An International Journal of Analytical Chemistry

ταλαντα

talanta

e Title Section, Contents List, Author
l Subject Indexes to Vol. 18, Nos. 1–6
are included in this issue

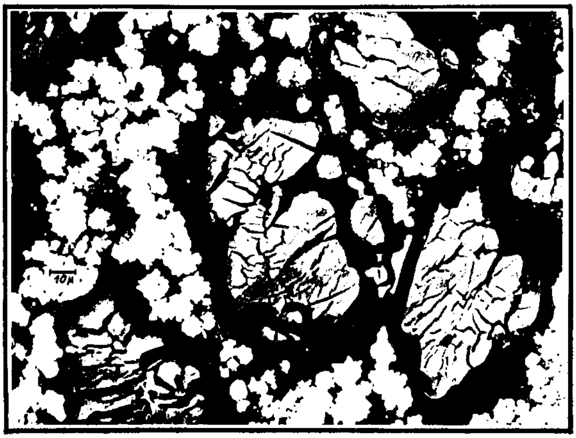
PERGAMON PRESS
OXFORD • LONDON • NEW YORK • PARIS

1971 VOLUME 18, NO. 6 JUNE

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).



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

Microphotograph of a DSK working layer.

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.

Some papers appearing in Vol 16 No 6:

R L KAY and T L BROADWATER:
Solvent structure in aqueous mixtures—I. Ionic mobilities in dioxane–water mixtures at 25°C

J-C JUSTICE:
An interpretation for the distance parameter of the Fuoss–onsager conductance equation in the case of ionic association.

R WACHTER and J BARTHEL:
A method for determining the precise dependence of conductivity data on temperature.

M KESTEN und H G FELLER:
Uber die rolle der Sulfationen bei der anodischen Auflösung und bei der Passivierung von Nickel.

W SMIT and J G HOOGLAND:
The mechanism of the anodic formation of the peroxodisulphate ion on platinum-II. Time dependence of the anode potential.

J AUGUSTYNSKI, F DALARD et J C SOHM:
Etude de la pile oxyde-d'argent–magnesium.

Published monthly

Subscription: £44/$110 per annum

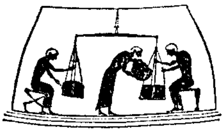
Pergamon Press

OXFORD · NEW YORK · SYDNEY · TORONTO

6/71

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., Pennwalt 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(£3.50)—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 $25(£8) 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 and Advertising 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 © 1971 Pergamon Press Ltd.

ห้องสมุด กรมวิทยาศาสตร์
ก.ค. 2514

Advisory Board

Chairman: Professor R.Belcher, University of Birmingham, England

Professor G.Ackermann, School of Mines, Freiberg, German Democratic Republic
Dr.D.M.W.Anderson, University of Edinburgh, Scotland
Professor F.E.Beamish, University of Toronto, Ontario, Canada
Professor E.Cerrai, C.I.S.E., Milan, Italy
Professor Fritz Feigl, Ministry of Agriculture, Rio de Janeiro, Brazil
Professor H.Flaschka, Georgia Institute of Technology, Atlanta, U.S.A.
Professor H.Freiser, University of Arizona, Tucson, U.S.A.
Professor T.Fujinaga, University of Kyoto, Japan
Professor G.Gottschalk, Technical University, Berlin, German Federal Republic
Mr.S.Greenfield, Albright & Wilson (Mfg.) Ltd., Birmingham, England
Dr.A.Hulanicki, University of Warsaw, Warsaw, Poland
Professor K.Issleib, Martin Luther University Halle Wittenburg, German Democratic Republic
Professor K.J.Karrman, University of Lund, Sweden
Dr.R.Levy, C.N.R.S., Paris, France
Professor C.Liteanu, University of Cluj, Cluj, Romania
Professor H.Malissa, Technical University, Vienna, Austria
Professor L.Meites, Clarkson College of Technology, Potsdam, New York, U.S.A.
Dr.L.C.Pasztor, Jones & Laughlin Steel Corporation, Pittsburgh, Pennsylvania, U.S.A.
Professor W.F.Pickering, University of Newcastle, New South Wales, Australia
Professor E.Pungor, Technical University, Budapest, Hungary
Dr.James E.Rein, Los Alamos Scientific Laboