_{\text{Ox}} > E_{\text{M}} > E_{\text{Red}}$$

(*b*) the direct interaction of Red with Ox which is thermodynamically permitted is hindered kinetically, whereas the oxidation of M^{n+} by Ox proceeds readily.

REACTIONS WITH ORGANIC SUBSTRATES

Reactions of this type usually involve the oxidation of an arylamine, phenol or dye-stuff. The oxidation of arylamines and phenols leads to the formation of coloured products, whereas the oxidation of dyestuffs most frequently involves decolorization. Thus the kinetics of such reactions are usually followed colorimetrically.

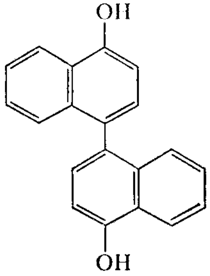
These oxidations are usually slow, but are catalysed by metal ions. When transition metal ions (and other one-electron oxidants) are used, the first step of arylamine or phenol oxidation is always homolytic:[7,8]

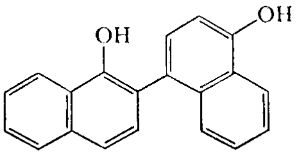
$$RH + M^{(n+1)+} \rightarrow R^{\cdot} + H^{+} + M^{n+} \tag{3}$$

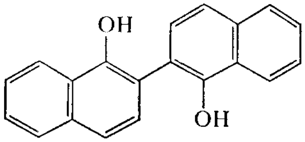
where $R^{\cdot}$ represents an arylamine radical $ArNH^{\cdot}$ or an aryloxy radical $ArO^{\cdot}$. The low ionization energy of arylamines and phenols permits the ready removal of the electron.[9] The radicals are also stabilized by conjugation of the unpaired $2p_z$ electron from nitrogen or oxygen with the π-electron system of the aromatic ring.[10] Reactants with substituents which increase the electron density in the conjugated system are oxidized more easily, therefore, than the corresponding non-substituted or electrophilically substituted compounds. Thus, the homolytic oxidation of polyphenols, arylamines, aminophenols, alkyl- and alkoxy-substituted phenols and arylamines proceeds very readily.[11–14]

The homolytic mechanism of the one-electron oxidation of these compounds by metal ions has been confirmed by kinetic data, initiation of polymerization processes, reduction of mercury(II) chloride, *etc.*[15–18] Direct evidence of the formation of free radicals has been provided by electron paramagnetic resonance.[19–24]

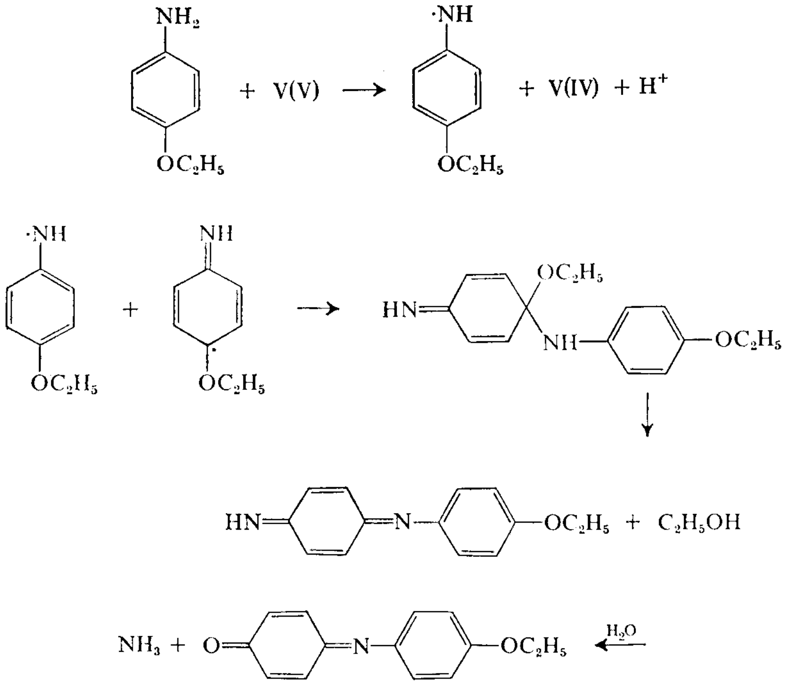
The large number of possible final reaction products arises because of the different ways in which the radical $R^{\cdot}$ can react further. These depend on its structure, reactivity and the reaction conditions,[7,14,25–28] and especially on the localization of the unpaired electron. For example, the localization of the electron at the 2 and 4 positions in the 1-naphthol radical results in the formation of three products when α-naphthol is oxidized by iron(III) chloride[29]:







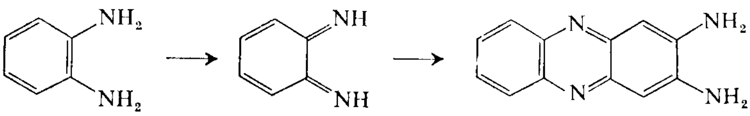
If a favoured position is hindered by a bulky substituent (such as phenyl, naphthyl, *etc*) at this position, the number of products is reduced. Less bulky substituents, however, do not prevent reaction at this position. Thus the catalytic oxidation of *p*-phenetidine by halates, with vanadium(V) as a catalyst, proceeds as follows[30]:



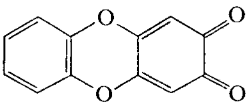
(4)

If the quinolide is stable it might form the final reaction product as in the oxidation of 1-methyl-2-naphthol (see ref. 14, p. 142).

Reaction of the radical in which the unpaired electron is localized *o*- to the —O or —NH group leads to the formation of heterocyclic compounds such as (see ref. 14, p. 149):

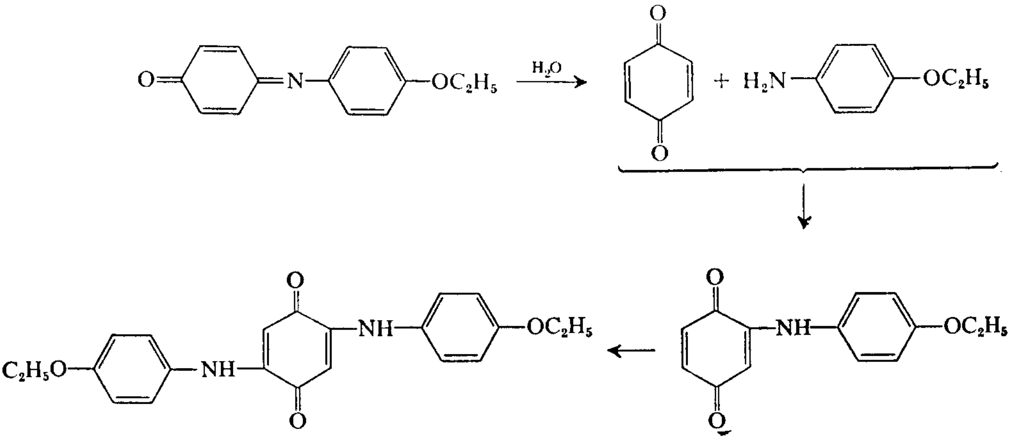


Catechol gives (see ref. 14, p. 146):



The formation of primary radicals from arylamines or phenols and their further reaction strongly depend on the acidity of the reaction medium. In acidic solutions the reactions usually lead to the formation of a smaller number of reaction products of relatively low molecular weight. There are many reasons for such a behaviour. Reaction (3) proceeds less easily in acidic solution, and the co-ordination of a metal ion with the free electron-pair of nitrogen or oxygen is more difficult in an acidic solution because of the competition of the hydrogen ions for the electron pair so that the radical formation is again hindered. The high rate of radical formation in alkaline solution increases the concentration of R$^{\cdot}$ so that the number of products likely to be formed is increased. Alkaline media also stabilize some types of radicals such as semiquinones, formed during the oxidation of polyphenols. The symmetric radical $^{\cdot}OPhO^{-}$ is formed.[31]

Acidity can also affect side-reactions such as hydrolyses, condensations, *etc.* Thus quinoneimines, formed during the oxidation of arylamines in neutral or alkaline solutions slowly hydrolyse to quinone and the amine. Further interaction gives mono- and diarylidoquinones as the final reaction products. Thus the oxidation of *p*-phenetidine shown by equation (4) in solutions of pH $\geqslant$ 5 proceeds further:[32]



(5)

Arylidoquinones are not very suitable as final reaction products for analytical procedures based on photometric measurements, because of their low water solubility; they form red-brown precipitates. This is yet another reason for avoiding alkaline reaction media for such reactions. Temperatures above 40–50° must be avoided because the rate of hydrolysis of quinoneimines according to equation (5) strongly increases on heating.

The disadvantage of the formation of polymeric or complex heterocyclic products (water-insolubility) is largely overcome by using compounds containing hydrophilic groups (OH, COOH, SO_3H *etc*). Thus sulphanilic acid, amino- and hydroxynaphthylsulphonic acids, aminocarboxylic acids, *etc*, have received great attention as reagents in catalytic analysis.[33–38] Alternatively, the solubility of the coloured reaction products can be enhanced by using water–organic solvent mixtures. Yatsimirskii and Philipov[39] used aqueous ethanol as solvent for the oxidation of 1-naphthylamine by potassium bromate, catalysed by molybdenum(VI).

Yatsimirskii has shown that the sensitivity of a catalytic method depends on the sensitivity of the method used to monitor the reaction.[6] Thus, when a spectrophotometric method is used, the reactants should be chosen so as to give a reaction product of high molar absorptivity. Quinoneimines and arylidoquinones are usually more intensely coloured than quinones, and their absorption bands fall in the spectral range where the sensitivity of the detectors is highest. These data, combined with those for the solubility of the corresponding compounds, indicate that quinoneimines are the reaction products most suitable for high sensitivity analysis.

Alternatively, the use of highly coloured products as indicator substances allows the reaction to be followed immediately after the start of the reaction, when the concentration x of the coloured reaction product is negligible compared to the initial reactant concentration C_0. The kinetic equation then simplifies to

$$\frac{dx}{dt} = kC_0 \tag{6}$$

where t is the time and k is the rate constant.

This equation gives a linear dependence between absorbance and time, which permits simple recording devices to be used and the time necessary for the analytical determinations to be shortened to 2–4 min.[40,41]

When both *o*- and *p*-positions in a phenol or arylamine molecule are hindered by bulky substituents, stable radicals are formed.[19] These radicals have molar absorptivities (in the visible part of the spectrum) of the order of 300–500 l. mole^{-1} mm^{-1} which makes them suitable for catalytic analysis purposes. Their main advantage is that usually reactions forming such radicals lead only to one product. Although the radicals are not very soluble in aqueous solution, organic solvent–water mixtures can be used as a reaction medium. However, such reactions have not yet been used in catalytic analysis, although their chemistry has been studied in some detail.[19]

Nature of the catalyst-reactant interaction

Most often, the first stage of the catalytic reaction is the substitution of water or another ligand attached to the metal ion, by the amine or phenol. In many instances this results in the formation of a charge-transfer complex. The catalyst, having free *d*-orbitals, acts as a strong Lewis acid and partially receives an electron from the highest energy nitrogen or oxygen orbital that is populated. The existence of such a complex was shown in the catalytic oxidation of *p*-phenetidine, discussed above.[42] The positively charged complex formed between the catalyst and the amine has an absorption band with a maximum at 540 nm and a molar absorptivity of 10^2–10^3 l. mole^{-1} mm^{-1}. At temperatures below 5° the complex is comparatively stable but at higher temperatures an oxidation process takes place, which results in the formation of an arylamino radical:

$$\begin{aligned} &\mathrm{V(V)} + \mathrm{H_2N\,.\,C_6H_4\,.\,OC_2H_5} \rightarrow \mathrm{V(V)\ldots H_2N\,.\,C_6H_4\,.\,OC_2H_5} \\ &\qquad \rightarrow \mathrm{V(IV)} + {}^{\cdot}\mathrm{NH\,.\,C_6H_4\,.\,OC_2H_5} + \mathrm{H^+} \end{aligned} \tag{7}$$

The process proceeds further according to reaction scheme (4).

The formation of such complexes makes it easier to understand, for example, why titanium(IV) catalyses oxidation processes with oxygen-containing ligands but not with nitrogen-containing ones and why silver(I) preferentially catalyses oxidation reactions of nitrogen-containing reactants. Thus the arylamine or phenol chosen must be suitable for complexation with the catalyst. The pH of the medium must also be chosen so as not to decrease the degree of complexation with the catalyst.

Copper(II) in alkaline solution catalyses the oxidation of arylamines and phenols but in slightly acidic solutions it catalyses only the arylamine oxidation. This can be ascribed to the different stability of copper(II) complexes with oxygen- and nitrogen-containing ligands.

Complex formation between the catalyst and the reactant offers possibilities for the regulation of the selectivity of catalytic methods. The tendency of the amine or phenol to complex with metal ions can be modified if suitable substituents are introduced in the substrate molecule or if the acidity of the reaction medium is adjusted to a suitable value.

Indirect catalytic oxidation

In this process the catalyst takes part in a reaction which produces the actual oxidant of the other reactant. Thus copper, iron and titanium compounds catalyse the oxidation of many organic substances by hydrogen peroxide. Most frequently the role of the catalyst in these processes is to produce hydroxyl radicals from hydrogen peroxide, and these are the real oxidant. For example, Fenton's reagent acts as follows:

$$Fe^{2+} + H_2O_2 \rightarrow FeOH^{2+} + {}^{\cdot}OH \qquad (8)$$

$${}^{\cdot}OH + RH \rightarrow H_2O + {}^{\cdot}R \qquad (9)$$

Catalytic systems of this type are very useful for the oxidation of compounds with sterically hindered donor atoms or with donor atoms which do not tend to form complexes with the catalyst. In such instances small uncharged radicals with a high oxidation potential (such as $^{\cdot}OH$) can be produced by a catalytic reaction and used up for the oxidation of the substrate.

Another example of this type is the accelerating action of phenols and hydroxy-carboxylic acids on the oxidation of arylamines catalysed by vanadium(V).[30,43–48] The tendency of oxygen donor atoms to complex with vanadium(V) is greater than that of nitrogen, so that charge-transfer complex formation and hence the oxidation processes with phenols proceed more readily than with arylamines. The phenoxy radicals produced oxidize the arylamine very rapidly, and therefore increase the overall reaction rate. These reactions are examples of activated catalytic processes, which will be discussed in detail in Part II.

The choice of a suitable oxidant for a catalytic oxidation is as important as the choice of the reductant, and is primarily governed by the two conditions stated in the introduction. Usually it is not difficult to find an oxidant with an oxidation potential higher than that of the reductant. The condition $E_{OX} > E_M$, however, restricts the number of possible oxidants especially when the oxidation potential of the couple $M^{(n+1)+}/M^{n+}$ is high. For example, there are only two oxidants used in the catalytic reactions of silver(I)—persulphate ion[33] and cerium(IV)[49] which can oxidize silver(I) to silver(II) ($E_M^0 = 2{\cdot}00$ V). Sometimes this restriction can be overcome by using a suitable complexing agent to lower the oxidation potential of the couple $M^{(n+1)+}/M^{n+}$.[33] In such instances the complexes of the ligand with the form of the catalyst that participates in the rate-limiting reaction step must be labile. Examples of this type will be discussed in detail in Part II.

The main difficulties in choosing a suitable oxidant arise from the second condition—the existence of kinetic obstacles to direct interaction between the reductant and the oxidant. Oxidants such as permanganate, cerium(IV), manganese(III), and cobalt(III) which react readily with organic compounds are seldom used for catalytic oxidation process with organic substances. When hydrogen peroxide is used as an oxidant, the greatest difficulty is the purification of the reagents from commonly occurring metals ions such as Cu^{2+}, Fe^{3+}, Mn^{2+}, Co^{2+} which catalyse the oxidations by hydrogen peroxide even when present in very small amounts. However, these catalytic effects can become an advantage when such ions are to be determined: many sensitive analytical catalytic procedures have been developed for the determination of these ions, using hydrogen peroxide as the oxidant.[50–55]

Halates are very suitable as oxidants for catalytic oxidations of organic substrates. At 20–50° they usually react only very slowly with organic compounds in spite of their relatively high oxidation potential. However, under such conditions they can oxidize rapidly many metal ions, especially the lower oxidation states of molybdenum, tungsten, vanadium and osmium.

Persulphate is another oxidant often used in catalytic analysis. It readily oxidizes silver(I) and copper(I) to higher oxidation states and thus is used in catalytic methods for the determination of these elements. However, the measurable rate of the uncatalysed oxidation is a serious disadvantage. This arises because persulphate dissociates in solution to give sulphate radicals:

$$S_2O_8^{2-} \rightarrow 2\,{}^{\cdot}SO_4^- \qquad (10)$$

which themselves oxidize the organic compound. Other authors[56] consider that persulphate acts through the production of hydroxyl radicals:

$${}^{\cdot}SO_4^- + H_2O \rightarrow HSO_4^- + {}^{\cdot}OH \qquad (11)$$

REDOX REACTIONS WITH INORGANIC SUBSTRATES

Inorganic reductants used in catalytic reactions are usually monodentate and charged, and, of course, are smaller than the organic molecules discussed above. Typical examples are I^-, Cl^-, $S_2O_3^{2-}$, AsO_2^- and NH_3.

Reactions in which more than one electron is transferred have been postulated as proceeding by one- or two-electron mechanisms, that is, by several one-electron steps or by a simultaneous transfer of two or even more electrons. The one-electron scheme has been supported by numerous experimental data not only for such reactions as

$$\begin{gathered} \mathrm{Ag(II)} + \mathrm{Fe(II)} \rightarrow \mathrm{Ag(I)} + \mathrm{Fe(III)} \qquad (12) \\ \mathrm{Ag(I)} + \mathrm{Fe(II)} \rightarrow \mathrm{Ag^0} + \mathrm{Fe(III)} \end{gathered}$$

but also for more complicated reations as, for example, the oxidation of sulphurous acid with iron(III), catalysed by copper(II)[57]:

$$\begin{gathered} \left.\begin{array}{r} \mathrm{Fe(III)} + H_2SO_3 \rightarrow \mathrm{Fe(II)} + {}^{\cdot}HSO_3 + H^+ \\ \mathrm{Fe(II)} + {}^{\cdot}HSO_3 + H^+ \rightarrow \mathrm{Fe(III)} + H_2SO_3 \end{array}\right\} \text{slow} \\ 2\,{}^{\cdot}HSO_3 \rightarrow H_2S_2O_6 \qquad (13) \\ \left.\begin{array}{r} \mathrm{Fe(III)} + {}^{\cdot}HSO_3 + H_2O \rightarrow \mathrm{Fe(II)} + SO_4^{2-} + 3H^+ \\ \mathrm{Cu(II)} + {}^{\cdot}HSO_3 + H_2O \rightarrow \mathrm{Cu(I)} + SO_4^{2-} + 3H^+ \end{array}\right\} \text{fast} \\ \mathrm{Cu(I)} + \mathrm{Fe(III)} \rightarrow \mathrm{Cu(II)} + \mathrm{Fe(II)} \end{gathered}$$

In some inorganic redox reactions, as for instance those involving thallium (III), *e.g.*,

$$\mathrm{Hg^0} + \mathrm{Tl(III)} \rightarrow \mathrm{Hg(II)} + \mathrm{Tl(I)} \qquad (14)$$

a two-electron mechanism is thought to occur.[58] Ashurst and Higginson, however, have shown that the kinetic data for similar reaction with iron(II) strongly indicate a one-electron mechanism:[59]

$$\mathrm{Fe(II)} + \mathrm{Tl(III)} \leftrightharpoons \mathrm{Fe(III)} + \mathrm{Tl(II)} \tag{15}$$

$$\mathrm{Tl(II)} + \mathrm{Fe(II)} \rightarrow \mathrm{Tl(I)} + \mathrm{Fe(III)}$$

As Basolo and Pearson emphasized "at the present time there is no good evidence that simultaneous, or near-simultaneous, transfer of more than one electron in a true electron-transfer reaction ever occurs".[60]

In most instances the existence of a two-electron mechanism is connected with the transfer of an atom or a group of atoms from one reactant to the other, as, for example:[61]

$$\mathrm{O_2SO^{2-}} + \mathrm{OCl^-} \rightarrow \mathrm{O_2SO_2^{2-}} + \mathrm{Cl^-} \tag{16}$$

It is of interest in this connection to quote the conclusions of Higginson[62] drawn after considering the mechanisms of many redox reactions:

(*a*) species derived from transition elements react by a set of one-electron steps;

(*b*) if both reacting species are derived from non-transition elements, two-electron reactions usually take place;

(*c*) if one of the reagents is a transition-element ion and the other compound is derived from a non-transition element, the one-electron mechanism occurs more often;

(*d*) if one of the reactants is a free radical, a one-electron reaction is to be expected.

In connection with catalytic analysis it is of interest to note that the reactions with the participation of transition-element species usually proceed by one-electron mechanisms. It can be seen that even in the few examples of two-electron reactions [of type (*c*)] the main reason that they were included in this group is that it had been impossible to detect the intermediates which correspond to one-electron mechanisms with the techniques then available. For this reason the importance of the application in this field of new physical methods such as EPR and NMR can hardly be overestimated.

The one-electron mechanism of many redox reactions catalysed by transition-element ions often results in the production of unstable intermediates. Duke has suggested the term "reactates" for such species,[63] which includes free radicals ($\cdot\mathrm{SO_4^-}$, $\cdot\mathrm{OH}$), atoms (Cl, O) or species in unfamiliar oxidation states [Mn(V), Sn(III)]. Many examples are known of the formation of reactates in the course of the catalytic reactions. For example, the role of $\cdot\mathrm{SO_4^-}$ and $\cdot\mathrm{OH}$ in redox reactions with $\mathrm{S_2O_8^{2-}}$ and $\mathrm{H_2O_2}$ has already been discussed.

The oxidation of hydrazine by iron(III), catalysed by copper(II),[64] proceeds through the formation of the radical $\cdot\mathrm{N_2H_3}$:

$$\begin{gathered}
\mathrm{N_2H_4} + \mathrm{Fe(III)} \xrightarrow{\text{fast}} \cdot\mathrm{N_2H_3} + \mathrm{Fe(II)} + \mathrm{H^+} \\
\cdot\mathrm{N_2H_3} + \mathrm{Fe(III)} \xrightarrow{\text{slow}} \mathrm{N_2H_2} + \mathrm{Fe(II)} + \mathrm{H^+} \\
\cdot\mathrm{N_2H_3} + \mathrm{Cu(II)} \xrightarrow{\text{fast}} \mathrm{N_2H_2} + \mathrm{Cu(I)} + \mathrm{H^+} \\
\mathrm{Cu(I)} + \mathrm{Fe(III)} \xrightarrow{\text{fast}} \mathrm{Cu(II)} + \mathrm{Fe(II)} \\
2\,\cdot\mathrm{N_2H_3} \rightarrow \mathrm{N_4H_6} \rightarrow 2\mathrm{NH_3} + \mathrm{N_2}
\end{gathered} \tag{17}$$

The catalytic effect is thus due to the greater reactivity of copper(II) in the oxidation of $^{\cdot}N_2H_3$ compared with iron(III), which is possibly due to the stronger tendency of copper(II) to complex with nitrogen-containing donors. The oxidation of iodide by dichromate, catalysed by iron(II), proceeds *via* the formation of Cr(V) and Cr(IV) as intermediates in the reduction of Cr(VI) and Cr(III) (see ref. 4, p. 309).

The catalysts of inorganic redox reactions act most often by a direct mechanism, by alternate oxidation–reduction processes with the oxidant and reductant. Thus in the oxidation of chloride by cerium(IV) the catalyst silver acts through the oxidation states Ag(I) and Ag(II).[49] The oxidation of iodide by halates in the presence of vanadium compounds proceeds *via* the consecutive formation of V(IV) and V(V).[65] Another example of this type of mechanism is provided by the oxidation of arsenic(III) with cerium(IV), catalysed by iodide or osmium(VIII). Thus, one of the most widely used catalytic reactions is considered[66] to proceed *via*

$$\begin{aligned} I^- + \mathrm{Ce(IV)} &\rightarrow \mathrm{Ce(III)} + I^0 \\ I^0 + \mathrm{As(III)} &\rightarrow \text{intermediate} \\ \text{intermediate} + \mathrm{Ce(IV)} &\rightarrow \mathrm{Ce(III)} + \mathrm{As(V)} + I^- \end{aligned} \tag{18}$$

An alternative is

$$\begin{aligned} I^0 + \mathrm{Ce(IV)} &\rightarrow \mathrm{Ce(III)} + I^+ \\ I^+ + \mathrm{As(III)} &\rightarrow \mathrm{As(V)} + I^- \end{aligned} \tag{19}$$

The catalytic action of osmium also involves its alternate reduction and oxidation.[67]

An indirect catalytic mechanism does sometimes occur, probably, for example, in the oxidation of ammonia by hydrogen peroxide, catalysed by copper compounds.[68] Copper(II) cannot oxidize ammonia, but it reacts with peroxide to form hydroxyl radicals, which oxidize the ammonia. The oxidation of iodide by hydrogen peroxide, catalysed by iron compounds, is probably another example of this type.[69]

In other instances, the catalyst is produced during the reaction as one of the reaction products, so that the process becomes autocatalytic, as in the oxidation of arsenite by iodate, catalysed by iodide:[70]

$$IO_3^- + 3AsO_2^- \rightleftharpoons I^- + 3AsO_3^- \tag{20}$$

Complex formation between the catalyst and the reagents during the reaction seems to be important in inorganic catalytic redox reactions although only in a few instances is there direct experimental evidence for intermediates of this type.[71,72] At the same time, many considerations indicate the formation of such complexes. For example, the addition of ligands that form stable, inert complexes with the catalyst usually results in an inhibition of the catalysis (ref. 6, p. 95). In some instances kinetic data are available for the formation of such complexes.[65]

The oxidation of many inorganic species used in catalytic analysis, such as chloride or ammonia, needs oxidants with higher oxidation potentials than those used to oxidize arylamines and phenols. For this reason oxidants such as cerium(IV), permanganate, chromate, molybdate, iodine and bromine are often used in such reactions, as are hydrogen peroxide, halates and other oxidants also used for oxidizing the organic compounds. For the same reason, the catalysts for these reactions are usually metal ions which in their highest oxidation state are strong oxidants [cobalt(III), nickel(III), silver(II), manganese(III), chromium(VI), osmium(VIII), vanadium(V), *etc.*]. Because of the higher oxidation potentials associated with the reagents and catalysts in this group of reactions, very often it is necessary to change the oxidation potential associated with either the catalyst or the oxidant by complex formation in order to fulfill the condition $E_{\text{Ox}} > E_{\text{M}} > E_{\text{Red}}$, which makes possible the catalytic action of the metal ion.

The sole use of inorganic reactants is analytically advantageous in that there are usually no side-reactions, or further reactions of the monitored reaction product. Even in reactions where dimerization of inorganic radicals is possible, together with further oxidation [see for instance reaction scheme (17)], the number of compounds formed is restricted. The absence of a number of products in the system makes possible the application of *different* methods to follow the reaction kinetics and this widens the limits of application of catalytic analysis. Amperometric methods are a good example. They have been applied to catalytic methods for the determination of sulphides and sulphur-containing compounds, chromium, molybdenum, germanium, *etc.*, by the oxidation of iodide by hydrogen peroxide or of azide by iodine.[73–77]

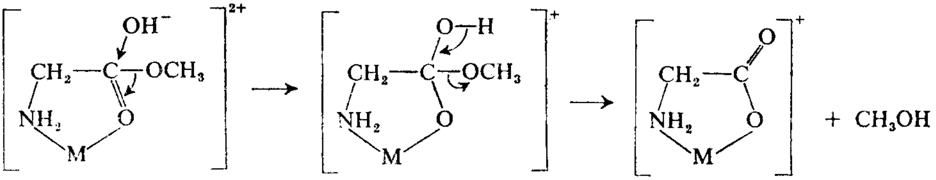
Polarography has similarly been applied in catalytic analysis, based on electrochemical reduction or oxidation processes with inorganic substances such as H^+, H_2O_2, NO_3^-, ClO_4^-, catalysed by metal ions.[78–81]

REACTIONS CATALYSED BY IONS NOT CHANGING THEIR OXIDATION STATE DURING THE COURSE OF THE REACTION

Reactions of this type include the catalytic rearrangement, decomposition, substitution and hydrolysis of organic and inorganic compounds in the course of which the catalyst does not change its oxidation state. The catalytic action can be due to the polarizing effect of the catalyst on bonds in the molecule of a reactant, or to the ability of the catalyst to bring the reactants together or to orientate them in a way suitable for the reaction to proceed.

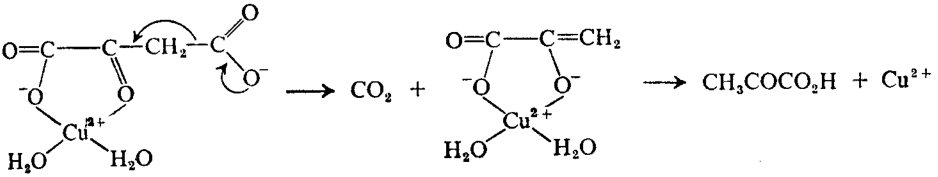
This group of catalytic reactions has not been developed as an analytical tool to such an extent as the preceding one, but it is important because it deals with reactions which make possible the determination of ions with filled outer *s*-, *p*- or *d*-electron shells, such as Al^{3+}, Ca^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}.

The hydrolysis of amino-acid derivatives and phosphate esters is the most studied of this type of reaction. These reactions are catalysed by metal ions such as Cu^{2+}, Zn^{2+}, Mn^{2+} and Cd^{2+}. The metal ion catalyst forms a chelate with the reactant. The positive charge of the metal ion affects the electron distribution in the ligand in such a way as to facilitate the attack of the hydroxide ion. For example, in the hydrolysis of alkyl- and aryl-esters of glycine,[82] the metal ion causes an electron shift from the carbon atom of the carbonyl group, thus facilitating attack by hydroxide:



(21)

The decarboxylation of β-keto acids was first used in catalytic analysis by Bontchev and his co-workers.[83,84] For example the decarboxylation of oxaloacetic acid is catalysed by metal ions such as Zn^{2+}, Mg^{2+}, Mn^{2+} and Cu^{2+}. In the presence of copper(II), the decarboxylation proceeds as follows:



(22)

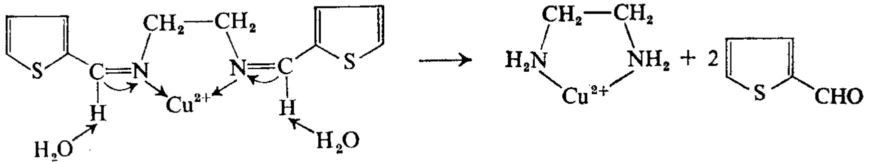
The catalyst forms chelates with both the substrate and the product, but the latter has a lower stability constant because of the change in inductive effect of the carboxyl group as it changes from the β- to the α-position. The substrate therefore displaces metal ion from the chelate with the product, and the cycle begins again. In such catalysed reactions any hindrance of chelate formation results in a decreased catalytic activity. Thus the presence of metal ions has no effect on the rate of decarboxylation of β-keto acids with a second carboxylic group too far from the keto group to form strong chelates, or on ketomonocarboxylic acids.[85] Hydrolytic reactions show the same dependence on the chelating ability of the substrate. Moreover, if the catalyst is already complexed by other ligands, so that the rate of substitution of these ligands by the substrate is very slow, or if stable inert complexes are formed with these ligands, the catalytic effect can decrease or even disappear.

Finally, the nature of the complex formed influences the catalysis. It was found, for example, in the catalytic decarboxylation of dimethyloxaloacetic acid that the catalyst forms two different complexes with the acid, only one of which can undergo decarboxylation.[86]

The metal ion acts in the catalytic, hydrolytic and decarboxylation reactions mainly because of its positive charge. It might be expected, therefore, that the effect of the dipositively charged ions will be of the same order and hence their overall catalytic action will depend on their complexing abilities. Numerous examples provide evidence for the validity of this assumption. In the hydrolytic reaction (21) the order of catalytic activity is

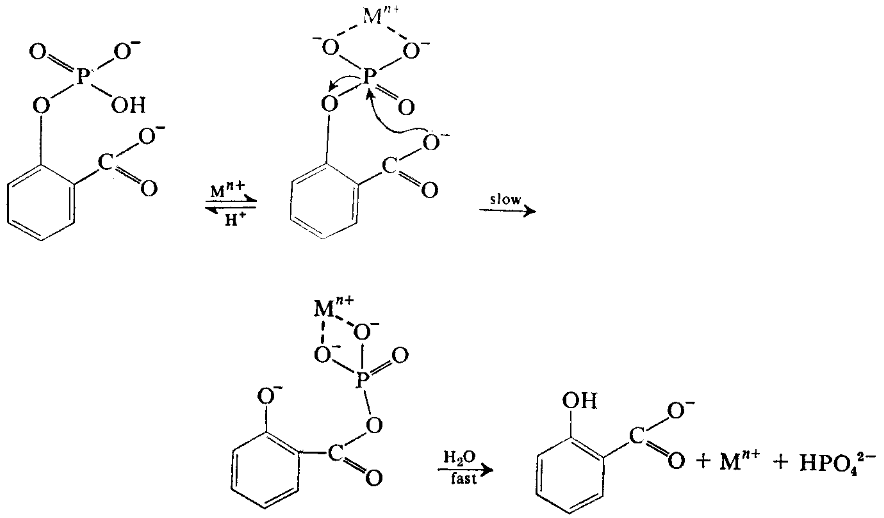
$$\mathrm{Cu(II)} > \mathrm{Co(II)} > \mathrm{Mn(II)} > \mathrm{Ca(II)},\ \mathrm{Mg(II)}$$

which is identical with the Irving-Williams order. The same reasons are responsible for the evident connection between the position of the metal-ion catalyst in Sidgwick's classification[87] and the character of the donor atoms in the substrate molecule. Metal ions of the third group of this classification which bond to nitrogen more strongly than to oxygen are good catalysts for reactions of substrates with nitrogen donor atoms. In the hydrolysis of a Schiff's base, for example:



(23)

copper(II) and nickel(II) are the best bivalent catalysts (ref. 85, p. 220). For the same reason mercury(II), lead(II) and silver(I) are the most effective catalysts for the hydrolysis of thiol esters (ref. 85, p. 217). Similarly hydrolysis of substrates containing only oxygen donors is catalysed preferentially by metal ions of the first group of Sidgwick's classification, which tend to form complexes with oxygen in preference to other donors. Thus the hydrolysis of salicyl phosphate:



(24)

is catalysed by UO_2^{2+}, VO^{2+}, ZrO^{2+}, Fe^{3+} and Cu^{2+} whereas Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} have no influence on the process.[88]

From an analytical point of view there are two main shortcomings of catalysed hydrolytic and decarboxylation reactions, namely, the low sensitivity and selectivity of these reactions. A comparatively large concentration of the catalyst is usually necessary to increase the reaction rate by a measurable extent. Yatsimirskii and Tikhonova,[89,90] the first authors to use a hydrolytic reaction in catalytic analysis, were able to determine 10 μg/ml of cadmium and 1 μg/ml of lead (total amounts of 250 μg of Cd^{2+} and 25 μg of Pb^{2+}), using the hydrolysis of the ethyl ester of cysteine. It is evident that this sensitivity is far less than that of a large number of other catalytic methods. The sensitivity of the decarboxylation reactions is also low. The catalytic effect becomes measurable at catalyst concentrations greater than about $10^{-3}M$, which is quite insufficient for trace analytical purposes. The sensitivity can be increased, however, by complexing the metal so as to increase the actual charge on the metal, as has been demonstrated[83,84] for the decarboxylation of oxaloacetic acid, which has been developed as a sensitive method for the determination of zinc.[84] The use of suitable complexing agents can contribute also to the selectivity of these catalytic reactions as will be discussed in Part II.

Catalytic substitutions of ligands in the co-ordination sphere of a metal ion are other examples of this group of reactions. They were first used in catalytic analysis by Asperger *et al.* for the determination of mercury.[91–94] These authors used the replacement of cyanide from hexacyanoferrate(II) by a water molecule:

$$[Fe(CN)_6]^{4-} + H_2O \rightleftharpoons [Fe(CN)_5H_2O]^{3-} + CN^- \qquad (25)$$

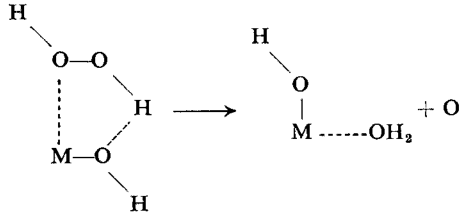
The reaction is monitored by adding nitrosobenzene, which readily replaces the water molecule in the inner co-ordination sphere of the product to form $[Fe(CN)_5PhNO]^{3-}$, a red-violet, soluble complex.[95]

The substitution of cyanide in hexacyanoferrate(II) by 2,2′-bipyridyl and 1,10-phenanthroline has also been used for the determination of mercury(II) and silver(I).[96,97]

The complete replacement of the cyanide ions in hexacyanoferrate(II) by water molecules gives $Fe(H_2O)_6^{2+}$, which is rapidly oxidized by atmospheric oxygen. The resulting iron(III) reacts with the unchanged hexacyanoferrate(II) and a blue colloidal solution of Prussian Blue is formed. Besides mercury(II), silver(I) and gold(III) also catalyse this reaction, which has been used for determination of these elements.[98–100]

The mechanism of these substitution processes and especially the role of the catalyst is at present not quite clear. It is worth noting, however, that the catalysts form stable complexes with the ligands whose substitution they catalyse.

The fact that in the reactions of this group the catalyst remains in the same oxidation state does not exclude the participation of the catalyst in oxidation processes. Thus the oxidation of iodide by hydrogen peroxide in acidic solution is catalysed by thorium(IV), zirconium(IV), hafnium(IV), niobium(V) and tantalum(V) which do not change their oxidation state during the course of the reaction.[6] In moderately acidic solutions they are present in the form of the corresponding oxo- or hydroxo-ions (for example ZrO^{2+}, $ThOH^{3+}$). Yatsimirskii has suggested[101] that the catalytic effect of these ions is due to the formation of cyclic peroxides, *e.g.*



(26)

The O—O bond is more labile in the complex, and it decomposes with the formation of free oxygen atoms, although it seems more probable that the reactates formed during the process are hydroxyl radicals, because the direct formation of oxygen atoms from the hydrogen peroxide molecule seems energetically less favourable than that of ˙OH. The reactates then oxidize the iodide. The catalyst does not react directly with the substrate and does not change its oxidation state during the reaction.

It is of interest to note that vanadium(V) and titanium(IV) oxo-ions, which are not among the catalysts for this reaction, catalyse the oxidation of thiosulphate by hydrogen peroxide as do Th(IV), Zr(IV), Nb(V), Ta(V) and Hf(IV).[6] If the role of the catalyst in these two reactions is only to produce reactates from H_2O_2 (or ˙OH) which then oxidize the substrate, the absence of a catalytic effect of V(V) and Ti(IV) in the first reaction is inexplicable. It seems possible, therefore, that the oxidation of the reductant occurs by interaction with a peroxide complex of the catalyst. When bond formation between the catalyst and the reductant is possible, and therefore a ternary complex can be formed, vanadium(V) and titanium(IV) catalyse the process (as for thiosulphate oxidation). If such a complex with the participation of the substrate cannot be formed [V(V) and Ti(IV) do not form iodide complexes] the oxo-ions of both elements do not influence the reaction (as for iodide oxidation).

Zusammenfassung—Die Mechanismen einiger bei der katalytischen Analyse verwendeter Reaktionen werden diskutiert. Die Kenntnis des Mechanismus einer katalytischen Reaktion kann bei der Auffindung neuer katalytischer Reaktionen und der Auswahl der besten Versuchsbedingungen von Nutzen sein. Ferner können Möglichkeiten zu weiterer Steigerung der Empfindlichkeit erkannt werden.

Résumé—On discute des mécanismes de quelques réactions utilisées en analyse catalytique. La connaissance du mécanisme d'une réaction catalytique peut aider dans le développement de nouvelles réactions catalytiques et le choix de conditions optimales, et montrer les possibilités de nouveaux accroissements de sensibilité.

REFERENCES

1. Z. Arkosi, *Ein Beitrag zur Mikrobestimmung einiger hochwertiger Schwermetallionen auf Grund ihrer katalytische Wirkung; Katalytische Analyse*, Juris-Verlag, Zürich, 1956.
2. R. A. Geitz, *Kinetic Analytical Methods*, in *Methods of Analysis of High Purity Substances*, Kharkov, 1962.
3. H. B. Mark, Jr., L. J. Papa and C. N. Reilley, *Advan. Anal. Chem. Instr.*, 1963, **2**, 255.
4. H. B. Mark and G. A. Rechnitz, *Kinetics in Analytical Chemistry*, Interscience, New York, 1968.
5. K. B. Yatsmirskii (ed.) *Methods for Analysis of Chemical Reagents*, 1966, No. 13. *Kinetic Methods of Analysis* (in Russ.). IREA, Moscow, 1966.
6. *Idem*, *Kinetic Methods of Analysis*, 2nd Ed., Khimia, Moscow, 1967; 1st Ed., Pergamon, Oxford, 1965.
7. R. G. R. Bacon, *Chem. Ind. London*, 1962, 19.
8. E. T. Denisov and N. M. Emanuel', *Usp. Khim.* 1960, **29**, 1409.
9. *Energies of Rupture of Chemical Bonds, Ionization Potentials, Electron Affinities* (in Russ.). Izdat. Akad. Nauk USSR, Moscow, 1962.
10. M. V. Bazilevskii and Kh. S. Bagdasar'yan, *Kinetics Catalysis*, (*USSR*), 1964, **5**, 215.
11. R. G. Caldwell and J. L. Ihrig, *J. Am. Chem. Soc.*, 1962, **84**, 2878.
12. D. S. Davies, H. L. Goldsmith, A. K. Gupta and G. R. Lester, *J. Chem. Soc.* 1956, 4926.
13. G. Engelsma and E. Havinga, *Tetrahedron*, 1958, **2**, 289.
14. W. A. Waters, *Mechanisms of Oxidation of Organic Compounds*, Methuen, London, 1964.
15. T. A. Cooper and W. A. Waters, *J. Chem. Soc.*, 1964, 1538.
16. J. S. Littler and W. A. Waters, *ibid.*, 1959, 1299.
17. S. K. Saha and A. K. Chaudhuri, *J. Indian Chem. Soc.*, 1965, **42**, 735.
18. R. I. Yadav and W. V. Bhagwat, *ibid.*, 1964, **41**, 25.
19. A. L. Bouchachenko, *Stable Radicals* (in Russ.). Izdat. Akad. Nauk USSR, Moscow, 1963.
20. B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.(B)*, 1966, 86.
21. C. J. W. Gutch and W. A. Waters, *ibid.*, 1965, 751.
22. T. J. Stone and W. A. Waters, *Proc. Chem. Soc.*, 1962, 253.
23. *Idem*, *J. Chem. Soc.*, 1964, 213.
24. J. R. Thomas, *J. Am. Chem. Soc.*, 1964, **86**, 1446.
25. R. Lundberg (ed.), *Autooxidation and Autooxidants*, Vol. I. Interscience, New York, 1961.
26. R. G. R. Bacon and D. J. Munro, *J. Chem. Soc.*, 1960, 1339.
27. H. Musso, *Angew. Chem.*, 1963, **75**, 965.
28. L. K. J. Tong and M. S. Glesmann, *J. Am. Chem. Soc.*, 1957, **79**, 583.
29. J. D. Edwards and J. L. Cashaw, *ibid.*, 1954, **76**, 4141.
30. P. R. Bontchev and B. G. Jeliazkowa, *Mikrochim. Acta*, 1967, 116.
31. C. Walling, *Free Radicals in Solution* (in Russ.), p. 362. Inlitizdat, Moscow, 1960.
32. P. R. Bontchev, *Mikrochim. Acta* 1962, 584.
33. P. R. Bontchev, A. A. Alexiev and B. Dimitrova, *Talanta*, 1969, **16**, 597.
34. Z. Jarabin and P. Szarvas, *Acta Univ. Debrecen*, 1962, **7**, 185.
35. S. U. Kreĭngol'd and E. A. Bozhevol'nov, *Zavodsk. Lab.*, 1965, **31**, 784.
36. R. Ralea and N. Jorga, *Analele Stiint Univ. A. I. Cuza, Iasi, Sect. I*, 1956, **2**, 211; *Chem. Abstr.*, 1959, **53**, 19688.
37. K. B. Yatsimirskii and L. I. Budarin, *Izv. Vysshikh Uchebn. Zavedenii Khim. i Khim. Tekhnol.*, 1963, **5**, 220.
38. K. B. Yatsimirskii and A. P. Filippov, *Zh. Neorgan. Khim.*, 1964, **9**, 2096.
39. *Idem*, *Zh. Analit. Khim.* 1965, **20**, 815.
40. L. I. Budarin and K. E. Prick, *Zavodsk. Lab.*, 1960, **26**, 1018.
41. H. V. Malmstadt and T. P. Hadjiioannou, *Anal. Chem.*, 1963, **35**, 2157.
42. P. R. Bontchev and B. G. Jeliazkowa, *Mikrochim. Acta*, 1967, 125.

43. P. R. Bontchev, *ibid.*, 1962, 592.
44. *Idem*, *Ukr. Khim. Zh.*, 1964, **30**, 1167.
45. P. R. Bontchev and K. B. Yatsimirskii, *Zh. Fiz. Khim.*, 1965, **39**, 1995.
46. P. R. Bontchev and G. St. Nikolov, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2609.
47. P. R. Bontchev and A. A. Alexiev, *Ukr. Khim. Zh.*, 1966, **32**, 1044.
48. P. R. Bontchev and B. Evtimowa, *Mikrochim. Acta*, 1967, 492.
49. A. A. Alexiev and P. R. Bontchev, *Z. Phys. Chem.*, 1969, **242**, 333.
50. I. F. Dolmanova and V. M. Peshkova, *Zh. Analit. Khim.*, 1964, **19**, 297.
51. H. Gôto and S. Suzuki, *Nippon Kagaku Zasshi*, 1950, **71**, 7.
52. S. U. Kreĭngol'd and E. A. Bozhevol'nov, see ref. 5, pp. 85, 88.
53. S. U. Kreĭngol'd, E. A. Bozhevol'nov and L. G. Sinyaver, *Zavodsk. Lab.*, 1965, **31**, 508.
54. V. M. Peshkova, I. F. Dolmanova and N. M. Semenova, *Zh. Analit. Khim.*, 1963, **18**, 1228.
55. T. Shiokawa and S. Suzuki, *Nippon Kagaku Zasshi*, 1951, **72**, 12.
56. D. A. House, *Chem. Rev.*, 1962, **62**, 185.
57. W. C. E. Higginson, D. Sutton and P. Wright, *J. Chem. Soc.*, 1953, 1380.
58. A. M. Armstrong and J. Halpern, *Can. J. Chem.*, 1957, **35**, 1020.
59. K. G. Ashurst and W. C. E. Higginson, *J. Chem. Soc.*, 1953, 3044.
60. F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd Ed., Wiley, New York, 1967.
61. H. Taube, *Record Chem. Progr. Kresge-Hooker Sci. Lib.*, 1956, **17**, 25.
62. W. C. E. Higginson and J. W. Marshall, *J. Chem. Soc.*, 1957, 447.
63. F. R. Duke, *Mechanisms of Oxidation-Reduction Reactions in Treatise on Analytical Chemistry*, eds. I. M. Kolthoff, P. J. Elving and E. B. Sandell, Part I, Vol. I, p. 637. Interscience, New York, 1959.
64. J. W. Cahn and R. E. Powell, *J. Am. Chem. Soc.*, 1954, **76**, 2568.
65. K. B. Yatsimirskii and V. E. Kalinina, *Izv. Vysshikn Uchebn. Zavedenii Khim. i Khim. Tekhnol.*, 1965, **8**, 378.
66. P. A. Rodriguez and H. L. Pardue, *Anal. Chem.*, 1969, **41**, 1369.
67. R. L. Habig, H. L. Pardue and T. B. Worthington, *ibid.*, 1967, **39**, 600.
68. V. G. Loshkareva, *Tr. Uralsk. Polytekhn. Inst.*, 1956, **57**, 61.
69. K. B. Yatsimirskii and G. A. Karacheva, *Zh. Neorgan. Khim.*, 1958, **3**, 352.
70. J. Bognår and S. Sarosi, *Anal. Chim. Acta*, 1963, **29**, 406.
71. G. A. Bogdanov, *Zh. Fiz. Khim.*, 1951, **25**, 332.
72. T. J. Lewis, D. H. Richards and D. A. Salter, *J. Chem. Soc.*, 1963, 2434.
73. W. Jedrzejewski, *Chem. Anal. Warsaw.*, 1960, **5**, 207.
74. W. Jedrzejewski and H. Gelowa, *ibid.*, 1962, **7**, 753.
75. E. Michalski and A. Wtorkowska, *ibid.*, 1962, **7**, 691, 783.
76. E. Michalski and H. Gelowa, *ibid.*, 1963, **8**, 643.
77. I. G. Shaftran, V. P. Rosenbaum and G. A. Steinberg, see ref. 5, p. 120.
78. J. Heyrovský, *Nature*, 1935, **135**, 870.
79. M. C. Johnson and R. J. Robinson, *Anal. Chem.*, 1952, **24**, 368.
80. G. B. Jones, *Anal. Chim. Acta*, 1954, **10**, 584.
81. G. S. Supin, see ref. 5, p. 132.
82. H. Kroll, *J. Am. Chem. Soc.*, 1952, **74**, 2036.
83. P. R. Bontchev and V. Michaylova, *J. Inorg. Nucl. Chem.*, 1967, **29**, 2945.
84. M. Michaylova, B. Evtimowa and P. R. Bontchev, *Mikrochim. Acta*, 1968, 922.
85. Q. Fernando, *Advan. Inorg. Chem. Radiochem.*, 1965, **7**, 234.
86. J. V. Rund and R. A. Plane, *J. Am. Chem. Soc.*, 1964, **86**, 367.
87. N. V. Sidgwick, *J. Chem. Soc.*, 1941, 433.
88. R. Hofstetter, Y. Murakami, G. Mont and A. E. Martell, *J. Am. Chem. Soc.* 1962, **84**, 3041.
89. L. P. Tikhonova and K. B. Yatsimirskii, *Zh. Neorgan. Khim.*, 1966, **11**, 2259.
90. K. B. Yatsimirskii and L. P. Tikhonova, *ibid.*, 1965, **10**, 2070.
91. S. Asperger and J. Murati, *Anal. Chem.*, 1954, **26**, 543.
92. S. Asperger and O. Cuprahi, *J. Chem. Soc.*, 1953, 1041.
93. S. Asperger and P. Pavlovic, *Anal. Chem.*, 1956, **28**, 1761.
94. P. Pavlovic and S. Asperger, *ibid.*, 1959, **31**, 939.
95. J. Kraljic and M. Mate, *Croat. Chem. Acta*, 1956, **28**, 273.
96. U. Kars and T. Pinter, *ibid.*, 1958, **30**, 141.
97. J. Kraljic, *Mikrochim. Acta*, 1960, 586.
98. M. N. Orlova and K. B. Yatsimirskii, *Izv. Visshikh Uchebn. Zavedenii Khim i Khim. Tekhnol.*, 1960, **3**, 630.
99. T. Pinter and H. Dresner, *Mikrochim. Acta*, 1955, 805.
100. K. B. Yatsimirskii and M. N. Orlova, *Zh. Neorgan. Khim.*, 1960, **5**, 2184.
101. K. B. Yatsimirskii, *Pure Appl. Chem.*, 1963, **6**, 117.

Talanta, 1970, Vol. 17, pp. 515 to 523. Pergamon Press. Printed in Northern Ireland

ACID DISSOCIATION AND SPECTROPHOTOMETRIC BEHAVIOUR OF 8-QUINOLINESELENOL IN WATER–DIOXAN MIXTURES

NOBORU NAKAMURA and EIICHI SEKIDO
Department of Chemistry, Faculty of Science, Kobe University, Kobe, Japan

(*Received* 26 *August* 1969. *Accepted* 21 *January* 1970)

Summary—The acid dissociation constants of 8-quinolineselenol, 8-quinolinol and 8-quinolinethiol in water–dioxan mixtures of varying solvent composition were determined potentiometrically or spectrophotometrically. The absorption spectra of 8-quinolineselenol in the same solvents were also obtained. The acid dissociation phenomena, stability towards oxidation and the absorption spectra of the reagents are discussed in connection with the existing forms. It is verified that 8-quinolineselenol exists as a zwitterion in water–dioxan mixtures of low or high dioxan content.

IN RECENT years, 8-quinolinethiol and 8-quinolineselenol have become of interest as analytical reagents.[1–4] 8-Quniolineselenol appears to be a more selective chelating agent than 8-quinolinol and 8-quinolinethiol, probably because of the lower electronegativity and larger size of the selenium atom.

Therefore, a study of metal complexes of 8-quinolineselenol is of value, especially as only a few studies of 8-quinolineselenol complexes have been reported.[2–4] This paper deals with a comparative study of the acid dissociation and spectrophotometric behaviour of 8-quinolineselenol, 8-quinolinethiol and 8-quinolinol in water–dioxan mixtures.

EXPERIMENTAL

Reagents

8-*Quinolineselenol.* The reagent was prepared by the modified method of Sekido, Fernando and Freiser.[3] The neutral salt of 8-quinolineselenol prepared from 8,8′-diquinolyldiselenide was dried under reduced pressure. This reagent was proved to be anhydrous and was stable for more than a week *in vacuo*.

The sodium salt of 8-*quinolinethiol.* 8,8′-Diquinolyldisulphide was first synthesized by the method of Edinger.[5] The sodium salt was then prepared by the following procedures. Pure disulphide, 5·5 g, was dissolved in a mixture of 20 ml of concentrated hydrochloric acid and 6 ml of 50% hypophosphorous acid, and the solution was heated under reflux for about 2 hr. The solution was cooled and filtered, and then a yellow precipitate was obtained by adding excess of saturated sodium hydroxide solution dropwise whilst a stream of nitrogen gas was passed through the solution. The pure sodium salt, obtained by recrystallization a few times from alcohol–ether, was dried *in vacuo*. The sodium salt prepared in this way was proved to contain 1–2 molecules of water of crystallization, and to be stable for several months under a nitrogen atomosphere.

8-*Quinolinol.* The reagent was reagent grade and was further purified by recrystallization from alcohol, m.p. 73·5–74·5°.

Dioxan. Commercial dioxan was treated with hydrochloric acid and metallic sodium and then distilled at 101·5–102·0°. Freshly distilled dioxan was further purified by freezing, and was used in a few days.

Carbonate-free sodium hydroxide solutions were prepared by the usual method and the other reagents used were reagent grade where possible.

Apparatus

pH meter. Horiba Model P, with glass and calomel electrodes, standardized against aqueous buffers (pH 4·01 and 6·86). The relationship between the pH meter reading (B) and the hydrogen ion concentration ($[H^+]$) in water–dioxan mixtures is defined as the following according to Van Uitert and Haas,[7]

$$-\log [H^+] = B + \log U_0 + \log \gamma_\pm \tag{1}$$

where U_0 is a conversion factor at zero ionic strength, $\gamma_\pm$ is the mean activity coefficient for the solvent composition and ionic concentration. The values of $\log U_0$ and $\log \gamma_\pm$ were taken from the data of Van Uitert and Haas,[7] and Harned and Owen,[8] respectively. Equation (1) was found to hold, with an error of 0·05 pH units, in this experiment.

Procedures

Nitrogen gas was bubbled through the sample solutions during titration, and the temperature was controlled to 25·0 ± 0·1° by circulating water through double-walled titration and reference cells. Titrations were made on the solutions which contain the reagents, perchloric acid and sodium perchlorate. The range of concentration was from $9{\cdot}4 \times 10^{-4}$ to $1{\cdot}0 \times 10^{-2}M$ for the reagents, and from $2{\cdot}0 \times 10^{-3}$ to $2{\cdot}0 \times 10^{-2}M$ for the acid, ionic strength varied from 0·001 to 0·1, and dioxan content ranged from 0 to 75% v/v.

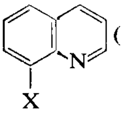
Spectrophotometric measurements were also made under various conditions; (*a*) in solvents of varying dioxan content, (*b*) at varying time, (*c*) in a stream of nitrogen gas, (*d*) by adding hypophosphorous acid as reducing agent.

CALCULATION

Acid dissociation of 8-quinolinol and its analogues takes place as follows

$$H_2R^+ \overset{k_{a_1}}{\rightleftharpoons} H^+ + HR \text{ and } H^+R^- \tag{2}$$

$$HR \text{ and } H^+R^- \overset{k_{a_2}}{\rightleftharpoons} H^+ + R^- \tag{3}$$

where R is 

(X = O, S or Se). The neutral and zwitterion forms are denoted by HR and H^+R^-, respectively, and k_{a_1} and k_{a_2} are stoichiometric acid dissociation constants. The formation function of the species HR and H_2R^+ corresponding to equations (2) and (3) is given by Bjerrum's method[13] as follows

$$\bar{N}_h - (\bar{N}_h - 1)\frac{[H^+]}{k_{a_2}} - (\bar{N}_h - 2)\frac{[H^+]^2}{k_{a_1} \cdot k_{a_2}} = 0 \tag{4}$$

where $\bar{N}_h$ is the average number of hydrogen ions bound to each reagent molecule. Since the difference between the numerical values of k_{a_1} and k_{a_2} for the reagents is large, the first term of equation (4) is negligible in the acidic region and thus rearrangement of equation (4) leads to equation (5), similarly the third term is negligible in the basic region and equation (6) is obtained:

$$k_{a_1} = \frac{(2 - \bar{N}_h)}{(\bar{N}_h - 1)}[H^+] \tag{5}$$

$$k_{a_2} = \frac{(1 - \bar{N}_h)}{\bar{N}_h}[H^+] \tag{6}$$

$\bar{N}_h$ is calculated by means of equation (7)

$$\bar{N}_h = \frac{[HR]_0 + [H]_0 + [OH^-] - [H^+] - [OH]_0}{T_R} \tag{7}$$

T_R is the total concentration of the reagent, $[HR]_0$ is the concentration of the reagent in the HR or H^+R^- form, and $[H]_0$, $[OH]_0$, $[H^+]$ and $[OH^-]$ are the concentrations of perchloric acid titrated, sodium hydroxide added, free hydrogen ion and free hydroxide ion, respectively. In the case of 8-quinolinethiol the $[HR]_0$ term in the numerator of equation (7) can be omitted because the sodium salt is used. The values of $[OH^-]$ are calculated by employing the values of K_w in water–dioxan mixtures, given by Harned and Owen.[8]

On the basis of values of k_{a_1} and k_{a_2} obtained thus, the constants, K_{a_1} and K_{a_2}, which are good approximations to the thermodynamic constants,[7,9] are determined according to the following equations, with the use of mean activity coefficients given for hydrochloric acid by Harned and Owen.[8]

$$pK_{a_1} = pk_{a_1} \tag{8}$$

$$pK_{a_2} = pk_{a_2} + 2\log\left(\frac{1}{\gamma_{\pm}}\right) \tag{9}$$

where it is assumed that $\gamma_{H^+} = \gamma_{R^-} = \gamma_{H_2R^+} = \gamma_{\pm}$ and $\gamma_{HR} = 1$. Association of solutes which may be expected to take place in solvents of high dioxan content was ignored.

RESULTS AND DISCUSSION

Potentiometric studies

Results. A number of titrations for 8-quinolinol, 8-quinolinethiol and 8-quinolineselenol were performed. In order to examine the accuracy of k_{a_2} calculated according to equations (5), (6) and (7), the formation curves were checked by comparing the experimental and theoretical values (Fig. 1).

For 8-quinolinol the agreement is quite satisfactory, but for 8-quinolinethiol and 8-quinolineselenol good agreement was not always obtained, because of experimental error. The causes of error were proved to be oxidation of the reagents by air or dioxan and the glass electrode error. Therefore, much attention was paid, especially

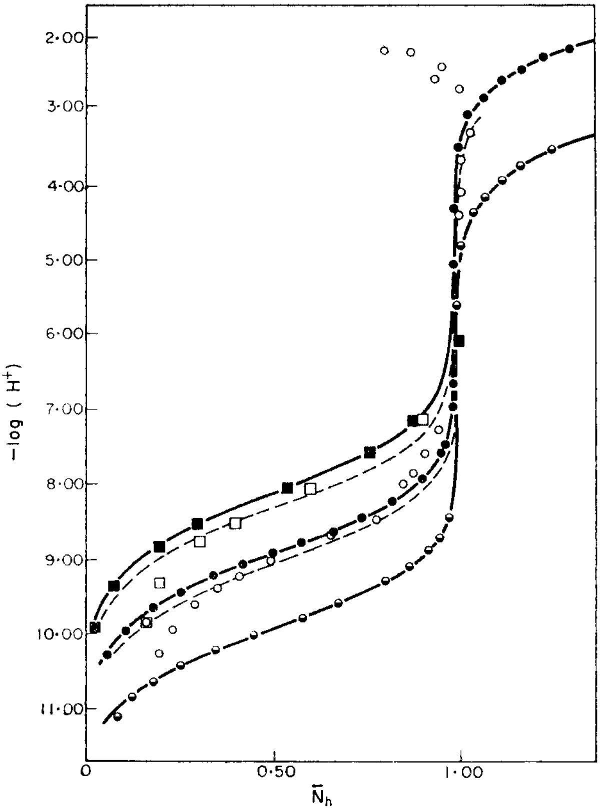


FIG. 1.—Formation curves for 8-quinolinol (—◓—), 8-quinolinethiol (—●—, - -○- -) and 8-quinolineselenol (—■—, - -□- -) in 50% water–dioxan mixture. The plots (- -○- -, - -□- -) are erroneous data.

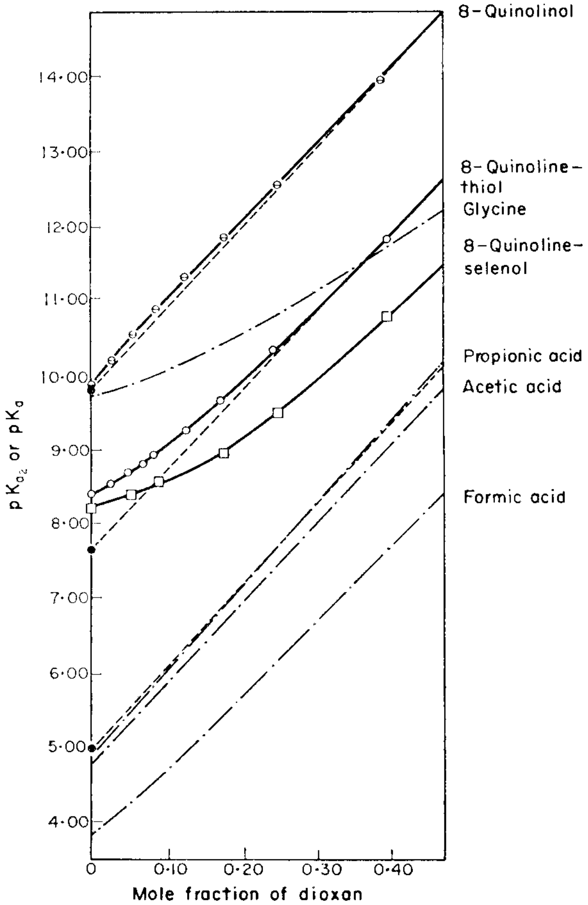


FIG. 2.—pK_{a_2} of the reagents and pK_a of monoprotic acids and glycine. Reliability of pK_{a_2} is ±0·07 for 8-quinolinol and 8-quinolinethiol, and ±0·1 for 8-quinolineselenol.

for 8-quinolineselenol, to titration procedure in order to minimize these errors. At first, titrations for 8-quinolineselenol were carried out under the same conditions as for 8-quinolinethiol, but the second equivalence point for 8-quinolineselenol did not coincide with that for 8-quinolinethiol. Disagreements of the formation functions corresponding to these titration curves are serious in the region $\bar{N}_h < 0{\cdot}5$ because of oxidation. Therefore the most reliable data for 8-quinolineselenol were obtained from the buffer region of the titration curve. To calculate the values of $\bar{N}_h$ for strongly acidic solution, the method of Irving and Rossotti[9] was applied to equation (7), otherwise serious disagreement for formation functions was observed in the region $-\log[H^+] < 3{\cdot}5$. The experimental results agreed with the theoretical ones. Only K_{a_1} for 8-quinolineselenol was determined spectrophotometrically. The acid dissociation constants (pK_{a_2}) obtained for these reagents are plotted as a function of dioxan content in Fig. 2.

Discussion. Activity coefficients in mixed solvents are defined as

$$\log \gamma = \log \gamma_0 + \log \gamma^* \qquad (10)$$

where $\log \gamma$, $\log \gamma_0$ ($= \lim_{\mu \to 0} \gamma$) and $\log \gamma^*$ correspond to the total, primary and secondary medium effect, respectively. Then the following relationship would hold[10]

$$pK_a = pK_a^0 + 2 \log \gamma_0 \tag{11}$$

where K_a and K_a^0 are the acid dissociation constants in the mixed solvent and in pure water, respectively. In the water–dioxan system the plots of $\log \gamma_0$ *vs.* mole fraction of dioxan in the range $n_2 = 0$–$0{\cdot}5$ have been found to be linear in the case of a monoprotic acid. Consequently the plots of pK_a *vs.* mole fraction of dioxan are linear. The values of pK_a of acetic acid, propionic acid, formic acid and glycine, which are given by Harned and Owen,[8] are shown in Fig. 2. The former three acids are monoprotic. In the case of glycine the zwitterion form is predominate in aqueous medium.

In Fig. 2, the pK_{a_2} values for 8-quinolinol, 8-quinolinethiol and 8-quinolineselenol are compared with pK_a for monoprotic acids and glycine. The values of pK_{a_2} all increase with mole fraction of dioxan. A substantially linear relationship is obtained for 8-quinolinol, but for 8-quinolinethiol there is deviation from linearity when the mole fraction is small.

In Fig. 2 the behaviour of the plot for 8-quinolinol is similar to that for acetic acid, and the behaviour for 8-qinolineselenol is similar to that of glycine. This suggests that in the neutral form, 8-quinolinol behaves as a monoprotic acid, and that 8-quinolineselenol as a zwitterion. For 8-quinolinethiol the behaviour is similar to that of 8-quinolineselenol in the region of low dioxan content but to that of 8-quinolinol in the region of high dioxan content.

If K_{aD} and K_{aC} are the acid dissociation constants for the neutral and zwitterion forms and K_t is the tautomeric constant, the following two equations hold:

$$\frac{1}{K_{a_2}} = \frac{1}{K_{aC}} + \frac{1}{K_{aD}} \tag{12}$$

$$K_t = \frac{[\text{Zwitterion}]}{[\text{Neutral}]} = \frac{K_{aD}}{K_{aC}}. \tag{13}$$

The values of pK_{aC} and pK_{aD} were evaluated from the results for pK_{a_2} and K_t. They are summarized in Table I.

TABLE 1.—EQUILIBRIUM CONSTANTS FOR 8-QUINOLINOL, 8-QUINOLINETHIOL AND 8-QUINOLINESELENOL IN WATER

	K_t	pK_{a_2}	pK_{aC}	pK_{aD}
8-quinolinol	0·04*	9·74	9·32	9·72
8-quinolinethiol	3·8†	8·36	8·26	7·68
8-quinolineselenol	1740‡	8·18	8·18	4·94

* Reference 11.
† Reference 12.
‡ Calculated value from the data of reference 3.

The calculated values of pK_{aD} are marked on the pK_{a_2} axis of Fig. 2. The black spot showing pK_{aD} for 8-quinolinol is in the vicinity of the straight line of pK_{a_2}, which suggests that 8-quinolinol behaves as the neutral form in water–dioxan mixtures.

Supposing that equation (11) is applied in this case, and that the reagent behaves only as the neutral form, the plots of pK_{a_2} *vs*, the mole fraction of dioxan are expected to be a straight line starting from the spot shown by values of pK_{aD} in Table I, and similarly for 8-quinolinethiol and 8-quinolineselenol. This is shown in Fig. 2. For 8-quinolinethiol, the plots of pK_{a_2} differ greatly from the expected when the mole fraction of dioxan is small but not when the mole fraction is higher. It is considered that this occurs because of a shift of the tautomeric equilibrium from the zwitterion to the neutral form with increase of the mole fraction of dioxan. Therefore, 8-quinolinethiol is considered to occur predominantly as the neutral form in the solvents with dioxan content > 70%, but 8-quinolineselenol is considered to be almost all in the zwitterion form in 75% water–dioxan mixture. This was also supported spectrophotometrically.

Spectrophotometric studies

Spectrophotometric measurements in water and water–dioxan mixtures were carried out both in air and in an atmosphere of nitrogen. Absorption spectra of 8-quinolinethiol, Fig. 3, are characterized by absorption maxima at 446, 316, 277 and 252 nm in water. The first two absorption bands have been attributed to the zwitterion form and the latter to the neutral form.[2] When the proportion of dioxan increases, the intensities of the first two bands decrease and those of the others increase (Fig. 3). The changes of the intensities for these bands suggest that the zwitterion form will be predominant in water and that the tautomeric equilibrium will be shifted towards the neutral form as the proportion of dioxan increases.

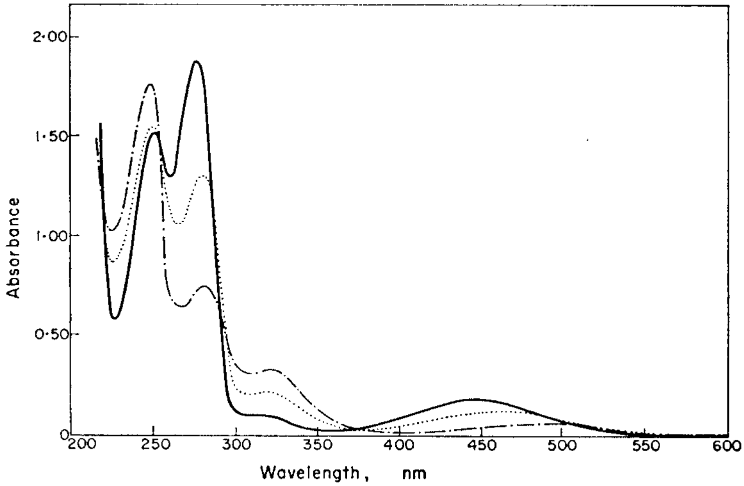


FIG. 3.—Absorption spectra of 8-quinolinethiol.
[NaR] = $1{\cdot}2 \times 10^{-4}M$, ($H_3PO_2$ or HCl added); pH = 4·2–5·1 Dioxan %: —— 0, ···· 30, —·— 50.

The absorption spectra for 8-quinolineselenol which were obtained in air were similar to those for 8-quinolinethiol. This fact is in conflict with the conclusion, obtained from potentiometric data, that the zwitterion form is predominant in spite of increase in dioxan content. However, different spectra, Fig. 4, were obtained when the measurements were made in an inert atmosphere and as quickly as possible. If the sample solution was allowed to stand for a certain time with the cell closed but in air, the spectra obtained become similar to those for 8-quinolinethiol. In Fig. 5, variation of the spectra as a function of time is represented. It is observed that the

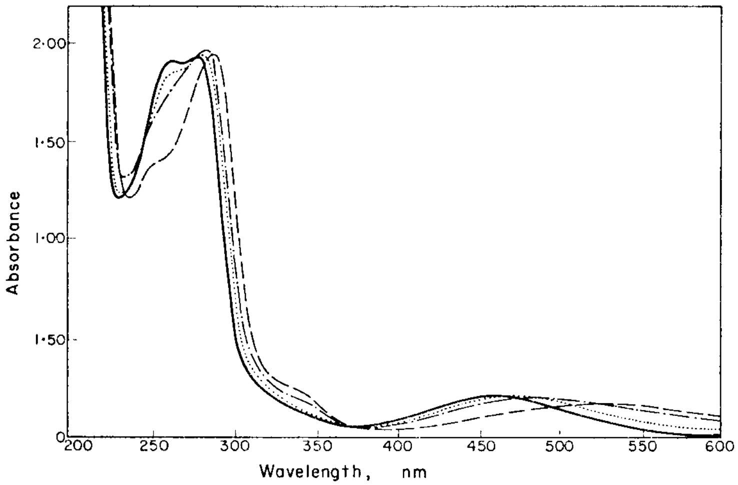


FIG. 4.—Absorption spectra of 8-quinolineselenol.
[HR] = 1·4 × $10^{-4}M$, [HCl] = 6 × $10^{-3}M$. Dioxan %: —— 0, ···· 30, —·— 50, — — 70.

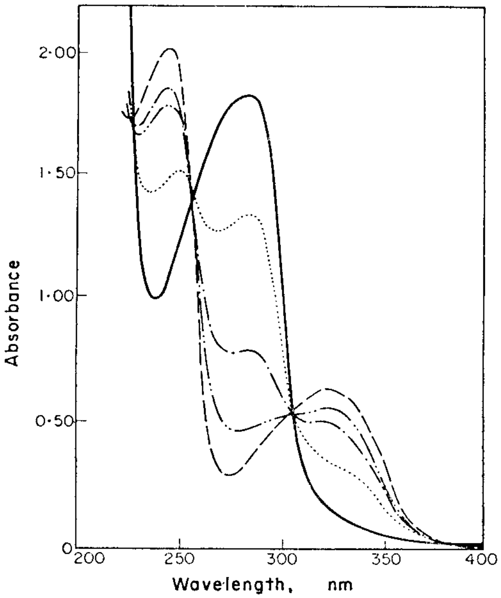


FIG. 5.—Variation of the spectra of 8-quinolineselenol in 50% water–dioxan mixture as a function of time.
[HR] = 1·2 × $10^{-4}M$, [$HClO_4$] = 5 × $10^{-3}M$. Time, *min*: —— 0, ···· 10, —·— 30, —··— 50. Diseleinde — —.

spectrum of 8-quinolineselenol approaches that of 8,8′-diquinolyldiselenide with time. The behaviour of the spectra for 8-quinolinethiol obtained under similar conditions was similar but the shifts were much slower.

To eliminate oxidation, measurements were carried out in the presence of hypophosphorous acid, and stable spectra were then obtained. In Fig. 4 it is shown that the absorption bands at 278 and 460 nm shift towards the red but the intensities of the bands change little with increase of dioxan content. The band at 260 nm shifts to red, and tends to overlap the band at 280 nm with increase of dioxan content. In other words the bands at 260, 278 and 460 nm undergo a blue shift as the solvent polarity is increased.

In Table II, spectrophotometric data obtained in this study or taken from the literature,[13] are summarized. All of the absorption coefficients are "apparent values" calculated from the total concentration of the reagent. Comparison suggests that the corresponding absorption bands undergo a red shift with decrease in basicity of ligand atoms. 8-Thiomethylquinoline has an absorption band at 251 nm which corresponds to the band at 252 nm of 8-quinolinol. 8-Selenomethylquinoline has a similar band at 252 nm. But the behaviour of the band at 260 nm for 8-quinolineselenol is different from these.

TABLE II.—ABSORPTION MAXIMA, *nm*, AND MOLAR ABSORPTIVITY (*l . mole*$^{-1}$. *mm*$^{-1}$)

8-quinolinol		8-quinolinethiol		8-quinolineselenol	
λ	ε	λ	ε	λ	ε
430	6·4	446	160	460	130
304	263	316	82	320(sh*)	
270	284	277	$1\cdot80 \times 10^{3}$	278	$1\cdot60 \times 10^{3}$
239	$3\cdot24 \times 10^{3}$	252	$1\cdot44 \times 10^{3}$	260	$1\cdot50 \times 10^{3}$

8-thiomethylquinoline		8-selenomethyl-quinoline		8,8′-diquinolyl-disulphide		8,8′-diquinolyldiselenide	
λ	ε	λ	ε	λ	ε	λ	ε
337	420	337	320	320		320	100
				310(sh*)		310(sh*)	
251	$2\cdot20 \times 10^{3}$	252	$2\cdot50 \times 10^{3}$	244		246	$3\cdot20 \times 10^{3}$
		232	$2\cdot10 \times 10^{3}$	232(sh*)		240(sh*)	

* Shoulder.

Consequently, the absorption bands at 278 and 460 nm for 8-quinolineselenol can be attributed to the zwitterion form, which correspond to the bands at 277 and 446 nm for 8-quinolinethiol and to 270 and 430 nm for 8-quinolinol. But the band at 260 nm for 8-quinolineselenol cannot be attributed to the neutral form. This suggests that in 8-quinolineselenol the zwitterion form is predominant in the solvent mixtures containing up to 70% dioxan. This conclusion agrees with the result obtained potentiometrically.

Acknowledgement—The authors acknowledge the invaluable assistance of Mr. Yoshiyuki Mido in this investigation.

Zusammenfassung—Die Säuredissoziationskonstanten von 8-Chinolinselenol, 8-Hydroxychinolin und 8-Chinolinthiol in Wasser-Dioxan-Gemischen wechselnder Lösungsmittelzusammensetzung wurden potentiometrisch oder spektrophotometrisch bestimmt. Die Absorptionsspektren von 8-Chinolinselenol in den selben Lösungsmittelgemischen wurden ebenfalls gemessen. Die Dissoziationseigenschaften, die Stabilität gegen Oxidation und die Absorptionsspektren der Reagentien werden in Verbindung mit den jeweils vorliegenden Formen diskutiert. Es wird nachgewiesen, daß 8-Chinolinselenol in Wasser-Dioxan-Gemischen mit niedrigem oder hohem Dioxananteil als Zwitterion vorliegt.

Résumé—On a déterminé potentiométriquement ou spectrophotométriquement les constantes de dissociation acide des 8-sélénolquinoléine, 8-hydroxyquinoléine et 8-thiolquinoléine dans des mélanges eau–dioxane de composition en solvant variable. On a aussi obtenu les spectres d'absorption de la 8-sélénolquinoléine dans les mêmes solvants. On discute des phénomènes de dissociation acide, de la stabilité vis-à-vis de l'oxydation et des spectres d'absorption des réactifs en relation avec les formes existantes. Il est vérifié que la 8-sélénolquinoléine esiste à l'état de zwitterion dans les mélanges eau-dioxane à basse ou haute teneur en dioxane.

REFERENCES

1. A. Corsini, Q. Fernando and H. Freiser, *Anal. Chem.*, 1963, **35,** 1424.
2. E. Sekido, Q. Fernando and H. Freiser, *ibid.*, 1963, **35,** 1550.
3. *Idem, ibid.*, 1964, **36,** 1768.
4. *Idem, ibid.*, 1965, **37,** 1556.
5. A. Edinger, *Ber.*, 1908, **41,** 937.
6. A. Weissberger and E. S. Proskauer, *Organic Solvents, 2nd Ed.*, p. 371. Interscience, New York, 1955.
7. L. G. Van Uitert and C. G. Haas, *J. Am. Chem. Soc.*, 1953, **75,** 451 and 455.
8. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions, 3rd Ed.*, pp. 716 and 756. Reinhold, New York, 1967.
9. H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1954, 2904 and 2910.
10. H. S. Harned and B. B. Owen, *op. cit.*, p. 671.
11. S. F. Mason, *J. Chem. Soc.*, 1957, 5010.
12. Yu. A. Bankovskii, L. M. Chera and A. F. Ievin'sh, *Zh. Analit. Khim.*, 1963, **18,** 668.
13. P. D. Anderson and D. M. Hercules, *Anal. Chem.*, 1966, **38,** 1703.
14. J. Bjerrum, *Metal Ammine Formation in Aqueous Solutions*, p. 35. Haase and Son, Copenhagen, 1957.
15. F. J. C. Rossotti and H. Rossotti, *Determination of Stability Constants*, p. 59. McGraw-Hill, New York, 1961.

Talanta, 1970, Vol. 17, pp. 525 to 536. Pergamon Press. Printed in Northern Ireland

THEORY OF TITRATION CURVES—VII

THE PROPERTIES OF DERIVATIVE TITRATION CURVES FOR STRONG ACID-STRONG BASE AND OTHER ISOVALENT ION-COMBINATION TITRATIONS

THELMA MEITES and LOUIS MEITES
Department of Chemistry, Clarkson College of Technology, Potsdam,
New York 13676, U.S.A.

(*Received* 27 *October* 1969. *Accepted* 2 *January* 1970)

Summary—This paper deals with isovalent ion-combination titrations based on reactions that can be represented by the equation $M^{n+} + X^{n-} \rightarrow MX$, where the activity of the product MX is invariant throughout a titration, and with the derivative titration curves obtained by plotting $d[M^+]/df$ versus f for such titrations. It describes some of the ways in which such curves can be obtained; it compares and contrasts them both with potentiometric titration curves, which resemble them in shape, and with segmented titration curves, from which they are derived; and it discusses their properties in detail.

DERIVATIVE titrations are little known and rarely if ever performed, even though it is possible to envision circumstances in which they should have significant advantages over other more familiar titration techniques. Malmstadt and Roberts[1] performed some spectrophotometric titrations in which the reagent was added at a nearly, though not quite, constant rate from a conventional burette while the dynode voltage of a photomultiplier was amplified, inverted, and differentiated with respect to time by a simple R-C network. Recording the output of this network against time would have given a true derivative titration curve had the rate of reagent addition been constant, but Malmstadt and Roberts chose instead to use a second-derivative autotitrator to terminate the addition of reagent at the inflection point of that curve. A similar approach was later adopted by De Leo and Stern.[2] Zenchelsky and Segatto[3] performed derivative thermometric titrations in which the temperature of the titration mixture was sensed by a thermistor connected as one arm of a d.c. Wheatstone bridge; the out-of-balance voltage of this bridge was differentiated with respect to time by an R-C network, the output from which was filtered and recorded against time. Very heavy filtering had to be used to eliminate noise caused by stirring irregularities, power dissipation in the thermistor,[4] and other high-frequency phenomena, and severely distorted curves were obtained. Similar experiences were reported by Perchec and Gilot[5] and Bark and Doran.[6]

Recent advances in the art of signal processing should simplify the task of obtaining reasonably faithful derivative titration curves. There is no detector employed in titrations for which the signal/noise ratio is worse than it is for a dropping electrode in an amperometric titration, and the very low frequency of the noise (*i.e.*, the variation of instantaneous current during the drop-life) at a dropping electrode introduces a further complication, yet Kelley and Fisher[7] were able to obtain derivative polarograms conforming closely to theoretical expectations, by techniques that should be easy to adapt to the trivially different conditions arising in titrations. One obvious digital approach would be to compute successive values of $\Delta S/\Delta t$, S being the signal provided by the detector and t the elapsed time since the start of the titration, and plot them against t in a constant-rate titration. Signal smoothing or averaging would of course be advantageous. Another approach would be to equip the motor-driven burette (or other device used for reagent addition) with a transmitting potentiometer, or its equivalent, to furnish a signal proportional to the volume V of reagent added at any instant, thereby making it possible to compute $\Delta S/\Delta V$ and plot it against V, and further enabling anticipation circuitry to be added so that equilibration could be ensured for a reaction that becomes slow near the equivalence point.

Derivative titrations are based on the apparatus and experimental techniques of segmented titration-curve procedures, and, like the latter, are therefore more versatile than potentiometric titrations. Thermometric, spectrophotometric, conductometric, fluorometric, and other kinds of detectors can all be used in familiar ways, and the problem of selecting an indicator electrode that will respond to the concentration of some suitable species does not arise. Moreover, although derivative titration curves have shapes strongly reminiscent of the shapes of potentiometric titration curves, they have very different properties. Like a potentiometric titration curve, a derivative titration curve has a point of maximum slope that almost coincides with the equivalence point when the equilibrium constant, K_t, for the chemical reaction and the concentrations of the two reacting solutions are reasonably large. But the range of variation is much larger for the derivative than it is for the potential, and in addition the derivative undergoes a larger fraction of that variation in the immediate vicinity of the inflection point. For these reasons it is possible to locate the inflection point on a derivative titration curve even under conditions so unfavourable that none can be perceived on the corresponding potentiometric titration curve.

Comparison of derivative titration curves with the segmented ones from which they are obtained indicates that neither has much, if any, advantage over the other for end-point location in the extreme situations that arise when K_t and the concentrations of the reacting solutions are small. The segmented curve then has a wide region of curvature around the equivalence point, and end-point location consequently entails long extrapolations of the short linear portions. The discomfort and error thus produced will not differ materially from those caused by the fact that the derivative curve for the same titration is approximately linear for some distance on either side of the inflection point, so that it will not be possible to attain greater accuracy in locating the inflection point, and by the additional fact that the inflection point differs appreciably from the equivalence point under these extreme conditions. All of these considerations will be illustrated by Figs. 1 and 3.

It is when K_t and the concentrations of the solutions are moderately large that derivative curves will be superior to segmented ones for end-point location. Then, by appropriate selection of the experimental conditions, the derivative can be made to undergo a very large variation in the immediate vicinity of the equivalence point. This variation is so sudden and so sharp that it should permit far more precise and accurate end-point location than can be attained with segmented curves. It is of course well known that, other things being equal, sigmoid curves are superior for end-point location to segmented ones.

The advantage of derivative titrimetry is even more pronounced in the fairly common situation in which the solution being titrated contains two substances that can react with the reagent. Consider, for example, the thermometric titration of a mixture of zinc(II) and strontium(II) with ethylenediaminetetra-acetate in a medium in which zinc is not appreciably complexed. The zinc will react with the reagent first because the formation constant of its chelonate is much higher than that of the strontium chelonate. But the two enthalpies of formation differ so little (*ca.* 25%) that the end-point of the titration of zinc will be very difficult to locate with reasonable precision. On the corresponding derivative titration curve, however, the rate of change of temperature with respect to either time or volume of reagent would drop abruptly to a value only about $\frac{3}{4}$ as large, as the last of the zinc was titrated: inspection of computed titration curves suggests that the accuracy and precision attainable in the determination of zinc in this mixture can be little, if at all, inferior to those that can be secured in work with pure solutions.

Titration curves are also often employed for the evaluation of equilibrium and rate constants, and for these purposes derivative curves seem markedly superior to segmented ones. Equilibrium constants were first deduced from amperometric titration curves by Kolthoff and Laitinen[8] and by Bobtelsky and Jordan,[9] whose lead has been followed by many others; the ways in which they have been obtained from thermometric titration curves have been reviewed by Tyrrell[10]; any segmented-curve technique may be used in similar ways. In any case, the computation has to be based on the relatively small difference between the curve actually obtained and the one that would be obtained if the titration reaction were complete at every point, and precise results are therefore very difficult to obtain. Although the corresponding derivative curve really presents the same information, its shape is more sensitive to variations of the equilibrium constant.

The use of constant-rate titrimetry in studies of homogeneous kinetics was introduced by Cover and Meites[11] and Kozak and Fernando.[12] Its applications to date include studies of the rate of the disproportionation of uranium(V)[13] and the rate of the reaction between diphenyl sulphide and bromine.[14] One situation in which the superiority of derivative titration curves (which for purposes like this must portray the behaviour of the derivative with respect to time rather than volume of reagent) would be clearly evident would be that in which some side-reaction consuming the substance M^{n+} being titrated was induced by the main reaction. Other kinds of titrimetry would then reveal only that the end-point preceded the expected equivalence point; it would be easy to infer that the induced reaction was taking place, but its rate would not be at all easy to evaluate. Derivative titrimetry, on the other hand, would provide values of $d[M^{n+}]/dt$ that could be directly compared with those expected in the absence of the induced reaction, and the difference between these, and the manner in which it varied as the titration progressed, would be easy to interpret in mechanistic and kinetic ways.

Whether the advantages of derivative titrations for all these purposes can be realized in practice is of course a question that will have to be settled experimentally. To provide a firm basis for such work we have undertaken a detailed investigation of their theory for the simplest case: that of an isovalent ion-combination titration.[15] This has entailed a more extensive study of the properties of the third derivative of the titration curve than has been undertaken previously.

We shall consider the general equation

$$M^{n+} + X^{n-} = MX \tag{1}$$

omitting charges henceforth for simplicity of notation. Assuming that a $C_M{}^0F$ solution of M is titrated with a C_XF solution of X, we define the dilution parameter r and the titration parameter f by the equations

$$r = C_M{}^0/C_X \tag{2}$$

$$f = V_XC_X/V_M{}^0C_M{}^0 \tag{3}$$

where $V_M{}^0$ is the volume of the solution of M being titrated and V_X is the volume of the reagent added to it at the point under consideration. We assume that the equilibrium constant of the titration reaction

$$K_t = 1/[\mathrm{M}][\mathrm{X}] \tag{4}$$

is invariant and is satisfied at every point. Similar definitions and assumptions have been made and discussed in earlier papers in this series.[15,16]

The fundamental titration-curve equation for a titration involving reaction (1) is

$$[\mathrm{M}] = C_M{}^0\frac{1-f}{1+rf} + \frac{1}{K_t[\mathrm{M}]}\,. \tag{5}$$

We shall consider the derivative titration curve to be a plot of d[M]/df, which we shall henceforth denote by D, against f. Descriptions of this plot are applicable, *mutatis mutandis*, to one of d[X]/df against f.

Differentiation of equation (5) yields

$$D = -\frac{(rK_t[\mathrm{M}]^2 + C_M{}^0K_t[\mathrm{M}] - r)^2}{(1+r)C_M{}^0K_t(K_t[\mathrm{M}]^2+1)} \tag{6}$$

which is the fundamental equation of the derivative titration curve for an isovalent ion-combination titration. Figures 1, 2, and 3 show how the curve is affected by variations of K_t, r, and $C_M{}^0$, respectively. To facilitate comparisons of these curves we have normalized them by plotting D/D_0, rather than D itself, on the ordinate axis; D_0 is the value of D at $f = 0$. In any practical titration the value of [M] at this point would be indistinguishable from $C_M{}^0$, and the product $K_t(C_M{}^0)^2$ would also be very much larger than unity, although a few curves for which neither of these things is true are included in Figs. 1–3 to show degenerate forms. When both are true, the value of D_0 is given by

$$D_0 = -(1+r)C_M{}^0 \tag{7}$$

which is useful in interpreting most of the curves in these figures. It indicates, for example, that the decrease of D/D_0 as r increases, which is shown by Fig. 2, is partly attributable to an increase of D_0. The value of D at $f = 1$, which we shall represent by the symbol D_1, may be found by substituting $[\mathrm{M}] = 1/K_t^{1/2}$ into equation (6), and is given by

$$D_1 = -C_M{}^0/2(1+r) \tag{8}$$

Differentiating equation (6) yields a description of the slope dD/df of the derivative curve:

$$\frac{\mathrm{d}D}{\mathrm{d}f} = \frac{2(rK_t[\mathrm{M}]^2 + C_M{}^0K_t[\mathrm{M}] - r)^3(rK_t[\mathrm{M}]^3 + 3r[\mathrm{M}] + C_M{}^0)}{(1+r)^2(C_M{}^0)^2K_t(K_t[\mathrm{M}]^2+1)^3} \tag{9}$$

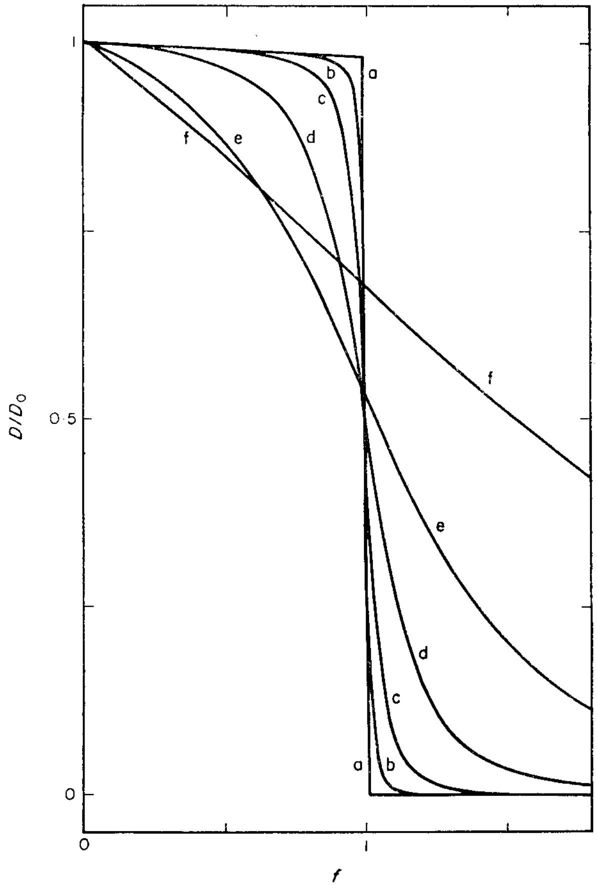


FIG. 1.—Calculated derivative titration curves.
$C_M{}^0 = 0{\cdot}1M$, $r = 0{\cdot}01$ and K_t = (*a*) 10^{10}, (*b*) 10^6, (*c*) 10^5, (*d*) 10^4, (*e*) 10^3, and (*f*) 10^2.

On introducing the expression for $K_t[\mathrm{M}]^2$ obtained by rearranging equation (5), it can be shown that

$$rK_t[\mathrm{M}]^2 + C_M{}^0K_t[\mathrm{M}] - r = C_M{}^0K_t[\mathrm{M}](1 + r)/(1 + rf).$$

Since the right-hand side of this equation must evidently be positive for all values of $f \geqslant 0$, and since the same thing is true of both the denominator and the quantity within the second parentheses in the numerator on the right-hand side of equation (9), $\mathrm{d}D/\mathrm{d}f$ must be positive everywhere, as is intuitively apparent.

At the equivalence point

$$\left(\frac{\mathrm{d}D}{\mathrm{d}f}\right)_1 = (4r + C_M{}^0K_t^{1/2})C_M{}^0/4(1 + r)^2. \qquad (10a)$$

On inspection of Fig. 2 it is clear that the choice of a small value of r is advantageous, because it maximizes the variation of D around the equivalence point in the same way that it decreases the necessity for applying a dilution correction in the parent segmented-curve technique. As a basis for estimating the relative precision of a derivative

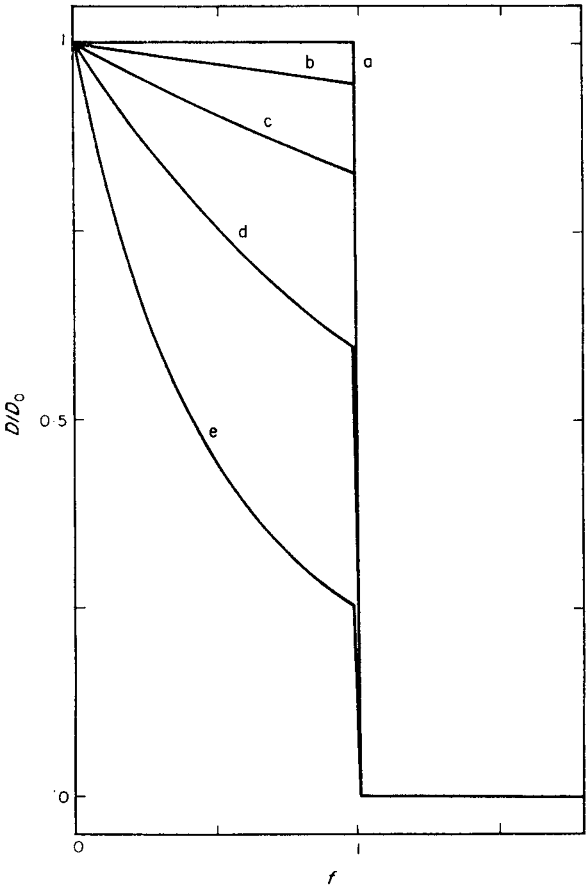


FIG. 2.—Calculated derivative titration curves.
$C_M{}^0 = 0{\cdot}1M$, $K_t = 10^{14}$, and r = (*a*) 0, (*b*) 0·03, (*c*) 0·1, (*d*) 0·3, and (*e*) 1.

titration we shall therefore rewrite equation (10*a*) in the approximate form

$$\left(\frac{\Delta D}{\Delta f}\right)_1 = (C_M{}^0)^2 K_t^{1/2}/4\,. \qquad (10b)$$

Benedetti-Pichler[17] defined the relative precision of a potentiometric titration as the value of Δf corresponding to a fixed uncertainty in the pH or indicator-electrode potential at the equivalence point. An exactly analogous definition seems inappropriate here, since there is very little basis for estimating the absolute uncertainty that can be expected in measuring a derivative signal. We shall instead assume that the uncertainty in the value of the derivative at the equivalence point is $\pm 10\%$ of its value at $f = 0$, so that $\Delta D_1/D_0 = \pm 0{\cdot}1$, and define the relative precision as the corresponding value of Δf. This appears to us to be an extremely conservative assumption, but experimentation will be needed to obtain a more reliable one.

Combination of equations (7) and (10*b*) with the assumption that again r will be made small, and the introduction of the description above of $\Delta D_1/D_0$, gives

$$\Delta f = \mp 0{\cdot}4/C_M{}^0 K_t^{1/2}. \qquad (11)$$

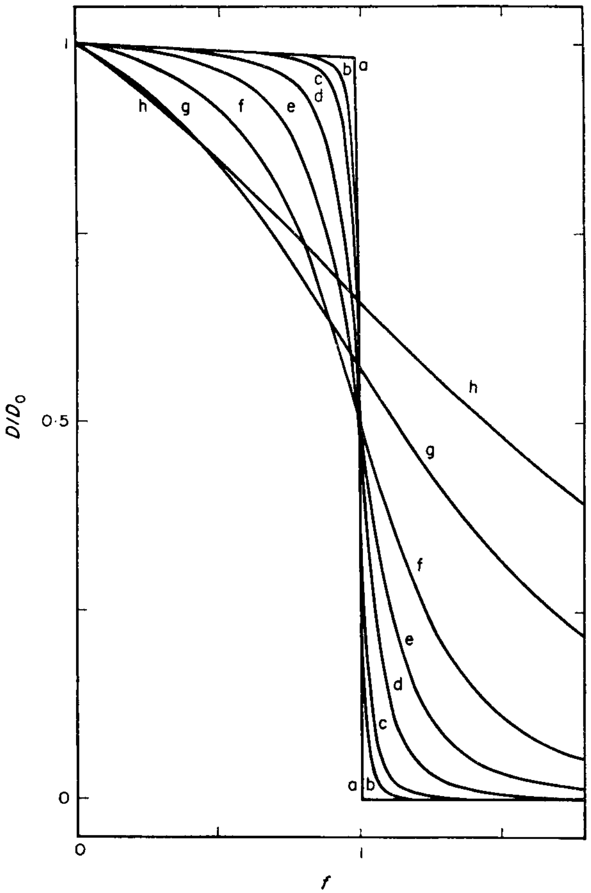


FIG. 3.—Calculated derivative titration curves.
$r = 0{\cdot}01$, $K_t = 10^{14}$, and $C_M{}^0 =$ (*a*) 1, (*b*) 10^{-5}, (*c*) 5×10^{-6}, (*d*) 2×10^{-6}, (*e*) 1×10^{-6}, (*f*) 5×10^{-7}, (*g*) 2×10^{-7}, and (*h*) $1{\cdot}1 \times 10^{-7}M$.

As usual,[18] it is the quantity $(C_M{}^0)^2K_t$ that governs the precision attainable in an isovalent ion-combination titration. The expected relative precision of a derivative titration is 0·4% even if $(C_M{}^0)^2K_t$ is as small as 10^1; this figure compares very favourably with the precision expected in an ordinary segmented-curve titration and is definitely superior to the corresponding figure for a potentiometric titration.

Differentiating equation (9) yields a description of the second derivative of the derivative curve:

$$\frac{d^2D}{df^2} = \frac{\begin{aligned}-6(rK_t[M]^2 + C_M{}^0K_t[M] - r)^4\{[(K_t[M]^2)^3 + 5(K_t[M]^2)^2 \\ + 11(K_t[M]^2) - 1]r^2 - [K_t[M]^2 - 1](C_M{}^0)^2K_t + 8rC_M{}^0K_t[M]\}\end{aligned}}{(1 + r)^3(C_M{}^0)^3K_t{}^2[K_t[M]^2 + 1]^5} \tag{12}$$

At the equivalence point

$$\left(\frac{d^2D}{df^2}\right)_{r=1} = -3rC_M{}^0(2r + C_M{}^0K_t^{1/2})/2(1 + r)^3. \tag{13}$$

If $r = 0$, the second derivative vanishes at the equivalence point: like the corresponding potentiometric titration curve, the derivative titration curve has an inflection point that coincides with the equivalence point if there is no dilution during the titration. Moreover, when $r = 0$, equation (12) becomes

$$\left(\frac{\mathrm{d}^2D}{\mathrm{d}f^2}\right)_{r=0} = 6(C_{\mathrm{M}}{}^0)^3K_{\mathrm{t}}{}^3[\mathrm{M}]^4(K_{\mathrm{t}}[\mathrm{M}]^2 - 1)/(K_{\mathrm{t}}[\mathrm{M}]^2 + 1)^5. \tag{14}$$

The value of $K_{\mathrm{t}}[\mathrm{M}]^2$ exceeds 1 everywhere up to the equivalence point, is equal to 1 at the equivalence point, and is smaller than 1 everywhere beyond the equivalence point. Therefore, if $r = 0$, $\mathrm{d}^2D/\mathrm{d}f^2$ is positive at $f = 0$, remains positive until it vanishes at $f = 1$, and is negative for all values of f exceeding 1: there is only one point of inflection on the titration curve.

These things are also true if r is finite but very small. However, increasing r causes the terms in r^2 and r within the braces in equation (12) to increase rapidly, and there is a certain critical value of r at which $\mathrm{d}^2D/\mathrm{d}f^2$ just becomes equal to zero when $f = 0$. If r exceeds this critical value, $\mathrm{d}^2D/\mathrm{d}f^2$ is negative at $f = 0$, increases until it passes through zero at a point that corresponds to a point of minimum slope on the titration curve, attains positive values over a certain range of values of f, then decreases abruptly, passing through zero at a point that corresponds to a point of maximum slope on the titration curve, and finally remains negative for all values of f beyond this second inflection point. The critical value of r is approximately $1/(C_{\mathrm{M}}{}^0)^2K_{\mathrm{t}}$ and is thus indistinguishable from zero in practical titrations.

Decreasing either K_{t} or $C_{\mathrm{M}}{}^0$ causes the value of $\mathrm{d}^2D/\mathrm{d}f^2$ at $f = 0$ to become more negative when r is finite, and narrows the range of values of f over which $\mathrm{d}^2D/\mathrm{d}f^2$ is positive. There is a degenerate case in which the second derivative never does attain positive values, so that there is no inflection point on the titration curve.

In connection with equation (13) it was stated above that the point of maximum slope coincides with the equivalence point if $r = 0$. In the light of the foregoing discussion, however, it can be seen that this is not true if r has any finite value, for then $\mathrm{d}^2D/\mathrm{d}f^2$ is negative at $f = 1$; in any real derivative titration (as in any real potentiometric titration[16]) the point of maximum slope precedes the equivalence point.

The locations of the inflection points, where the quantity within braces in equation (12) must vanish, are most conveniently described by equating this quantity to zero in the form

$$\frac{(C_{\mathrm{M}}{}^0)^2K_{\mathrm{t}}}{r^2}(1 - K_{\mathrm{t}}[\mathrm{M}]^2) + 8\left[\frac{(C_{\mathrm{M}}{}^0)^2K_{\mathrm{t}}}{r^2}\right]^{1/2}(K_{\mathrm{t}}[\mathrm{M}]^2)^{1/2}$$
$$+ [(K_{\mathrm{t}}[\mathrm{M}]^2)^3 + 5(K_{\mathrm{t}}[\mathrm{M}]^2)^2 + 11(K_{\mathrm{t}}[\mathrm{M}]^2) - 1] = 0. \tag{15}$$

This has the solution described by the equation

$$\frac{C_{\mathrm{M}}{}^0K_{\mathrm{t}}^{1/2}}{r} = \frac{4K_{\mathrm{t}}^{1/2}[\mathrm{M}] + (K_{\mathrm{t}}[\mathrm{M}]^2 + 1)^2}{K_{\mathrm{t}}[\mathrm{M}]^2 - 1} \tag{16}$$

from which the negative sign in the numerator of the general quadratic solution has been omitted because it can give rise only to negative or indeterminate values of $C_{\mathrm{M}}{}^0K_{\mathrm{t}}^{1/2}/r$, which are physically meaningless. From equation (16) it is again apparent that any inflection point must precede the equivalence point, so that $K_{\mathrm{t}}[\mathrm{M}]^2$ at the inflection point will exceed 1, if r has any finite value.

It is appropriate to begin by considering the locations of the inflection points when $C_M{}^0K_t^{1/2}/r$ is large, because this is the situation that is most important in practical titrations. The second inflection point, which is the point of maximum slope, will then occur just before the equivalence point, where $K_t[\mathrm{M}]^2$ barely exceeds 1.* Substituting

$$K_t[\mathrm{M}]^2 = 1 + \delta \qquad (\delta \ll 1) \tag{17}$$

into equation (16), replacing $(1 + \delta)^{1/2}$ by $1 + \delta/2$, we obtain

$$\frac{C_M{}^0K_t^{1/2}}{r} = \frac{4[1 + \delta/2] + (2 + \delta)^2}{\delta} = \frac{8}{\delta}. \tag{18a}$$

Comparison of equations (5) and (17) provides a value for δ:

$$\delta = C_M{}^0K_t[\mathrm{M}](1 - f)/(1 + rf). \tag{18b}$$

By combining equations (18*a*) and (18*b*), letting $[\mathrm{M}] = 1/K_t^{1/2}$ and $rf = r$ because the inflection point under discussion almost coincides with the equivalence point, we obtain

$$1 - f = 8r(1 + r)/(C_M{}^0)^2K_t. \tag{19}$$

Thus, for example, if $r = 1$ and $K_t = 10^{14}$, as would be the case for the titration of C^0F strong acid with C^0F strong base in an aqueous medium of low ionic strength at 25°, the point of maximum slope will occur at $(1 - f) = 1{\cdot}6 \times 10^{-13}/(C^0)^2$; this is quite close enough to the equivalence point to justify the approximations embodied in equation (19) unless C^0 is very small. It is unexpected that this result should be exactly identical with that for the point of maximum slope on the potentiometric titration curve under the same conditions.[16]

The location of the first inflection point when $C_M{}^0K_t^{1/2}/r$ is large can be obtained by noting that equation (16) becomes very nearly

$$\frac{C_M{}^0K_t^{1/2}}{r} = K_t[\mathrm{M}]^2 \tag{20}$$

if $K_t[\mathrm{M}]^2$ is large. As will presently appear, when $C_M{}^0K_t^{1/2}/r$ is large the point of minimum slope is close enough to the equivalence point to justify the approximation $(1 + rf) = (1 + r)$, and is yet far enough away from the equivalence point to justify writing $[\mathrm{M}] = C_M{}^0(1 - f)/(1 + rf)$. Introducing these two simplifications into equation (20) and rearranging yields

$$1 - f = (1 + r)/(rC_M{}^0K_t^{1/2})^{1/2} \tag{21}$$

so that in the strong acid–strong base titration mentioned in the preceding paragraph, where $r = 1$ and $K_t = 10^{14}$ and where the point of maximum slope occurs at $(1 - f) = 1{\cdot}6 \times 10^{-13}/(C^0)^2$, the point of minimum slope occurs at $(1 - f) = 6{\cdot}32 \times 10^{-4}/(C^0)^{1/2}$.

As the value of $C_M{}^0$ decreases, the values of $(1 - f)$ at both of the inflection points increase, but that at the point of maximum slope increases much the more rapidly of

---

* It is the ease with which situations important in practice can be described by simplifications like this that justifies the appearance of $K_t[\mathrm{M}]^2$ in these equations. The superficially preferable course of solving equation (5) for [M] and differentiating with respect to f yields equations so complex that the useful simplifications are impossible to discern.

the two. The behaviour of these values in the typical case in which $r = 1$ is shown in Fig. 4. With equation (16) in mind, it is convenient to focus attention on the behaviour of $K_t[M]^2$ at the inflection points. As $C_M{}^0K_t^{1/2}/r$ decreases, the value of $K_t[M]^2$ at the point of minimum slope, which is large when $C_M{}^0K_t^{1/2}/r$ is large, decreases more and more; meanwhile the value of $K_t[M]^2$ at the point of maximum slope, which is barely above 1 when $C_M{}^0K_t^{1/2}/r$ is large, increases. There is a minimum value of $C_M{}^0K_t^{1/2}/r$ at which an inflection point is possible. This minimum may be found by differentiating equation (16) to obtain

$$\frac{d(C_M{}^0K_t^{1/2}/r)}{d(K_t[M]^2)} = \frac{(K_t[M]^2 - 1)[2/(K_t^{1/2}[M]) + 2(K_t[M]^2 + 1)] - [4(K_t^{1/2}[M] + (K_t[M]^2 + 1)^2]}{(K_t[M]^2 - 1)^2} . \qquad (22)$$

On equating the numerator of the right-hand side of this equation to zero it is found that the minimum value of $C_M{}^0K_t^{1/2}/r$ occurs at $K_t[M]^2 = 4$. On substituting the latter value into equation (16), this minimum value of $C_M{}^0K_t^{1/2}/r$ is found to be 11. By combining these results with equation (5), it can be shown that

$$f = (22r - 3)/25 \qquad (23)$$

at the point where the two inflection points coincide. This limiting value of f is represented by the small circle in Fig. 4. It is especially curious, because similar functions derived from titration curves have heretofore seemed to be uniformly

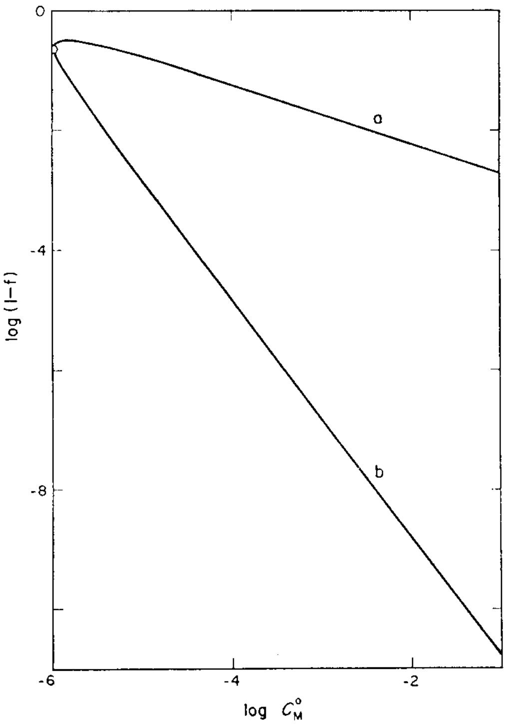


FIG. 4.—Effects of log $C_M{}^0$ on the values of $(1 - f)$ at (a) the first and (b) the second inflection points of titration curves for which $r = 1$ and $K_t = 10^{14}$.

monotonic, that the value of $(1 - f)$ at the point of minimum slope should pass through a maximum as this limit is approached.

All these considerations can be summarized as follows

1. If r is zero or extremely small the curve has only one inflection point: this is a point of maximum slope, and it coincides with the equivalence point if $r = 0$.

2. In a practical titration, in which r has a finite and appreciable value, there may be either two inflection points or none. There is no inflection point if $C_M{}^0K_t^{1/2}/r$ is equal to or less than 11; there are two inflection points if $C_M{}^0K_t^{1/2}/r$ exceeds this value. The first inflection point is a point of minimum slope; if $C_M{}^0K_t^{1/2}/r$ is very large, as will be true in practical titrations, the value of $K_t[M]^2$ is large at this point, and its location is described by equation (21). The second inflection point is a point of maximum slope and must always precede the equivalence point; if $C_M{}^0K_t^{1/2}/r$ is large, the value of $K_t[M]^2$ is barely above 1 at this point, and its location is described by equation (19). As $C_M{}^0K_t^{1/2}/r$ decreases, the value of $K_t[M]^2$ at the first inflection point decreases while that at the second inflection point rises, and the ratio of the values of $(1 - f)$ at the two inflection points approaches 1. When $C_M{}^0K_t^{1/2}/r$ becomes equal to 11, $K_t[M]^2$ becomes equal to 4 at each of the inflection points, and the corresponding values of $(1 - f)$ become equal to $(28 - 22r)/25$; the inflection points coincide and therefore vanish.

Zusammenfassung—Diese Arbeit befaßt sich mit isovalenten Ionenkombinations-Titrationen, die man durch die Gleichung $M^{n+} + X^{n-} \rightarrow MX$ darstellen kann, wenn sich die Aktivität des Produkts MX bei der ganzen Titration nicht ändert, sowie mit den differenzierten Titrationskurven, die man durch Auftragen von d $[M^-]/\mathrm{d}f$ gegen f bei solchen Titrationen erhält. Die Arbeit beschreibt einige Verfahren, wie man solche Kurven erhalten kann; sie zeigt Ähnlichkeiten und Unterschiede zu potentiometrischen Titrationskurven, die ähnliche Form haben, und zu segmentierten Titrationskurven, von denen sie abgeleitet sind. Die Eigenschaften dieser Kurven werden bis ins Einzelne diskutiert.

Résumé—Ce mémoire traite des titrages par combinaison d'ions isovalents basés sur des réactions que l'on peut représenter par l'équation $M^{n+} + X^{n-} \rightarrow MX$, où l'activité du produit MX est invariante tout à travers un titrage, et des courbes de titrage dérivées obtenues en portant $\mathrm{d}[M^+]/\mathrm{d}f$ par rapport à f pour de tels titrages. Il décrit quelques-unes des voies dans lesquelles de telles courbes peuvent être obtenues; il les compare et les oppose tant aux courbes de titrages potentiométriques, qui leur ressemblent en allure, qu'aux courbes de titrage segmentées, desquelles elles sont dérivées; et il discute en détail de leurs propriétés.

REFERENCES

1. H. V. Malmstadt and C. B. Roberts, *Anal. Chem.*, 1956, **28**, 1408.
2. A. B. De Leo and M. J. Stern, *J. Pharm. Sci.*, 1965, **54**, 911.
3. S. T. Zenchelsky and P. R. Segatto, *Anal. Chem.*, 1957, **29**, 1856.
4. L. Meites, T. Meites and J. N. Jaitly, *J. Phys. Chem.*, 1969, **73**, 3801.
5. H. Perchec and B. Gilot, *Bull. Soc. Chim. France*, 1964, 619.
6. L. S. Bark and K. Doran, unpublished results cited by L. S. Bark and S. M. Bark, *Thermometric Titrimetry*, p. 29. Pergamon, Oxford, 1969.
7. M. T. Kelley and D. J. Fisher, *Anal. Chem.*, 1958, **30**, 929; 1959, **31**, 1475.
8. I. M. Kolthoff and H. A. Laitinen, *Rec. Trav. Chim.*, 1940, **59**, 922.
9. M. Bobtelsky and J. Jordan, *J. Am. Chem. Soc.*, 1945, **67**, 1824.
10. H. J. V. Tyrrell, *Talanta*, 1967, **14**, 843; *cf.* also R. J. Raffa, M. J. Stern and L. Malspeis, *Anal. Chem.*, 1968, **40**, 70.

11. R. E. Cover, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1962; R. E. Cover and L. Meites, *J. Phys. Chem.*, 1963, **67**, 1528, 2311.
12. G. S. Kozak and Q. Fernando, *J. Phys. Chem.*, 1963, **67**, 811; G. S. Kozak, Q. Fernando and H. Freiser, *Anal. Chem.*, 1964, **35**, 296.
13. P. W. Carr and L. Meites, *J. Electroanal. Chem.*, 1966, **12**, 373.
14. J. Janata and O. Schmidt, *ibid.*, 1966, **11**, 224.
15. L. Meites and J. A. Goldman, *Anal. Chim. Acta*, 1964, **30**, 18.
16. *Idem*, *ibid.*, 1963, **29**, 472.
17. A. A. Benedetti-Pichler, *The Essentials of Quantitative Analysis.* Ronald Press, New York, 1956.
18. L. Meites, *Polarographic Techniques*, 2nd Ed., pp. 470–474. Interscience, New York, 1965.

Talanta, 1970, Vol. 17, pp. 537 to 540. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

Mass spectrometric analysis of carbon monoxide–nitrogen mixtures

(*Received* 12 *December* 1969. *Accepted* 14 *January* 1970)

THE PRODUCTS of a hydrocarbon flame burning in oxygen will contain combustion gases consisting largely of carbon monoxide, carbon dioxide and water. Analysis of samples of such mixtures with a conventional single-focussing mass spectrometer such as the A.E.I. M.S.2 or the Atlas CH 4 presents no difficulties. When, however, the oxidant is air, or the fuel contains nitrogen, or the samples withdrawn from the flame include some of the surrounding air, the analytical problem becomes more difficult. The most abundant ions in the mass spectra of both nitrogen and carbon monoxide are the molecular-ions which are responsible for nearly all the ion current. Both these ions have an integral mass of 28, so when a mixture of nitrogen and carbon monoxide is admitted to the mass spectrometer the ion currents due to CO^+ and N_2^+ ions cannot be separated and are responsible for a single peak in the mass spectrum. When such a state of affairs is encountered with other pairs of compounds it is frequently still possible to carry out a satisfactory analysis by using the mass peaks which are due to fragment ions. Some of these may make up a substantial part of the total ion current and differ in their occurrence and abundance for pairs of compounds having the same integral mass. From the mass spectra of carbon monoxide and nitrogen which are shown in Table I, it can be seen that the fragment ions are of low abundance so that any analysis based on the measurement of their ion currents would be subject to considerable error. Such an analysis made for example from the $^{12}C^+$ peak from carbon monoxide and the $^{14}N^+$ peak from nitrogen would have an error approximately 50 times that of a method based on the ion current due to the molecular ions.

TABLE I.—RELATIVE PEAK HEIGHTS FROM MASS SPECTRA

m/e	CO_2	CO	N_2
44	100	—	—
29	0·07	1·12	0·77
28	8·10	100	100
22	1·50	—	—
16	4·08	0·44	0·01
14	—	5·0	5·0
12	7·0	1·0	—

Relative sensitivities

Carbon dioxide $\left(\frac{H_{44}}{H_{40}} \cdot \frac{P_{Ar}}{P_{CO_2}}\right) = 0·83$

Carbon monoxide $\left(\frac{H_{28}}{H_{40}} \cdot \frac{P_{Ar}}{P_{CO}}\right) = 0·77$

Nitrogen $\left(\frac{H_{28}}{H_{40}} \cdot \frac{P_{Ar}}{P_{N_2}}\right) = 0·87$

In fact, the masses of the molecule ions of carbon monoxide and nitrogen are not exactly the same; the precise mass of CO^+ is 27·994914, that of N_2^+ is 28·006148, and the difference is about 1 part in 2500.

The resolution of a single-focussing mass spectrometer operated under conditions of high sensitivity is only 1 part in 1000, so that CO^+ and N_2^+ mass peaks cannot be resolved. Modern double-focussing mass spectrometers such as the A.E.I. M.S.9 have resolutions of the order of 1 part in 70000 so that it is possible by using such an instrument to analyse mixtures of carbon monoxide and nitrogen directly by measuring the intensity of the ion currents at masses 27·994915 and 28·006148. These instruments are, however, extremely costly and a method was therefore developed in which the normal analytical routine of a single-focussing machine was modified to permit the analysis of mixtures of combustion products containing both carbon monoxide and nitrogen.

In conventional methods of gas analysis it is convenient to convert the inert carbon monoxide into carbon dioxide which can be absorbed by alkaline solutions. A number of procedures for carrying out this conversion have been devised, involving oxidation of carbon monoxide to carbon dioxide with molecular oxygen or solid metal oxides at high temperatures. These procedures are not sufficiently simple or quantitative to be useful. Recently, however, a suitable oxidant has been proposed for the conversion of carbon monoxide into carbon dioxide at room temperature. It consists of a mixture of iodine pentoxide and sulphuric acid adsorbed upon pumice and is available commercially in the form of a fine powder under the name of Schütze catalyst.

The method described in this paper involves the recording of mass spectra of a sample containing both carbon monoxide and nitrogen before and after conversion with the oxidant. The intensity of the peak at mass 28 would be reduced by an amount directly proportional to the increase in the 44-peak produced by the conversion of carbon monoxide into carbon dioxide. The amount of carbon monoxide in the sample could be calculated from either the decrease in mass-28 peak intensity or the increase in mass-44 peak intensity.

EXPERIMENTAL

Materials

Schütze catalyst was obtained from Kodak Ltd. All gases were obtained from the British Oxygen Co.

Apparatus

The inlet system of an A.E.I. M.S.2 mass spectrometer was modified by attaching a small Pyrex glass chamber into which a porcelain boat filled with the oxidant could be introduced. The chamber could be pumped out and isolated from both the pumping system and the mass spectrometer inlet by means of taps. The sample volume could be connected to the mass spectrometer by opening a tap.

Method

A sample was introduced into the inlet reservoir of the mass spectrometer from the sample volume and its pressure was measured by means of a diaphragm micromanometer. The mass spectrum was then recorded and the reservoir pumped out. A second sample was then admitted from the sample volume and the reservoir connected to the chamber containing the catalyst. The pressure was measured on the micromanometer and the mass spectrum again recorded.

Calculation of results

Let the pressure in the reservoir for the first sample be P and the pressure after oxidation be P', and p and p' be the partial pressures of any component before and after oxidation. Let the sensitivities of the mass spectrometer for carbon monoxide, carbon dioxide and nitrogen be S_{CO}, $S_{\mathrm{CO_2}}$ and $S_{\mathrm{N_2}}$. If H is the peak height before oxidation and H' that recorded after oxidation, then, if no carbon dioxide is present initially,

$$\begin{aligned}\frac{H'_{44}}{S_{\mathrm{CO_2}}} &= p'_{\mathrm{CO_2}}\\ &= \frac{P}{P'}\cdot p_{\mathrm{CO}}\end{aligned}$$

The partial pressure of carbon monoxide in the original sample may thus be derived from H'_{44}. If carbon dioxide is present in the original sample then this must be corrected for, *i.e.*,

$$p_{\mathrm{CO}} = \frac{P'[H'_{44} - H_{44}P'/P]}{PS_{\mathrm{CO_2}}}$$

In either case the nitrogen concentration may be determined from the residual H'_{28} from

$$p_{\mathrm{N_2}}' = \frac{H'_{28} - 0{\cdot}081H'_{44}}{S_{\mathrm{N_2}}}$$

An additional check may be made by calculating the nitrogen concentration from the residual H_{28} as given by

$$p_{\mathrm{N_2}} = \frac{[H_{28} - 0{\cdot}081H_{44} - H'_{44}P/P' + H_{44}P'/P]}{S_{\mathrm{N_2}}}$$

In order to compensate for instrumental variations, it is common practice to use a standard substance, to express all sensitivities relative to the sensitivity for this substance, and to make a daily check on the sensitivity of the instrument for this one substance, thus avoiding a lengthy daily calibration for all gases. A suitable calibrating substance for this work is argon, and sensitivities for the three gases, expressed as a fraction of the argon sensitivity, are shown in Table I.

RESULTS AND DISCUSSION

The method was tested in a number of ways to check whether the oxidation of carbon monoxide to carbon dioxide was complete under all the experimental conditions expected to be encountered.

1. Mixtures of nitrogen and carbon monoxide were made in a gas mixing plant. The carbon monoxide content was varied from 84·81% to 12·00%.
2. The total pressure of the gas mixture at the inlet system of the mass spectrometer and hence over the oxidant was varied from 1·3 to 130 mbar.
3. The mixture of carbon monoxide and nitrogen was diluted with equal volumes of carbon dioxide to determine whether carbon dioxide had any effect on the oxidation.
4. A mixture of argon and carbon monoxide was oxidized and checked for any residual carbon monoxide.
5. Mixtures of carbon monoxide and nitrogen were oxidized at the gas inlet system of a gas chromatography apparatus to check both for complete oxidation and for the effect of varying the time of exposure of the gas to the oxidant.

TABLE II.—ANALYTICAL RESULTS ON BLENDED GAS MIXTURES

	P_1	P_2	Composition, %						
			Ar		CO		N_2		CO_2
Blend			50·3		42·6		7·7		—
Result	93·0	67·3	50·1	50·4	41·2	41·6	7·7	8·0	—
Blend			47·2		33·0		19·8		—
Result	101·7	73·5	48·0	48·3	32·1	32·6	19·9	19·1	—
Blend			50·7		24·2		25·1		—
Result	123·0	96·9	50·2	50·0	24·7	24·3	25·1	25·7	—
Blend			43·9		23·7		33·4		—
Result	70·0	52·5	45·2	45·7	25·7	25·9	29·9	29·3	—
Blend			55·5		9·2		35·3		—
Result	70·0	52·5	51·4	51·7	10·5	10·5	38·1	37·8	—
Blend			50·7		24·2		25·1		—
Result	53·0	39·3	50·4	51·0	24·6	24·9	25·0	24·1	—
Result	27·7	21·0	50·2	50·5	24·7	25·0	25·1	25·3	—
Result	12·2	8·1	50·5	50·1	24·8	24·8	24·7	25·1	—
Result	1·4	1·1	50·5	50·2	24·2	24·6	25·3	26·2	—
Blend			54·4		45·6		—		—
Result	111·0	83·8	52·0	52·4	48·0	47·6	—		—
Blend			10·0		22·8		25·8		41·4
Result	97·2	74·3	8·7	8·9	24·5	24·9	23·7	23·2	43·7

The results of carrying out these tests are summarized in Table II. It can be seen that the results are in fair agreement with the blend values. It is in fact very difficult to make up a gas mixture of known composition merely by connecting reservoirs of the components at different pressures and allowing free diffusion. The blend values are therefore derived only from the gas pressures of the reservoirs and should not be considered as standard compositions, from which the results may deviate by a few per cent. A good test of the method is the agreement between the pairs of results obtained by different methods. A conservative estimate of the errors would be 2–3%. The results are not affected by the pressure at which oxidation takes place and satisfactory results may be achieved at pressures of ~1 mbar. The oxidation of carbon monoxide is complete and is unaffected by the addition of an excess of carbon dioxide. In a series of experiments in which small volumes of carbon monoxide were swept with a stream of nitrogen over a boat containing the Schütze catalyst in the inlet system of a gas chromatography apparatus, the extent of oxidation was determined by measuring the peak area obtained for the carbon dioxide peak. The time of exposure of the carbon monoxide to the oxidant was varied both by altering the gas flow and admitting the sample at different times. The results obtained were in agreement with those reported above and the time of exposure could not be made sufficiently brief to demonstrate incomplete oxidation of a carbon monoxide sample.

Chemistry Department
University of Birmingham
P.O. Box No. 363
Birmingham, 15

J. R. MAJER

Summary—A method for the analysis of gas mixtures containing both carbon monoxide and nitrogen, by using a single-focussing mass spectrometer, is described. It involves measurement of the mass spectrum of a gas sample before and after conversion of the carbon monoxide present into carbon dioxide by means of the Schütze catalyst.

Zusammenfassung—Die Analyse von Kohlenmonoxid und Stickstoff enthaltenden Gasgemischen unter Verwendung eines einfach fokussierenden Massenspektrometers wird beschrieben. Das Massenspektrum einer Gasprobe wird zweimal gemessen: einmal vor und einmal nach der Umsetzung des vorhandenen Kohlenmonoxids zu kohlendioxid mit Hilfe von Schütze-Katalysator.

Résumé—On décrit une méthode pour l'analyse de mélanges de gaz contenant à la fois de l'oxyde de carbone et de l'azote en utilisant un spectromètre de masse à une seule focalisation. Elle comprend la mesure du spectre de masse d'un échantillon de gaz avant et après conversion de l'oxyde de carbone présent en gaz carbonique au moyen du catalyseur de Schütze.

Talanta, 1970, Vol. 17, pp. 540 to 543. Pergamon Press. Printed in Northern Ireland

Analytical applications of mixed ligand extraction equilibria

Nickel–dithizone–phenanthroline complex

(*Received* 4 *December* 1969. *Accepted* 14 *January* 1970)

THE POPULAR metal reagent dithizone (diphenylthiocarbazone) normally is not useful as a reagent for nickel because the complex forms very slowly and is less intensely coloured than most dithizonates. Recently, however, it was discovered[1] that in the presence of pyridine or other nitrogen bases together with dithizone, a mixed ligand nickel complex of unusually high absorbance is formed relatively rapidly. This reaction is not only potentially useful as a highly sensitive method for nickel but should permit an independent evaluation of the equilibrium extraction constant for nickel dithizonate. Although this had been previously reported[2] to have the value of $10^{-2\cdot 9}$ with chloroform as solvent, a more recent publication[3] cited $10^{-0\cdot 2}$ as a more reliable value because a longer (10 day) equilibration period had been employed in order to overcome the slow rate of the nickel–dithizone reaction.

The extraction constant of the mixed ligand complex, $NiDz_2{\cdot}phen$, (where Dz is the dithizonate anion and phen is 1,10-phenanthroline) is defined as the equilibrium constant of the reaction

$$\mathrm{Ni^{2+} + 2HDz_{org} + phen_{org}} \xrightleftharpoons{K'_{ex}} \mathrm{NiDz_2{\cdot}phen_{org} + 2H^+}$$

and may be evaluated by using the expression

$$D = K'_{\mathrm{ex}} \frac{[\mathrm{HDz}]^2_{\mathrm{org}}[\mathrm{phen}]_{\mathrm{org}}}{[\mathrm{H^+}]^2} \mu_{\mathrm{Ni}} \tag{1}$$

where μ_{Ni} represents the fraction of the total aqueous nickel concentration that is in the uncomplexed hydrated form, and the subscript org indicates a species in the organic phase.

This reaction can be seen to be the sum of (*a*) the extraction of nickel dithizonate

$$\mathrm{Ni^{2+} + 2HDz_{org} \overset{K_{ex}}{\rightleftharpoons} NiDz_{2org} + 2H^+}$$

and (*b*) the formation of the mixed ligand adduct in the organic phase

$$\mathrm{NiDz_{2org} + phen_{org} \overset{K_{AD}}{\rightleftharpoons} NiDz_2{\cdot}phen_{org}}$$

so that K'_{ex}, the mixed ligand extraction constant, can be seen to be the product of the extraction constant of nickel dithizonate, K_{ex}, and the organic phase mixed-ligand adduct formation constant, K_{AD}. Hence, if K_{AD} is known,[4] K_{ex} can be evaluated.

It was therefore decided to determine K_{ex}' in order to evaluate K_{ex} and to provide a rational basis on which to design a procedure for determining nickel by use of this reaction.

EXPERIMENTAL

Materials

All materials were of analytical reagent grade.

Extraction equilibration procedure

A 20-ml portion of a chloroform solution containing the desired concentrations of dithizone and phenanthroline was added to a 60-ml screw-cap vial, followed by 20-ml of an aqueous solution that was $1{\cdot}0 \times 10^{-4}M$ in nickel(II) and buffered to the desired pH with either formate or acetate buffer at an ionic strength of 0·1, and the vial was then closed with a fitted polyethylene thimble before capping. The mixture was then shaken for 60 min (found to be sufficiently long for equilibration), allowed to stand several minutes for phase separation, and then aliquot of the phase having the lower nickel content was analysed in the manner below. The nickel content of the other phase was then obtained by difference.

Procedure for determination of nickel (aqueous phase)

Buffer the sample containing up to 15 μg of Ni in 5–10 ml solution with ammonium chloride–ammonia (pH 10). Add 15·0 ml of chloroform solution of dithizone ($6 \times 10^{-4}M$) and phenanthroline ($3 \times 10^{-4}M$). Shake vigorously for 2 min. Let the phases settle, remove the upper (aqueous) layer with a pipette and aspirator. Add 20 ml of $0{\cdot}2M$ sodium hydroxide and shake for 2 min. Deliver an aliquot of the chloroform phase through a dry filter paper into a 10-mm cuvette. Read the absorbance at 520 nm against a reagent blank prepared in the same way.

Procedure for nickel (chloroform phase)

Dilute an aliquot of the chloroform phase to 15·0 ml with chloroform, then proceed as for aqueous phase, starting at addition of sodium hydroxide.

RESULTS AND DISCUSSION

On the basis of preliminary studies it was found that although quantitative nickel extraction could be obtained from solutions having pH values as low as 3, this would require higher reagent concentrations and inconveniently long equilibration times. Therefore the procedure finally developed employed an ammonium chloride–ammonia buffer at pH 10. This pH could be varied within at least ±0·3 pH units without effect. The mixed ligand complex was stable enough towards alkali for 1–$2M$ sodium hydroxide to be used without decomposition of the complex; however, shaking with $0{\cdot}2M$ sodium hydroxide removed excess of dithizone with adequate efficiency. A calibration curve obtained by this procedure was found to be linear to better than 4 ppt and could be used on known nickel samples with an agreement of about 5 ppt (Table I). It is likely that the method could be extended to even lower levels of nickel, but it would probably be necessary to purify reagents before use, either by shaking with portions of dithizone–phenanthroline solutions for reagents of pH under 8–9 or, as with ammonia, distilling before use. Without any special effort being made to purify reagents, the blanks observed in this study had absorbances corresponding to about 0·6–0·8 μg of nickel. It should easily be possible to extend the method down to 0·05–0·10 μg of nickel by using 100-mm cells.

In the presence of phenanthroline, the rate of extraction of nickel (as a mixed ligand complex, of course) is much faster than with dithizone alone. In fact, the rate of extraction is related to processes involving mainly nickel phenanthroline complexes.[5] Nevertheless, the overall extraction is faster at higher pH values and equilibration can require as long as 30 min in the pH range 3–4. In evaluating

TABLE I.—ANALYSES OF NICKEL SAMPLES

Absorbance at 520 nm	Total nickel, μg		Error	
	Taken	Found	Abs., μg	Rel., ppt
0·128	2·33	2·28	−0·05	22
0·131	2·33	2·33	0·00	0
0·260	4·67	4·70	+0·03	6
0·259	4·67	4·68	+0·01	2
0·385	7·00	6·99	−0·01	1
0·385	7·00	6·99	−0·01	1
0·517	9·36	9·41	+0·05	5
0·516	9·36	9·39	+0·03	3
0·890	16·36	16·25	−0·11	7
0·900	16·36	16·43	+0·07	4

Calibration curve from least squares: $A_{520} = (0{\cdot}05453 \pm 0{\cdot}00021) W_{\mathrm{Ni}} + 0{\cdot}0039$ where W_{Ni} is the weight of nickel, in μg.

extraction equilibria involving phenanthroline it is necessary to take into account the effect of metal-phenanthroline complex formation in the aqueous phase.[6,7] This can readily be done by evaluating μ_{Ni} in equation (1) from the expression

$$\mu_{\mathrm{Ni}} = \{1 + \beta_1[\mathrm{phen}] + \beta_2[\mathrm{phen}]^2 + \beta_3[\mathrm{phen}]^3\}^{-1} \tag{2}$$

where β_1, β_2 and β_3 are the cumulative Ni^{2+}–phen formation constants, and [phen] is the phenanthroline concentration in the aqueous phase, obtained by dividing the organic phase phenanthroline concentration, $[\mathrm{phen}]_{\mathrm{org}}$, by the phenanthroline distribution constant ($K_{\mathrm{DR}} = 10^{3{\cdot}0}$)[7]. In Table II are

TABLE II.—EQUILIBRIUM EXTRACTION OF BIS(DIPHENYLTHIOCARBAZONATO)NICKEL(II)–PHENANTHROLINE INTO CHLOROFORM FROM WATER AT 25°C AND 0·1 IONIC STRENGTH

pH	log D_{Ni}	$-\log\,[\mathrm{HDz}]^{*}_{\mathrm{org}}$	$-\log\,[\mathrm{phen}]^{*}_{\mathrm{org}}$	$-\log\,\mu_{\mathrm{Ni}}$	log K_{ex}'
4·75	1·50	3·21	4·21	2·7	5·1
3·80	0·43	2·66	4·00	3·3	5·4
4·25	0·66	3·17	4·06	3·1	5·6
4·80	1·28	3·21	4·21	2·7	5·0
				Mean	5·3 ± 0·3

* Initial concentration corrected for amount consumed in Ni reaction.

listed values of μ_{Ni} for various equilibrium runs, calculated from $\log \beta_1 = 8{\cdot}60$, $\log \beta_2 = 16{\cdot}70$, $\log \beta_3 = 24{\cdot}25$,[8] and values of log K_{ex}' from equation (1). With the average value 5·3 for log K'_{ex}, and the previously determined[4] value 5·96 for log K_{AD}, the extraction constant for nickel dithizonate, $K_{\mathrm{ex}} = K'_{\mathrm{ex}} \mid K_{\mathrm{AD}}$, yields a value $\log K_{\mathrm{ex}} = -0{\cdot}7$ which is in fair agreement with $\log K_{\mathrm{ex}} = -0{\cdot}2$, obtained from direct measurement by McClellan and Sabel[3] in a 10-day equilibration run. This not only confirms McClellan's interpretation of the low value of the previously reported $\log K_{\mathrm{ex}} = -2{\cdot}9$ but emphasizes the importance of 1,10-phenanthroline in substantially accelerating the rate of nickel extraction in this system.

Acknowledgement—The authors gratefully acknowledge financial support of the U.S. Atomic Energy Commission in this work.

Department of Chemistry
University of Arizona
Tucson, Arizona 85721, *U.S.A.*

BEN S. FREISER
HENRY FREISER

Summary—The mixed ligand nickel-dithizone-phenanthroline complex provides a sensitive method for determination of nickel and also permits evaluation of the extraction constant for nickel dithizonate. The value $\log K_{\mathrm{ex}} = -0{\cdot}7$ was obtained, in agreement with a value of −0·2 obtained by others, and in contrast to an earlier value of −2·9. The addition of phenanthroline substantially increases the rate of extraction.

Zusammenfassung—Der gemischte Komplex von Nickel mit Dithizon und Phenanthrolin bietet eine empfindliche Methode zur Bestimmung von Nickel und erlaubt auch die Ermittlung der Extraktionskonstanten von Nickeldithizonat. Der Wert log $K_{ex} = -0{,}7$ wurde erhalten; er stimmt überein mit dem von anderen Autoren erhaltenen Wert $-0{,}2$, nicht jedoch mit dem älteren Wert $-2{,}9$. Die Zugabe von Phenanthrolin erhöht die Extraktionsrate beträchtlich.

Résumé—Le complexe mixte nickel-dithizone-phénanthroline fournit une méthode sensible pour le dosage du nickel et permet aussi l'évaluation de la constante d'extraction pour le dithizonate de nickel. On a obtenu la valeur log $K_{ex} = -0{,}7$, en accord avec une valeur $-0{,}2$ obtenue par d'autres, mais en opposition avec une valeur plus ancienne de $-2{,}9$. L'addition de phénanthroline accroît nettement la vitesse d'extraction.

REFERENCES

1. K. S. Math, K. S. Bhatki and H. Freiser, *Talanta* (1969), **16**, 412.
2. G. Iwantscheff, *Das Dithizon and seine Awendung in der Mikro-und Spurenanalyse*, Verlag Chemie, GMBH, Weinheim, 1958.
3. B. E. McClellan and P. Sabel, *Anal. Chem.*, 1969, **41**, 1077.
4. K. S. Math and H. Freiser, *ibid.*, 1969, **41**, 1682.
5. G. Colovos and H. Freiser, unpublished work.
6. C. Woodward and H. Freiser, *Anal. Chem.* 1968, **40**, 345.
7. H. G. Hamilton and H. Freiser, *ibid.*, 1969, **41**, 1310.
8. L. G. Sillén and A. E. Martell, *Stability Constants of Metal Ion Complexes*, 2nd. Ed. Chem. Soc. Spec. Publn. No. 17, London, 1964.

Talanta, 1970, Vol. 17, pp. 543 to 548. Pergamon Press. Printed in Northern Ireland

Use of a filter in atomic-fluorescence spectroscopy

(*Received* 24 *June* 1969. *Revised* 12 *January* 1970. *Accepted* 22 *January* 1970)

In ATOMIC-FLUORESCENCE flame spectroscopy, the limit of detection (defined as the solution concentration producing a given signal:noise ratio, usually 2) may generally be improved by increasing (*a*) the intensity of the source of primary radiation, (*b*) the amount of sample reaching the flame, or (*c*) the signal:noise ratio by reducing noise or increasing the signal by using an optical system with a higher light-gathering power.

High-intensity light sources, mainly microwave-excited electrodeless discharge tubes, have been used to obtain very low limits of detection, particularly for zinc and cadmium.[1] Heated spray chamber burners[2,3] enable more sample to enter the flame, while separated flames[4,5] and diffusion flames[6] have reduced flame noise, consequently increasing the signal:noise ratio.

Attempts to increase the light-gathering power have incorporated lenses to focus radiation from the flame onto the monochromator slit,[7] and the use of a concave mirror to collect radiation from the opposite side of the flame to the monochromator and focus this onto the slit.[7,8] Although the use of a mirror increases the signal it also increases the noise so the limit of detection is often not improved. The light-gathering power of the conventional system is mainly limited by the *f*-number of the monochromator used to separate the signal from background radiation.

This communication reports on the use of an interference filter, with auxiliary optics of low *f*-number to obtain a large light-gathering power, in place of the conventional monochromator in atomic-fluorescence spectroscopy. The light-gathering power of this system will effectively be limited by the *f*-number of the auxiliary optics. The use of a filter in atomic-fluorescence spectroscopy has previously been suggested by Jenkins[9] and West.[10] The filter is used to attenuate background radiation rather than to select a certain fluorescence wavelength.

Most of the background radiation can be attributed to flame emission above 300·0 nm, so the filter–photomultiplier combination should have a low response in this region to reduce noise and photomultiplier fatigue. By choosing a filter with a suitably wide bandpass below 300·0 nm and a photomultiplier with suitable response characteristics in this region, it should be possible to use one filter–photomultiplier combination for the determination of several elements which have fluorescence wavelengths below 300·0 nm.

Because larger background scatter and flame noise signals result from the increase in light-gathering power, for a system incorporating a filter to show an advantage over conventional systems both signals must be limited. Background scatter has been reduced to a tolerable level by shielding the sources of primary radiation and using a light trap. The increase in flame noise has been limited by using a bandpass of the a.c. amplifier that rejects most of the flame–noise signal.

Results obtained with the filter–photomultiplier combination are compared with those from another non-dispersive detecting system, incorporating a solar-blind photomultiplier, that has previously been used in atomic-fluorescence spectroscopy analysis.[12,13] Also, results from the non-dispersive systems are compared with those obtained from a conventional dispersive system incorporating a monochromator.

EXPERIMENTAL

The arrangement of the apparatus is shown in Fig. 1.

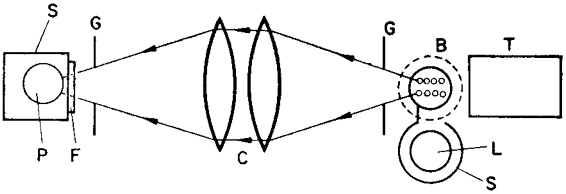


FIG. 1.—Arrangement of apparatus. *C*—condensing lenses, *B*—burner, *L*—lamp, *G*—stop, *P*—photomultiplier, *F*—filter, *S*—screening, *T*—light trap.

Primary sources of radiation

A Philips zinc vapour discharge lamp, operated from a variable transformer and a ballast leak transformer, was used for the investigation on zinc. A specially constructed mercury discharge tube (internal diameter 18·4 mm, length 0·20 m, argon gas pressure 2·7 mbar, weight of mercury 100 mg) was used for the determination of mercury. The lamp was operated on full-wave rectified, unsmoothed a.c. *via* a 100-ohm power resistor. The full-wave rectification unit was operated from a variable transformer supplied from a constant voltage source (Advance Volstat CV5 750A).

Aluminium screening, painted flat black, placed around the lamps, limited background scatter of radiation. A 50 × 20 mm hole in the screening allowed radiation from a selected region of the positive column of the mercury discharge and from the whole length of the zinc discharge to illuminate the flame. A protrusion on the detecting system side of this hole prevented radiation from the lamps entering the detecting system directly.

Flame

An air–town-gas flame was supported on an Evans Electroselenium burner head (from an EEL flame photometer model 100) the gases and sample solution being mixed in a spray chamber from a Unican SP90 atomic-absorption spectrophotometer. The holes in the burner head were aligned along the lens–filter axis. The flame produced by this burner had an approximate cross section o 20 × 10 mm and a height of 0·10 m. All gases were regulated with needle valves and monitored by flowmeters.

Detecting system

The condensing lenses were of quartz, diameter 80 mm, focal length 80 mm. The photomultiplier (R.C.A. 1P28) was housed in an aluminium box with a hole cut to the size of the photocathode. The filter (Baird-Atomic Prominent Ultraviolet Line Filter A.1.) was placed in front of this hole and secured with a black rubber washer which prevented stray radiation from entering at the edges of the filter. The spectral response of the filter–photomultiplier combination is shown in Fig. 2, curve *e*. An Isotopes Development Ltd. E.H.T. unit 532/D provided power for the photomultiplier, the signal from which was fed into a lock-in a.c. amplifier (Brookdeal Electronics Ltd. FL 355). The signal from the amplifier was then fed into a phase shifter-meter unit (Brookdeal Electronics Ltd. MS 320) the output from which was recorded on a Honeywell pen recorder. The 100 Hz reference signal for the phase shifter was obtained by the full wave rectification of the output of a 6·3-V transformer. A time constant of 1 sec was used for all measurements.

A light trap was constructed from a circular box, diameter 0·30 m, length 0·40 m, open at one end and lined with black velvet. This was placed on the opposite side of the flame to the detecting system, with the open end facing the flame, thus reducing the amount of background scattered radiation entering the detecting system.

Procedure

Standard 1000-ppm solutions of the elements were prepared by dissolving mercury(II) chloride in demineralized water, and zinc oxide in the minimum quantity of hydrochloric acid, and diluting with demineralized water. Less concentrated solutions were obtained by further dilution.

A photomultiplier voltage of 1·00 kV was used, and the lamp placed as close to the flame as possible (50 mm). The air flow-rate to the flame was fixed at 5·0 l./min and the fuel flow-rate for optimum signal-noise ratio was 1·6 l./min for both mercury and zinc. The aspiration rate of the solution was 3·1 ml/min.

The condensing lens system was placed 0·10 m from the center of the burner head and the aperture of the stop adjusted so that the lens system was just filled with radiation from the flame. The photomultiplier–filter position was adjusted by aspirating a zinc solution into the flame, irradiating with zinc resonance radiation and finding the position giving a maximum reading. The position of the burner head below the optical axis was adjusted until the signal resulting from scattering of primary radiation from the head was reduced to a tolerable level when the maximum gain of the amplifier was used. Approximately the middle third of the flame was focussed on to the photocathode. The fluorescence signal from a 1-ppm solution of both zinc and mercury remained essentially constant when the burner head was raised until the tips of the inner cones were just below the bottom of the front stop.

Choice of lamp operating conditions

The lamp currents were adjusted by means of a variable transformer to give a maximum fluorescence signal for a 1-ppm solution of the respective elements. The zinc lamp showed a maximum fluorescence signal at between 0·45 and 0·55 A and the mercury lamp at between 0·15 and 0·30 A.

Tests for scattering

Demineralized water was aspirated at all times when measurements were not being taken. To verify that the recorded signal was a fluorescence signal and was not caused by scattering within the flame the following procedure was used: with the amplifier at maximum gain, a 1-ppm mercury solution was aspirated and the flame irradiated with zinc 213·9-nm resonance radiation. No increase in signal above background resulted. A similar result was obtained with a 1-ppm zinc solution and mercury 253·7-nm radiation, and a 1-ppm lead solution with either mercury or zinc radiation.

Measurements made using a monochromator and solar-blind photomultiplier

To make a meaningful comparison of the results obtained when using a filter with those when using a monochromator, the condensing lenses and filter were replaced by a Jarrel-Ash 0·5-m grating monochromator incorporating an R.C.A. 1P28 photomultiplier. The flame was placed 40 mm from the entrance slit with the tips of the inner cones of the flame approximately 10 mm below the bottom of the slit. Both entrance and exit slits were set at 2·00 mm. The other parameters remained unchanged.

For measurements with a solar-blind photomultiplier, a Hamamatsu H.T.V. R.166 photomultiplier replaced the R.C.A. 1P28, the filter was removed and radiation from the flame was focussed directly onto the photocathode, all other parameters remaining unchanged.

RESULTS AND DISCUSSION

Table I lists the optimum lamp currents and limits of detection for zinc and mercury obtained with a monochromator, a filter–photomultiplier combination, or a solar-blind photomultiplier. Calibration curves of fluorescence signal against concentration for each system are essentially the same as

Table I.—Lamp currents and limits of detection for zinc and mercury

		Limit of detection, *ppm*		
Element	Lamp current, *A*	Monochromator	Filter	Solar-blind
Zinc	0·50	0·007	0·00001	0·00002
Mercury	0·30	0·02	0·002	0·00025

those obtained by Mansfield *et al.*,[11] being approximately linear from the limit of detection up to 5 ppm for zinc and 1000 ppm for mercury.

The limit of detection for zinc is improved by a factor of 700 by replacing the monochromator with a filter. This result is accounted for by the increased light-gathering power of the optical system, and a larger portion of the flame being focussed onto the photocathode. The optimum limit of detection of 10^{-5} ppm for zinc is an improvement on other recorded values obtained by using a Philips zinc vapour discharge lamp.[8,11]

For mercury, the limit of detection with the present filter and photomultiplier is an order of magnitude lower than that obtained by using a monochromator. This smaller improvement (compared with that obtained for zinc) is accounted for by the increase in light-gathering power being partially offset by the approximately 10-fold decrease in response of the filter-photomultiplier combination at 253·7 nm compared with that at 213·9 nm, Fig. 2, curve *e*. The optimum limit of detection of $2{\cdot}5 \times 10^{-4}$ ppm obtained with the solar blind photomultiplier is an improvement on the value of 0·08 ppm obtained by Browner *et al.*[7] from an aqueous solution in an air–hydrogen flame, and on the value of 0·1 ppm obtained by Mansfield *et al.*[11] from an aqueous solution in an oxy-hydrogen flame.

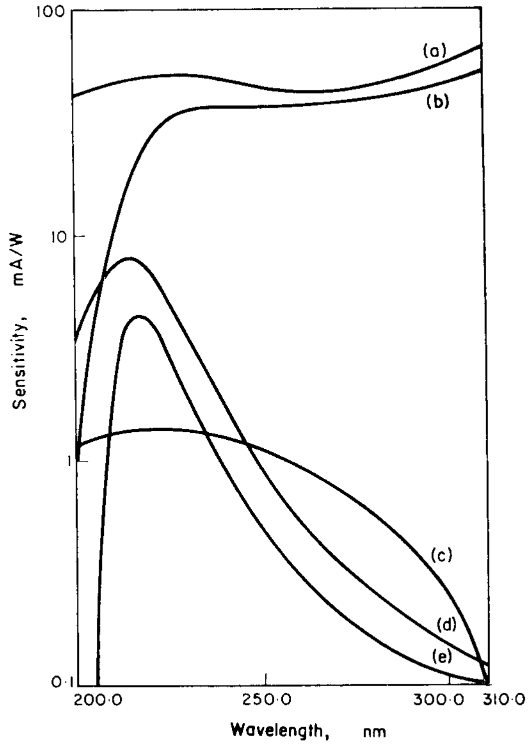


FIG. 2.—Approximate spectral response characteristics for various photocathodes and filter-photocathode combinations.
(*a*) S19; (*b*) S5; (*c*) Hamamatsu R166;
(*d*) Baird-Atomic Prominent Ultraviolet Line Filter A.1. and S19 photocathode;
(*e*) Baird-Atomic Prominent Ultraviolet Line Filter A.1. and S5 photocathode;

The spectral response characteristics of the filter–photomultiplier combination and the solar-blind photomultiplier are compared in Fig. 2, curves *e* and *c*. The combination shows an approximately 5-fold greater sensitivity than the solar-blind photomultiplier at 213·9 nm, while the solar-blind photomultiplier shows an approximately 5-fold greater sensitivity at 253·7 nm. Experimentally, the sensitivity of the solar-blind photomultiplier was found to be approximately 5-fold greater at 213·9 and 253·7 nm compared with the curve estimated from published data, Fig. 2, curve *c*. Consequently, the apparent signal from a given concentration of zinc was approximately the same with either system, but that from a given concentration of mercury was approximately an order of magnitude greater when the solar-blind photomultiplier was used. The flame-noise signal for the solar-blind photomultiplier was approximately twice that for the combination.

Comparisons have been made with a single solar-blind photomultiplier. Manufacturers state that it is extremely difficult to reproduce the solar-blind photocathode to an exact sensitivity, so that a 5-fold variation in sensitivity compared with published figures is quite possible. The use of a photomultiplier with an S19 response, Fig. 2, curve *a*, in place of the R.C.A. 1P28 with an S5 response, Fig. 2, curve *b*, would enhance the sensitivity of the filter-photomultiplier combination in the short-wavelength region, Fig. 2, curve *d*, the response around 300·0 nm being little affected.

Because of differences in apparatus it is difficult to compare accurately results of various recorded investigations. The most valid comparison of limits of detection obtained when a filter–photomultiplier combination, a solar-blind photomultiplier or a monochromator is used, is that in which results are obtained under otherwise identical experimental conditions, as in the present investigation.

The results of this investigation confirm that limits of detection can be improved by using a filter in place of a monochromator in atomic-fluorescence spectroscopy. With a suitable choice of filter and photomultiplier the 200·0–300·0 nm region can be covered with a single combination, giving comparable results to those from a solar-blind photomultiplier. For other wavelength regions a filter–photomultiplier combination should provide superior limits of detection compared with a monochromator, providing background noise, from the flame or other source of ground-state atoms, is low. In particular, the filter–photomultiplier combination should be most useful in conjunction with the carbon filament.[14]

General Electric Company Ltd.
Central Research Laboratories
Hirst Research Centre
Wembley, England

P. D. WARR

Summary—A detecting system incorporating an interference filter is described for use in atomic-fluorescence spectroscopy analysis in the 200·0–300·0 nm spectral region. Results obtained by using this system are compared with those from a detecting system incorporating either a monochromator or a solar-blind photomultiplier. Improvements of approximately 700-fold and 10-fold respectively in the limits of detection for zinc and mercury result from replacing the monochromator with the filter, while results with the filter are similar to those from a solar-blind photomultiplier. Limits of detection of 10^{-5} ppm for zinc and $2{\cdot}5 \times 10^{-4}$ ppm for mercury, both in aqueous solutions aspirated into an air–town-gas flame, are an improvement on other published results for these elements, obtained by atomic-fluorescence flame spectroscopy.

Zusammenfassung—Ein Nachweissystem mit Interferenzfilter zum Gebrauch bei der atomfluoreszenzspektrometrischen Analyse im Spektralbereich 200–300 nm wird beschrieben. Damit erhaltene Ergebnisse werden verglichen mit solchen, die mit anderen Nachweissystemen, entweder mit Monochromator oder mit tageslichtblindem Photomultiplier erhalten wurden. Bei den Nachweisgrenzen von Zink und Quecksilber erzielt man Verbesserungen um den Faktor 700 bzw. 10, wenn man den Monochromator durch das Filter ersetzt; dagegen sind die Ergebnisse mit dem Filter ähnlich wie mit dem tageslichtblinden Photomultiplier. Nachweisgrenzen von 10^{-5} ppm für Zink und $2{,}5 \times 10^{-4}$ ppm für Quecksilber, jeweils in wäßrigen Lösungen in eine Luft–Stadtgas–Flamme gesaugt, bedeuten eine Verbesserung gegenüber anderen publizierten Ergebnissen, die durch Atomfluoreszenz-Flammenspektrometrie an diesen Elementen erhalten wurden.

Résumé—On décrit un système détecteur comprenant un filtre interférentiel pour emploi en analyse par spectroscopie de fluorescence atomique dans la région spectrale 200,0–300,0 nm. Les résultats obtenus en utilisant ce système sont comparés à ceux d'un système

détecteur comprenant soit un monochromateur, soit un photomultiplicateur aveugle à la lumière solaire. Il résulte des améliorations d'approximativement 700 fois et 10 fois respectivement dans les limites de détection pour le zinc et le mercure du remplacement du monochromateur par le filtre, tandis que les résultats avec le filtre sont semblables à ceux d'un photomultiplicateur aveugle à la lumière solaire. Des limites de détection de 10^{-5} *ppm* pour le zinc et 2,5 × 10^{-4} *ppm* pour le mercure, tous deux en solutions aqueuses aspirées dans une flamme air-gaz de ville, sont une amélioration par rapport à d'autres résultats publiés pour ces éléments et obtenus par spectroscopie de flamme de fluorescence atomique.

REFERENCES

1. K. E. Zacha, M. P. Bratzel, Jr., J. D. Winefordner and J. M. Mansfield, Jr., *Anal. Chem.*, 1968, **40**, 1733.
2. A. A. Venghiattis, *Appl. Optics*, 1968, **7**, 1313.
3. A. Hell, W. F. Ulrich, N. Shifrin and J. Ramírez-Muñoz, *ibid.*, 1968, **7**, 1317.
4. R. S. Hobbs, G. F. Kirkbright, M. Sargent and T. S. West, *Talanta*, 1968, **15**, 997.
5. D. N. Hingle, G. F. Kirkbright and T. S. West, *Analyst*, 1968, **93**, 522.
6. R. M. Dagnall, K. C. Thompson and T. S. West, *Talanta*, 1967, **14**, 1467.
7. R. F. Browner, R. M. Dagnall and T. S. West, *ibid.*, 1969, **16**, 75.
8. N. Omenetto and G. Rossi, *Anal. Chim. Acta*, 1968, **40**, 195.
9. D. R. Jenkins, *Spectrochim. Acta*, 1967, **23B**, 167.
10. T. S. West and X. K. Williams, *Anal. Chem.*, 1968, **40**, 335.
11. J. M. Mansfield, J. D. Winefordner and C. Veillon, *ibid.*, 1965, **37**, 1049.
12. P. L. Larkins, R. M. Lowe, J. V. Sullivan and A. Walsh, *Spectrochim. Acta*, 1969, **24B**, 187.
13. T. J. Vickers and R. M. Vaught, *Anal. Chem.*, 1969, **41**, 1476.
14. T. S. West and X. K. Williams, *Anal. Chim. Acta*, 1969, **45**, 27.

Talanta, 1970, Vol. 17, pp. 548 to 551. Pergamon Press. Printed in Northern Ireland

Thermometric titration of sulphate

(*Received* 21 *October* 1969. *Accepted* 14 *January* 1970)

A VOLUMETRIC determination of sulphate with barium ions is often preferred to a gravimetric one despite difficulties with reliable detection of the end-point. Visual end-point detection is most vulnerable to interferences, because barium cations form only rather weak complexes with indicators. Frequently the colour change is not well defined and standardized titration conditions are usually required. However, the situation can be improved considerably by employing instrumental end-point detection. These methods were recently reviewed in connection with the determination of sulphur in organic samples.[1] Application of a specific ion-sensitive electrode for this purpose was reported recently.[2]

We have investigated the possibility of thermometric end-point detection and its applicability to practical sulphate determination. Thermometric titration of sulphate by barium ions was reported by Dean and Watts[3] and later by Mayr and Fisch[4] but with controversial results. Determination of sulphate by precipitation with barium ions is also mentioned in work on injection enthalpimetry.[5]

EXPERIMENTAL

Apparatus

A modified a.c.-thermistor bridge by Richards[6] with an LTC 23F thermistor was used to detect the temperature changes. The output of this bridge, which was used at a sensitivity of 5 V/deg was fed into a Servoscribe recorder; 50-ml or 100-ml polytetrafluoroethylene (PTFE) beakers mounted in a block of polystyrene foam served as titration vessels. Efficient and constant mixing was provided by a vibrating paddle mounted on the glass body of the thermistor.[7] The paddle was driven by a V-1 vibrator (Advance Instruments Ltd.) at 50 Hz. A motorized Agla micrometer syringe was used in the early experiments but was later replaced by a Radiometer ABU-12 burette. The titrant and all other solutions were kept in a water thermostat in order to minimize the temperature drift.

Reagents

Barium perchlorate, 1–2M aqueous solution, was standardized gravimetrically. Organic sulphur compounds were microanalytical standards and all other chemicals were analytical-reagent grade. Distilled demineralized water was used in all experiments.

RESULTS AND DISCUSSION

Effect of ethanol

An ethanol (or acetone)-water medium is frequently used, particularly in sulphate titrations with visual indicators. It was found that the stoichiometry of the precipitation depends on the concentration of ethanol (Fig. 1). Adsorption of soluble sulphate on freshly precipitated barium sulphate was suggested as a possible explanation of negative errors observed in the earlier thermometric work.[3,4] It is therefore conceivable that concentrations of ethanol above 50% v/v eliminate this co-precipitation. Other surface-active compounds such as thymol were found to have no effect on the stoichiometry of the reaction. It should be noted from Fig. 1 that the results at concentrations of ethanol less than 50% have much lower precision than those at above this level.

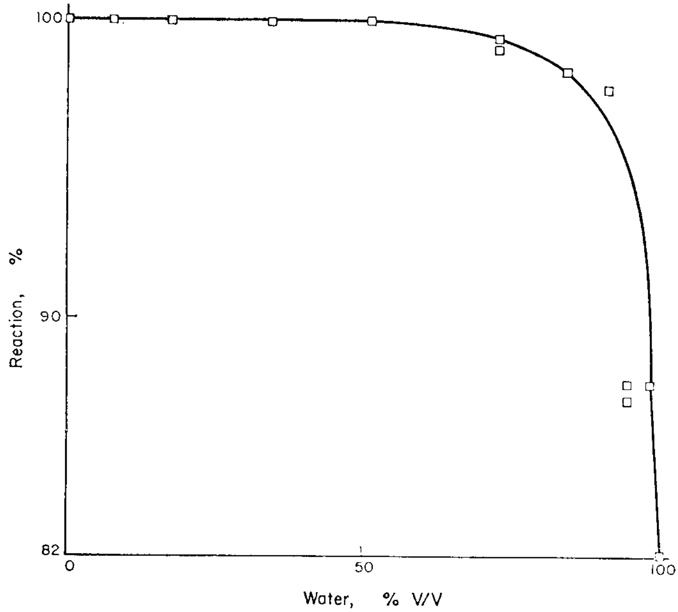


FIG. 1.—Effect of composition of ethanol/water mixture on the stoichiometry of the titration of 1 ml of 0.1N sulphuric acid.

Determination of sulphate

Results of determinations of sulphate both in inorganic and organic samples (following oxygen flask combustion or fusion with sodium peroxide) are summarized in Table I. The general procedure for a titration is as follows.

The sample, containing 1–25 mg of sulphate, is placed in a PTFE beaker and diluted to 30 ml with ethanol and water (together with 1 ml of a 10% solution of perchloric acid) in such proportions as to give a 70% ethanolic solution. After equilibration in a water-bath for approximately 10 min the beaker is fixed in the polystyrene block and the vibrator switched on. Depending on the size of the sample, the burette speed, recorder chart speed and the bridge sensitivity are adjusted to give a suitable rate of deflection; typical chart speeds are 30 or 120 mm/min. From the rate of addition of titrant and chart speed the volume of barium perchlorate can be calculated and hence the amount of sulphate present.

For the given volume of titration mixture the temperature rise is approximately 0·1° per ml of 0·1N sulphuric acid. The titration itself takes approximately 1–3 min to complete. The minimum

TABLE I.—ANALYSIS OF SULPHUR COMPOUNDS

Sample	Amount taken *mg*	S,% Theory	S,% Mean found	Rel. std devn.,%§
H_2SO_4	0·9807	32·7	31·8	1·6
H_2SO_4	2·451	32·7	33·2	2·2
H_2SO_4	4·902	32·7	33·0	3·6
H_2SO_4	9·804	32·7	32·7	1·1
H_2SO_4	24·50	32·7	32·2	1·6
Na_2SO_4	14·20	22·5	22·9	1·8
Sulphonal*	10–13	28·1	28·9	7·1
Sulphonal†	10–13	28·1	27·0	1·6
Benzyl* thiuronium chloride	19–24	15·8	16·3	2·7

* After oxygen flask combustion.
† Following fusion with 1–2 g of sodium peroxide.
§ Calculated from at least 7 determinations.

amount of sulphate which can be determined by this method with reasonable accuracy is about 1 mg.

Interferences from various inorganic compounds were also investigated both in equimolar amounts and in a slight excess. No interference was found from excess of iron(III) chloride, copper(II) chloride, nickel choride or silver nitrate. Interferences from excess of sodium fluoride can be eliminated by addition of boric acid. Phosphate and arsenate do not interfere in equimolar concentrations but low results for sulphate were found if they were present in higher concentrations. When an inorganic compound was present which was precipitated on addition of the ethanol, low results were always obtained.

CONCLUSIONS

The proposed method is very rapid and suffers from only a few interferences. On the other hand-the accuracy is lower than in other instrumental methods. This might be due to the fact that the short titration time which is required for the semi-adiabatic arrangement is not long enough for barium sulphate to be formed exactly stoichiometrically, because of adsorption phenomena which occur during the precipitation.

Acknowledgement—The authors express their gratitude to Mr. C. E. O'Brien for his help with oxygen, flask combustions.

Imperial Chemical Industries Ltd.
Petrochemical & Polymer Laboratory
P.O. Box 11, *The Heath, Runcorn, Cheshire, England*

M. B. WILLIAMS
J. JANATA

Summary—Direct thermometric titration of sulphate with a solution of barium perchlorate is proposed. The stoichiometry of the titration is shown to be critically dependent on the concentration of ethanol in the titration medium. The titration is rapid and suffers from only a few interferences.

Zusammenfassung—Die direkte thermometrische Titration von Sulfat mit einer Lösung von Bariumperchlorat wird vorgeschlagen. Es wird gezeigt, daß die Stöchiometrie der Titration empfindlich von der Äthanolkonzentration im Titrationsmedium abhängt. Die Titration geht schnell und unterliegt nur wenigen Ströungen

Résumé—On propose un titrage thermométrique direct du sulfate avec une solution de perchlorate de baryum. On montre que la stoechiométrie du titrage dépend de manière essentielle de la concentration de l'éthanol dans le milieu de titrage. Le titrage est rapide et ne souffre que de seulement quelques interférences.

REFERENCES

1. J. P. Dixon, *Modern Methods in Organic Microanalysis*, Chap. 7. Van Nostrand, London, 1968.
2. J. W. Ross and M. S. Frant, *Anal. Chem.*, 1969, **41**, 967.
3. P. M. Dean and O. O. Watts, *J. Am. Chem. Soc.*, 1924, **46**, 855.
4. C. Mayr and J. Fisch, *Z. Anal. Chem.*, 1929, **76**, 418.
5. I. Sajó and B. Sipos, *Talanta*, 1967, **14**, 203.
6. J. C. S. Richards, *Electron. Eng.*, 1967, 674.
7. P. T. Priestley, *Analyst*, 1963, **88**, 194.

Talanta, 1970, Vol. 17, pp. 551 to 553. Pergamon Press. Printed in Northern Ireland

Di-n-butyl carbamoylphosphonate as an extractant of inorganic ions from hydrochloric acid solutions

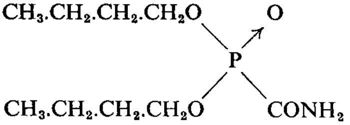
(*Received* 9 *October* 1969. *Accepted* 24 *January* 1970)

Di-n-butyl carbamoylphosphonate (DBCP)* was found to extract readily the elements scandium, zirconium, hafnium, thorium, protactinium, uranium and neptunium from their solutions in nitric acid.[1]

This study comprises the measurement of the extracting ability of DBCP for 33 elements from their solutions in 0·5—12*M* hydrochloric acid. A 0·1*M* solution of DBCP in chloroform was used as the extractant. In most cases radioisotopes of the elements were used as tracers for the extraction experiments. Extraction coefficients of uranium(VI) and thorium were determined spectrophotometrically.[2,3]

EXPERIMENTAL

DBCP was synthesized in the laboratory[4] and purified by recrystallization from ethanol. It is a white crystalline solid (m.p. 175–176°) with the structure



The radioisotopes used were prepared as described earlier.[1] For the determination of the distribution ratio, *D*, 1 mg of the element was added to hydrochloric acid solutions of various concentrations, except in the cases of neptunium, technetium and protactinium, where the behaviour of carier-free ^{239}Np, ^{99m}Tc and ^{233}Pa was studied. The distribution ratios were measured as in our earlier work.[1]

RESULTS AND DISCUSSION

The obtained *D* values for all the elements studied are compiled in Fig. 1 in a graph of log *D vs* molarity of hydrochloric acid. Elements showing *D* values less than 10^{-2} are presented in a single group. An examination of Fig. 1 shows that the univalent and bivalent ions studied are non-extractable in the whole range of acidity 0·5–12*M* hydrochloric acid, showing *D* values lower than 10^{-2}. Of the trivalent ions, only indium and chromium show less than 1% extraction in the whole range of acidity, while all the others, including the lanthanides, show high extraction values in acidities greater than 6*M* hydrochloric acid. It is important to note here that among the trivalent ions, scandium was the only one extracted by DBCP to an appreciable extent from nitric acid solutions, while, with the exception of cerium(IV), lanthanides are extracted by DBCP only 5% or less from this medium.[1] A striking difference is observed between the behaviour of niobium and tantalum, the former being much the more extractable (maximum for Nb 92% and for Ta 16%, both from 10*M* hydrochloric acid).

The maximum extraction values of zirconium and hafnium are 96% and 98% respectively from 12*M* hydrochloric acid. They present larger differences at the lower acidities. Among all the elements studied, thorium shows the highest extractability. It is extracted nearly quantitatively even from

---

* Originally named by the authors as *N*-(di-n-butylphosporo)urea, (N–DBPU).

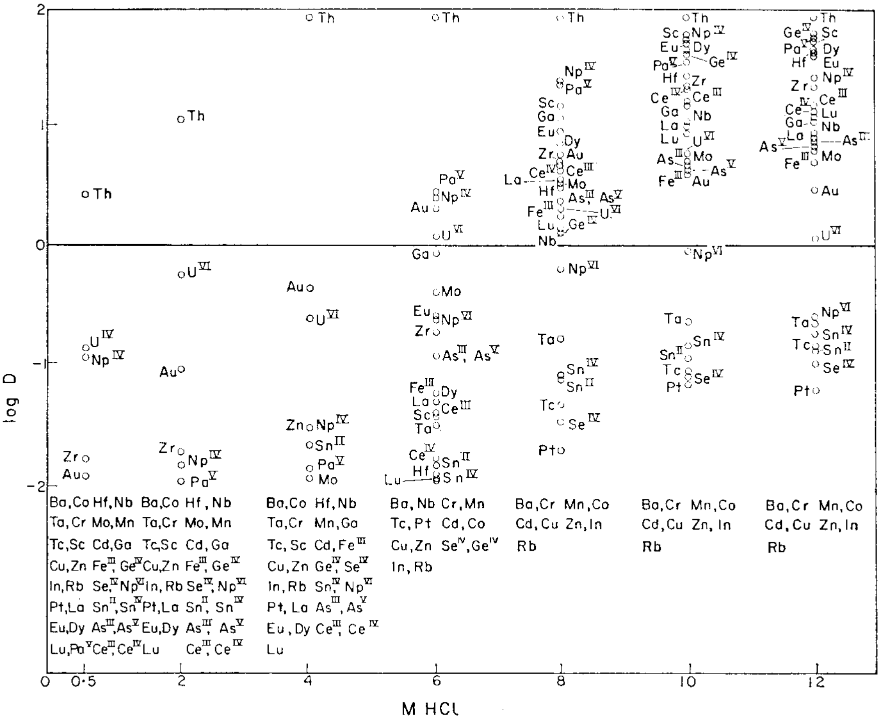


FIG. 1.—Log *D* values in 0·1*M* DBCP–HCl system [the values for As(III) and Ge(IV) correspond to the extraction by chloroform].

4*M* hydrochloric acid, while the extraction of carrier-free protactinium is very small up to this acid concentration. The extraction of uranium in the form of UO_2^{2+} is relatively high even at low acidities, with a maximum value of 87% from the 10*M* acid. The distribution ratios of carrier-free neptunium (IV) and (VI) are very different at all acid concentrations studied, the former being always the more extractable [maximum extraction values are 98% and 49% for neptunium(IV) and (VI) respectively from 10*M* hydrochloric acid].

Blank experiments with the pure solvent did not show any measurable extraction for any of the elements examined except for arsenic(III) and germanium(IV) which are extracted to a high degree by chloroform.

In summary, the extraction ability of DBCP is greater at high hydrochloric acid concentrations, a trend which was also observed for the extraction from nitric acid solutions.[1] On the other hand fewer elements are extracted from nitric acid solutions, which means that the selectivity of this new extractant is lower when the extractions are carried out from hydrochloric acid solutions. There are reasons to believe that the phosphoroamide moiety in the structure of DBCP is important in the extraction and future work is planned for the study of the extraction mechanism and the structure of the solvates involved.

Acknowledgements—The authors wish to express their thanks to Mr. S. C. Archimandritis and to Miss M. Foka for their valuable assistance in the present study.

Chemistry Division
Nuclear Reactor Center "Democritus"
Athens, Greece

D. C. PERRICOS
A. K. TSOLIS
E. P. BELKAS

Summary—The extraction of 33 elements by a 0·1*M* solution of di-n-butyl carbamoylphosphonate in chloroform has been investigated as a function of hydrochloric acid concentration. The results show that this new extractant readily extracts most of the elements in a high oxidation state, including the trivalent rare earths, from hydrochloric acid at concentrations greater than 6*M*.

Zusammenfassung—Die Extraktion von 33 Elementen durch eine 0,1 *M* Lösung von Di-n-butylcarbamoylphosphonat in Chloroform wurde in Abhängigkeit von der Salzsäurekonzentration untersucht. Die Ergebnisse zeigen, daß dieses neue Extraktionsmittel die meisten höherwertigen Elemente extrahiert, einschießlich der dreiwertigen seltenen Erdenen, wenn die Salzsäurekonzentration höher als 6 *M* ist.

Résumé—On a étudié l'extraction de 33 éléments par une solution 0,1*M* de carbamoylphosphonate de di-*n*-butyle en chloroforme, en fonction de la concentration en acide chlorhydrique. Les résultats montrent que ce nouvel agent d'extraction extrait aisément la plupart des éléments qui sont dans un état d'oxydation élevé, y compris les terres rares trivalentes, de l'acide chlorhydrique à des concentrations plus grandes que 6*M*.

REFERENCES

1. A. K. Tsolis, E. P. Belkas and D. C. Perricos, *Radiochim. Acta*, 1969, **11**, 117.
2. F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, Vol. II, p. 493. Van Nostrand, New York, 1961.
3. J. Akaishi, *J. At. Energy Soc. Japan*, 1962, **4**, 32.
4. R. A. Wiesboeck, *J. Org. Chem.*, 1965, **30**, 3161.

Talanta, 1970, Vol. 17, p. 555. Pergamon Press. Printed in Northern Ireland

LETTER TO THE EDITOR

Determination of manganese(II) in the presence of vanadium(V) and chromium(VI)

SIR,

Since Lingane and Karplus[1] in 1946 introduced the determination of Mn(II) by titration with $KMnO_4$ in pyrophosphate solution, this method of analysis is frequently used. Both Mn(II) and Mn(VII) are converted into Mn(III), which forms a very stable complex with pyrophosphate. Since the intense red colour of the complex precludes the use of a colour indicator, the titration is generally performed potentiometrically. The titration may be performed at pH 1–8, but the potential break at the equivalence point is maximal at pH 6–7. Furthermore, several components that interfere at low pH values do not do so at pH 6–7.[2] Vanadium(V), however, if present in more than small amounts, interferes at pH 6–7. At lower pH this interference is eliminated,[1] but other difficulties then arise. Chromium(VI), often present after oxidative attack on samples containing chromium, interferes by oxidizing Mn(II) to Mn(III) in the solution used.

We have found that amounts of vanadium up to 100 mg do not interfere at pH 6–7, but that larger amounts make the potential stabilization very slow, although the final result is still correct. The effect of chromium can be eliminated if the Cr(VI) is first reduced to Cr(III) by addition of 210 mg of sodium nitrite (for a maximum of 1 mmole of dichromate), followed by dilution to about 100 ml, adjustment to pH 1 with alkali or hydrochloric acid, heating at 40° for a few minutes, addition o 500 mg of urea and heating near the boiling point for 30 min (to remove excess of nitrite and the gases evolved in that process), then addition of this solution to 300 ml of saturated sodium pyrophosphate solution, adjustment to pH 6–7, and, after an hour, titration potentiometrically with permanganate. If larger amounts than 100 mg of vanadium are present, the titration is performed at 60°. The increased temperature is necessary to give rapid potential equilibration. An alternative is to add most of the titrant at room temperature and the rest after heating the solution to 55–60°. The rest period of an hour when chromium is present is necessary because the formation of the chromium complex with pyrophosphate is slow, as noted by Scribner,[3] who first developed this method of preventing chromium from interfering.

Relative errors ranged from 0·0% to +0·3% for up to 1200 mg of vanadium present (15 experiments), and from +0·2% to +0·5% for 50 mg of chromium (6 experiments). Experiments with 100 mg of chromium gave errors of +0·7%.

I thank C. Slagt, Miss J. de Neef, and J. F. G. van der Grift for experimental help.

Laboratory for Analytical Chemistry
State University, Utrecht
Croesestraat 77-*A*
The Netherlands
25 *September* 1969

J. AGTERDENBOS

REFERENCES

1. J. J. Lingane and R. Karplus, *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 191.
2. W. G. Scribner and R. A. Andersen, *Anal. Chem.*, 1961, **33**, 771.
3. W. G. Scribner, *ibid.*, 1960, **32**, 970.

Tantala, 1970, Vol. 17, p. i. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

High-voltage spark excitation of some organic molecules in nitrogen and argon atmospheres: R. M. DAGNALL, D. J. SMITH, K. C. THOMPSON and T. S. WEST. (23 *March* 1970)

Substoichiometric determination of traces of palladium by radioactive isotope-dilution analysis: G. B. BRISCOE and S. HUMPHRIES. (23 *March* 1970)

Spectrophotometric determination of the protolytic dissociation constants of the new chromogenic reagent "Palladiazo"—I. Investigations carried out in sodium hydroxide, perchloric acid and differently buffered aqueous solutions: J. A. PÉREZ-BUSTAMANTE and F. BURRIEL-MARTÍ. (24 *March* 1970)

Spectrophotometric determination of the protolytic dissociation constants of the new chromogenic reagent "Palladiazo"—II. Study of the protonation processes undergone by the azo groups of the reagent in sulphuric acid media: J. A. PÉREZ-BUSTAMANTE and F. BURRIEL-MARTÍ. (24 *March* 1970)

Solvent extraction and spectrophotometric determination of vanadium(V) with *N*-phenyl-3-styrylacrylohydroxamic acid: D. C. BHURA and S. G. TANDON. (25 *March* 1970)

Precipitation of zirconium tetramandelate from homogeneous solution: HARBIR SINGH and N. K. MATHUR. (25 *March* 1970)

Indirect atomic-absorption method for the determination of selenium: HERBERT K. Y. LAU and PETER F. LOTT. (7 *April* 1970)

Extraction and separation of ^{137}Cs and ^{86}Rb by means of 4-t-butyl-2-(α-methylbenzyl)phenol: J. RAIS, J. KRTIL and V. CHOTÍVKA. (9 *April* 1970)

Analytical kinetics of the titanium(III)–perchlorate reaction: E. BISHOP and N. EVANS. (13 *April* 1970)

Differential titrimetric determination of selenium and tellurium in mixtures: P. P. NAIDU and G. G RAO. (14 *April* 1970)

Talanta, 1970, Vol. 17, p. ii. Pergamon Press. Printed in Northern Ireland

NOTICE

FOURTEENTH CONFERENCE ON ANALYTICAL CHEMISTRY IN NUCLEAR TECHNOLOGY

Mountain View Hotel and Motor Lodge, Gatlinburg, Tennessee 37738, U.S.A.
13–15 October 1970

THE FOURTEENTH Conference on Analytical Chemistry in Nuclear Technology will be held in Gatlinburg, Tennessee, 13–15 October 1970, under the sponsorship of the Analytical Chemistry Division, Oak Ridge National Laboratory.

Papers up to 25 minutes in length, that describe original, unpublished work related to the following topics are solicited by the Program Committee.

1. Applications of Digital Computers in Analytical Chemistry.
2. New Sensors and Detectors for use in Studies Related to Environmental Pollution.
3. Problems Associated with the Purity of Reagents for use in Chemical Analysis.
4. Sample Preparation and Dissolution—Vital Steps in Chemical Analysis.
5. Papers on Topics of General Interest Related to Analytical Chemistry in Nuclear Technology.

Those who wish to make contributions should submit an abstract of 200–500 words not later than 20 June 1970. The title, name of the author, an estimate of the time that will be required for the presentation, and in case of multiple authorship, an indication of the name of the speaker should accompany the abstract.

Abstracts of papers and inquiries concerning the conference including request for programmes, should be directed to the Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee 37830, Attention: L. J. Brady, Chairman.

The registration fee, except for full-time students, is $10.00 per person. A registration fee of $5.00 will be required for attendance of one day or any part thereof.

Reservation for lodging should be made by direct communication with The Mountain View Hotel and Motor Lodge, Gatlinburg, Tennessee 37738, U.S.A.

SUMMARIES FOR CARD INDEXES

End-point evaluation in instrumental titrimetry—II. Confidence intervals in extrapolation of linear titration curves: PAVEL JANDERA, STANISLAV KOLDA and STANISLAV KOTRLÝ, *Talanta*, 1970, **17**, 443. (Department of Analytical Chemistry, College of Chemical Technology, Pardubice, Czechoslovakia.)

Summary—The random titration error has been evaluated by single linear regression analysis of both linear branches of titration curves. As a simplification the confidence interval of a titration is estimated by substituting divergent linear confidence limits for the curved confidence limits of both branches of the curve. The influence of the angle between both branches upon the confidence interval of a titration has also been evaluated. The procedure has been proved advantageous by applying it to several amperometric and photometric titrations of lead and by comparing the results with those obtained by the complementary approach of Liteanu and Cörmös, and by the usual statistical treatment of end-points obtained by graphical extrapolation. The method allows a critical consideration of the experimental conditions with regard to the desired level of precision.

Preparative gas chromatography of volatile metal compounds—I. Separation of aluminium, chromium and iron β-diketonates: R. BELCHER, C. R. JENKINS, W. I. STEPHENS and P. C. UDEN, *Talanta*, 1970, **17**, 455. (Department of Chemistry, The University of Birmingham, P.O. Box 363, Birmingham, England.)

Summary—The analytical gas chromatography of a range of fluorinated and unfluorinated β-diketonates of aluminium, chromium and iron has been studied in detail and conditions have been established for their complete separation; the complexes of trifluoroacetylpivaloylmethane show the best characteristics for this purpose. A range of liquid phases and column conditions have been considered and Apiezon substrates have been shown to give optimal resolution. The technique has been extended to a preparative scale with up to 0·1-g chelate samples, and the efficiency of the process demonstrated by the removal of 2% proportions of two metal complexes from a sample of the third. Implications of the technique for the purification of metals are discussed.

ОБНАРУЖЕНИЕ КОНЦА ТИТРОВАНИЯ В ИНСТРУМЕНТАЛЬНОЙ ТИТРИМЕТРИИ—II. ИНТЕРВАЛЫ ДОВЕРИЯ ПРИ ЭКСТРАПОЛЯЦИИ ЛИНЕЙНЫХ ТИТРАЦИОННЫХ КРИВЫХ:

PAVEL JANDERS, STANISLAV KOLDA and STANISLAV KOTRLÝ, *Talanta*, 1970, **17**, 443.

Резюме—Случайная ошибка титрации вычислена единственным линейным регрессивным анализом обеих линейных ветв титрационных кривых. В упрощенной форме интервал доверия титрации получается замещением изогнутых пределах доверия дивергентными линейными пределами доверия для обеих ветв кривой. Также изучен эффект угла между ветвами на интервал доверия титрации. Метод оказался выгодным в случае его применения на амперометрические и фотометрические титрации свинца и в сравнении с результатами полученными методом Литеану и Кермеша или обыкновенной статистической обработкой концев титрования, полученных графической экстраполяцией. Метод позволяет критическое обсуждение опытных условий в отношении на желательную степень точности.

ПРЕПАРАТИВНАЯ ГАЗОВАЯ ХРОМАТОГРАФИЯ ЛЕТУЧИХ СОЕДИНЕНИЙ МЕТАЛЛОВ—β. РАЗДЕЛЕНИЕ I-ДИКЕТОНОВ АЛЮМИНИЯ, ХРОМА И ЖЕЛЕЗА:

R. BELCHER, C. R. JENKINS, W. I. STEPHENS and P. C. UDEN, *Talanta*, 1970, **17**, 455.

Резюме—Изучена аналитическая газовая хроматография ряда фторированных и нефторированных β-дикетонатов алюминия, хрома и железа и определены условия для их полного разделения. Найлучшие результаты в етом направлении получены с комплексами трифторацетилпивалоилметана. Изучен ряд стационарных фаз и условий колонок; оптимальное разделение получено с апиезоновыми субстратами. Метод расширен на разделение до 0,1 г хелатов на препаративной шкале. Эффективность метода показана уклонением 2 % примес двух комплексов металлов из пробы третего. Обсуждены возможности применения метода в очистки металлов.

Spectrophotometric study and analytical application of rare earth Tiron complexes—I. Determination of neodymium, holmium and erbium: TOMITSUGU TAKETATSU and NOBUYO TORIUMI, *Talanta*, 1970, **17**, 465. (College of General Education, Kyushu University, Fukuoka, Japan.)

Summary—The absorption spectra of neodymium, holmium and erbium Tiron complexes in aqueous solution have been measured from 340 to 650 nm. The absorbance at the wavelength of maximum absorption band of an aqueous medium containing neodymium (pH 4·5), neodymium (pH 12·0), holmium (pH 5·0) and erbium (pH 5·0) Tiron complexes was about 4 (at 578 nm), 9 (at 571 nm), 9 (at 450 nm) and 5 (at 376 nm) times greater, respectively, than for the same quantities of the corresponding chlorides. The spectrophotometric determination of these elements has been investigated. Combining ratios of Tiron to rare earth have been found to be 3:2 and 2:1.

Application of the Unterzaucher method to the determination of oxygen in coke: B. P. KIRK and H. C. WILKINSON, *Talanta*, 1970, **17**, 475. (The British Coke Research Association, Chesterfield, Derbyshire, U.K.)

Summary—The Unterzaucher method, used for the determination of oxygen in organic compounds and coal, has been adapted to the determination of oxygen in coke. Modifications were made to the conventional apparatus in order to eliminate any contribution made by the coke moisture to the determined oxygen content. The carbon dioxide produced from the combustion of the oxygen in the coke was estimated by a sensitive conductimetric method. Evidence is presented which indicates that additional liberation of oxygen from the coke mineral matter does not make a significant contribution to the total oxygen determined under the prescribed experimental conditions. The error of the determination is approximately 0·1%. A comparison is made between results obtained for a series of cokes and chars by the direct method and by an independent determination, based on neutron activation.

Macroreticular chelating ion-exchangers: R. F. HIRSCH, E. GANCHER and F. R. RUSSO, *Talanta*, 1970, **17**, 483. (Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079, U.S.A.)

Summary—Two macroreticular chelating ion-exchangers have been prepared and characterized. One contains the iminodiacetate group and the second contains the arsonate group as the ion-exchanging site. The macroreticular resins show selectivities among metal ions similar to those of the commercially available microreticular chelating resins. Chromatographic separations on the new resins are rapid and sharp.

ИЗУЧЕНИЕ СПЕКТРОФОТОМЕТРИЧЕСКИМ МЕТОДОМ И ПРИМЕНЕНИЕ В АНАЛИЗЕ КОМПЛЕКСОВ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ С ТИРОНОМ—I. ОПРЕДЕЛЕНИЕ НЕОДИМА, ГОЛМИЯ И ЭРБИЯ:

Tomitsugu Taketatsu and Nobuyo Toriumi, *Talanta*, 1970, **17**, 465.

Резюме—Измерены спектры поглощения комплексов неодима, голмия и эрбия с тироном в водном растворе в области 340–650 нм. Экстинкция при длини волн максимального светопоглощения водного раствора содержащего комплексы тирона с неодимом (pH 4,5), неодимом (pH 12,0), голмием (pH 5,0) и эрбием (pH 5,0) была 4крат (при 578 нм), ркрат (при 571 нм), 9крат (при 450 нм) и 5крат (при 376 нм) выше, соответственно, чем для тех же количеств соответственных хлоридов. Исследована возможность спектрофотометрического определения этих элементов. Определены отношения тирона и редкоземельных элементов 3:2 и 2:1.

ПРИМЕНЕНИЕ МЕТОДА УНТЕРЦАУХЕРА В ОПРЕДЕЛЕНИИ КИСЛОРОДА В КОКСЕ:

B. P. Kirk and H. C. Wilkinson, *Talanta*, 1970, **17**, 475.

Резюме—Метод Унтерцаухера, использован для определения кислорода в органических соединениях и угле, адаптирован для определения кислорода в коксе. Обыкновенный прибор изменен что бы избечь вклад влаги в коксе в определение кислорода. Двуокись углерода, образована сжиганием кислорода в коксе, определена чувствительным кондуктометрическим методом. Показано что дополнительное выделение кислорода из минерального вещества кокса не повышает в значительной мере общее количество кислорода определено при прописанных опытных условиях. Ошибка определения составляет приблизно 0,1 %. Сравнены результаты полученные на ряде образцов кокса и древесного угля непосредственным методом с результатами независимого метода основанного на нейтроноактивационном анализе.

МАКРОРЕТИКУЛЯРНЫЕ ХЕЛАТООБРАЗУЮЩИЕ ИОНООБМЕННЫКИ:

R. F. Hirsch, E. Gancher and F. R. Russo, *Talanta*, 1970, **17**, 483.

Резюме—Приготовлены и испытаны два макроретикулярных хелатообразующих ионообменныка. Один из них содержит иминодиацетат-группу в качестве ионообменной группы, другий—арсонат-группу. Макроретикулярные смолы показывают селективность для ионов металлов похоже селективности коммерческих микроретикулярных хелатообразующих смол. Новые смолы дают быстрые и острые хроматографические разделения.

Determination of some methylcarbamate insecticides by a.c. polarography and cyclic voltammetry: M. D. Booth and B. Fleet, *Talanta*, 1970, **17**, 491. (Chemistry Department, Imperial College, London, S.W.7.)

Summary—The study of adsorption–desorption phenomena represents an important extension to the range of organic compounds that can be determined by electrochemical methods. The present work has utilized this approach for the determination of a range of methylcarbamate insecticides. The tensammetric behaviour of this class of compound at the mercury electrode has been investigated by a.c. polarography and the optimum experimental conditions for their analytical determination have been derived. Cyclic voltammetry has also been used to study the electrode process and by using the peak obtained on the cathodic sweep it was possible to extend the limit of detection to the ppm level.

Catalytic reactions—I. Mechanisms: P. R. Bontchev, *Talanta*, 1970, **17**, 499. (Department of Analytical Chemistry, University of Sofia, 1 Anton Ivanov Str., Sofia 26, Bulgaria.)

Summary—The mechanisms of some reactions used in catalytic analysis are discussed. The knowledge of the mechanism of a catalytic reaction can help in the development of new catalytic reactions and the choice of optimal conditions, and to show the possibilities for further increases in sensitivity.

Acid dissociation and spectrophotometric behaviour of 8-quinolineselenol in water–dioxan mixtures: Noboru Nakamura and Eiichi Sekido, *Talanta*, 1970, **17**, 515. (Department of Chemistry, Faculty of Science, Kobe University, Kobe, Japan.)

Summary—The acid dissociation constants of 8-quinolineselenol, 8-quinolinol and 8-quinolinethiol in water–dioxan mixtures of varying solvent composition were determined potentiometrically or spectrophotometrically. The absorption spectra of 8-quinolineselenol in the same solvents were also obtained. The acid dissociation phenomena, stability towards oxidation and the absorption spectra of the reagents are discussed in connection with the existing forms. It is verified that 8-quinolineselenol exists as a zwitterion in water–dioxan mixtures of low or high dioxan content.

ОПРЕДЕЛЕНИЕ НЕКОТОРЫХ ИНСЕКТИЦИДОВ НА ОСНОВЕ МЕТИЛКАРБАМИНАТА МЕТОДАМИ ПЕРЕМЕННОТОКОВОЙ ПОЛЯРОГРАФИИ И ЦИКЛИЧЕСКОЙ ВОЛЬТАМПЕРОМЕТРИИ:

N. D. Booth and B. Fleet, *Talanta*, 1970, **17**, 491.

Резюме—Изучение явлений адсорбции-десорбции представляет собой важний класс органических соединений которые могут быть определены электрохимическими методами. В предлежащей стате эти методы использованы для определения ряда инсектицидов на основе метилкарбамината. Тенсамметрическое поведение этого класса соединений на ртутном электроде изучено методом переменнотоковой полярографии и определены оптимальные условия для их аналитического определения. Также использован метод циклической вольтамперометрии для изучения электродного процесса и применением пика полученного в катодном развитии удалось протянуть чувствительность метода до частей на миллион.

КАТАЛИТИЧЕСКИЕ РЕАКЦИИ—I. МЕХАНИЗМЫ:

P. R. Bontchev, *Talanta*, 1970, **17**, 499.

Резюме—Обсуждены механизмы некоторых реакций использованных в каталитическом анализе. Познавание механизма каталитической реакции может помогать в разработке новых каталитических реакций и при выборе оптимальных условий и может указывать пути улучшения чувствительности.

КИСЛОТНАЯ ДИССОЦИАЦИЯ И СПЕКТРОФОТОМЕТРИЧЕСКАЯ ХАРАКТЕРИСТИКА 8-ХИНОЛИНСЕЛЕНОЛА В СМЕСЯХ ВОДЫ И ДИОКСАНА:

Noboru Nakamura and Eiichi Sekido, *Talanta*, 1970, **17**, 515.

Резюме—Определены потенциометрическим или спектрофотометрическим методами константы кислотной диссоциации 8-хинолинселенола, 8-хинолинола и 8-хинолинтиола в смесях воды и диоксана различного состава. Также определены спектры светопоглощения 8-хинолинселенола в тех же растворителях. Обсуждены явления связанные с кислотной диссоциацией, стабильность против окисления и спектры светопоглощения реагентов в связы с существующими формами. Подтверждено наличие 8-хинолинселенола в форме амфотерного иона в смесях воды и диоксана с высоким и низким содержанием диоксана.

Theory of titration curves—VII. The properties of derivative titration curves for strong acid–strong base and other isovalent ion-combination titrations: Thelma Meites and Louis Meites, *Talanta*, 1970, **17**, 525. (Department of Chemistry, Clarkson College of Technology, Potsdam, New York 13676, U.S.A.)

Summary—This paper deals with isovalent ion-combination titrations based on reactions that can be represented by the equation $M^{n+} + X^{n-} \rightarrow MX$, where the activity of the product MX is invariant throughout a titration, and with the derivative titration curves obtained by plotting $d[M^+]/df$ versus f for such titrations. It describes some of the ways in which such curves can be obtained; it compares and contrasts them both with potentiometric titration curves, which resemble them in shape, and with segmented titration curves, from which they are derived; and it discusses their properties in detail.

Mass spectrometric analysis of carbon monoxide–nitrogen mixtures: J. R. Majer, *Talanta*, 1970, **17**, 537. (Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham 15.)

Summary—A method for the analysis of gas mixtures containing both carbon monoxide and nitrogen, by using a single-focussing mass spectrometer, is described. It involves measurement of the mass spectrum of a gas sample before and after conversion of the carbon monoxide present into carbon dioxide by means of the Schütze catalyst.

Analytical applications of mixed ligand extraction equilibria. Nickel–dithizone–phenanthroline complex: Ben S. Freiser and Henry Freiser *Talanta*, 1970, **17**, 540. (Department of Chemistry, University of Arizona, Tucson, Arizona 85721, U.S.A.)

Summary—The mixed-ligand nickel–dithizone–phenanthroline complex provides a sensitive method for determination of nickel and also permits evaluation of the extraction constant for nickel dithizonate. The value $\log K_{ex} = -0{\cdot}7$ was obtained, in agreement with a value of $-0{\cdot}2$ obtained by others, and in contrast to an earlier value of $-2{\cdot}9$. The addition of phenanthroline substantially increases the rate of extraction.

ТЕОРИЯ ТИТРАЦИОННЫХ КРИВЫХ—VII. СВОЙСТВА ПРОИЗВОДНЫХ ТИТРАЦИОННЫХ КРИВЫХ ДЛЯ ТИТРОВАНИЯ СИЛЬНЫХ КИСЛОТ И ОСНОВАНИЙ И ДРУГИХ ИЗОВАЛЕНТНЫХ КОМБИНАЦИЙ ИОНОВ:

THELMA MEITES and LOUIS MEITES, *Talanta*, 1970, **17**, 525.

Резюме—Предлежащая статья посвящена титрации комбинаций изовалентных ионов, основанных на реакциях представленных уравнением $M^{n+} + X^{n+} \rightarrow MX$, где активность продукта непеременная в течении титрации и в случае производных титрационных кривых приказана как функция $d[M^+]/df$ от f Описаны некоторые причины получения таких кривых; они сравнены с потенциометрическими кривыми титрования, которые имеют похожие формы, и с сегментированными кривыми титрования из которых они произведены. Статья также обсуждает подробно характеристики этих кривых.

АНАЛИЗ СМЕСЕЙ ОКИСИ УГЛЕРОДА И АЗОТА МЕТОДОМ МАСС-СПЕКТРОМЕТРИИ:

J. R. MAJER, *Talanta*, 1970, **17**, 537.

Резюме—Описан метод анализа газовых смесей содержащих окись углерода и азот с применением масс-спектрометра с единственным фокусированием. Метод состоит из измерения масс-спектра газообразной пробы пред и после конверсии присутствующейо в пробе окиси углерода в двуокись углерода с использованием катализатора Шютцеа.

ПРИМЕНЕНИЕ В АНАЛИЗЕ ЭКСТРАКЦИОННЫХ РАВНОВЕСИЙ СМЕШАННЫХ ЛИГАНДОВ: КОМПЛЕКС НИКЕЛЯ С ДИТИЗОНОМ И ФЕНАНТРОЛИНОМ:

BEN S. FREISER and HENRY FREISER, *Talanta*, 1970, **17**, 540.

Резюме—Смешанный комплекс никеля с дитизоном и фенантролином представляет собой основу для чувствительного метода определения никеля и также позволяет определить константу экстракции дитизоната никеля. Получена величина $\lg K_{ex} = -0{,}7$ которая соглашается с величиной $-0{,}2$ полученной другими авторами, а которая отличаестя от раньшей величины $-2{,}9$. Добавка фенантролина в значительной мере повышает скорость экстракции.

Use of a filter in atomic-fluorescence spectroscopy: P. D. Warr, *Talanta*, 1970, **17**, 543. (The General Electric Company Limited, Central Research Laboratories, Hirst Research Centre, Wembley, England.)

Summary—A detecting system incorporating an interference filter is described for use in atomic-fluorescence spectroscopy analysis in the 200·0–300·0 nm spectral region. Results obtained by using this system are compared with those from a detecting system incorporating either a monochromator or a solar-blind photomultiplier. Improvements of approximately 700-fold and 10-fold respectively in the limits of detection for zinc and mercury result from replacing the monochromator with the filter, while results with the filter are similar to those from a solar-blind photomultiplier. Limits of detection of 10^{-5} ppm for zinc and $2{\cdot}5 \times 10^{-4}$ ppm for mercury, both in aqueous solutions aspirated into an air–town-gas flame, are an improvement on other published results for these elements, obtained by atomic-fluorescence flame spectroscopy.

Thermometric titration of sulphate: M. B. Williams and J. Janata, *Talanta*, 1970, **17**, 548. (Imperial Chemical Industries Limited, Petrochemical and Polymer Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire, England.)

Summary—Direct thermometric titration of sulphate with a solution of barium perchlorate is proposed. The stoichiometry of the titration is shown to be critically dependent on the concentration of ethanol in the titration medium. The titration is rapid and suffers from only a few interferences.

Di-n-butyl carbamoylphosphonate as an extractant of inorganic ions from hydrochloric acid solutions: D. C. Perricos, A. K. Tsolis and E. P. Belkas, *Talanta*, 1970, **17**, 551. (Chemistry Division, Nuclear Reactor Center "Democritus", Athens, Greece.)

Summary—The extraction of 33 elements by a $0{\cdot}1M$ solution of di-n-butyl carbamoylphosphonate in chloroform has been investigated as a function of hydrochloric acid concentration. The results show that this new extractant readily extracts most of the elements in a high oxidation state, including the trivalent rare earths, from hydrochloric acid at concentrations greater than $6M$.

ПРИМЕНЕНИЕ ФИЛЬТРА В АТОМНО-ФЛУОРЕСЦЕНТНОЙ СПЕКТРОСКОПИИ:

P. D. WARR, *Talanta*, 1970, **17**, 543.

Резюме—Описана система датчика на основе интерференционного фильтра применима в анализе методом атомно-флуоресцентной спектроскопии в области спектра 200,0–300,0 нм. Полученные этой системой результаты сравнены с реэультатами полученными датчиками включающими монохроматор или solar-blind фотоусилитель. Заменой монохроматора с фильтром получено 700-кратное и 10-кратное повышение чувствительности для цинка и ртути, соответственно, а результаты полученные с фильтром сравнимые с результатами полученными с solar-blind фотоусилителем. Чувствительности 10^{-5} д.м. для цинка и $2{,}5 \times 10^{-4}$ д.м. для ртути, полученные вбрызгиванием водных растворов в пламя воздух/бытовой газ, представляют собой улучшение в сравнении с другими данными атомнофлуоресцентной пламенной спектроскопии, опубликованными для этих элементов.

ТЕРМОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ СУЛЬФАТА:

M. B. WILLIAMS and J. JANATA, *Talanta*, 1970, **17**, 548.

Резюме—Предложено непосредственное термометрическое титрование сульфата с раствором перхлората бария. Показано что стехиометрия титрования критически зависит от концентрации епирта в титруемом растворе. Титрация быстра и подлежает влиянию только небольшего числа веществ.

ДИ-Н-БУТИЛКАРБАМОИЛФОСФОНАТ В КАЧЕСТВЕ ЭКСТРАКТАНТА ДЛЯ НЕОРГАНИЧЕСКИХ ИОНОВ ИЗ СОЛЯНОКИСЛЫХ РАСТВОРАХ:

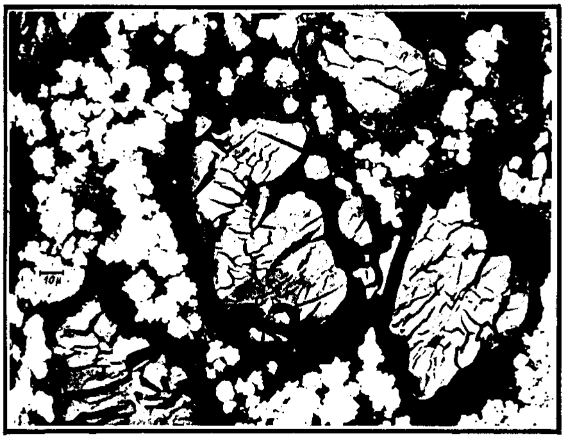
D. C. PERRICOS, A. K. TSOLIS and E. P. BELKAS, *Talanta*, 1970, **17**, 551.

Резюме—Изучено извлечение 33 элементов 0,1 *M* раствором ди-н-бутилкарбамоилфосфоната в хлороформе в зависимости от концентрации соляной кислоты. Результаты показывают что новый экстрактант легко извлекает большинство элементов в высшей степени окисления, включая трехвалентные редкоземельные элементы, из растворов соляной кислоты, концентрация которых больше чем 6 *M*.

ELECTROCHIMICA *Acta*

Editor-in-Chief: DR T P HOAR, Cambridge

Electrochimica Acta is published by Pergamon Press Ltd under the auspices of the International Committee for Electrochemical Thermodynamics and Kinetics (CITCE).



Microphotograph of a DSK working layer.

Executive Editorial Board:
DR T P HOAR
University of Cambridge, England
PROFESSOR J O'M BOCKRIS
University of Pennsylvania, USA
PROFESSOR N IBL
Swiss Federal Institute of Technology, Zurich, Switzerland
PROFESSOR P Van RYSSELBERGHE
Stanford University, USA
PROFESSOR G VALENSI
Faculté des Sciences de Poitiers, France

This is an international journal of pure and applied electrochemistry, publishing papers on every aspect of this subject. More than two hundred papers are presented each year, either in the form of original reports or as serious, critical reviews. Electrochimica Acta thus provides a comprehensive up-to-date coverage of current activity throughout the rapidly expanding field of electrochemistry.

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

Published monthly

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

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

1966

11/69

Volume 17, No. 6 June 1970

Contents

Short Communications

Letter to the Editor

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 thei use at a reduced rate of $15 (£5.5.) per annum.

Printed in Northern Ireland at The Universities Press, Belfast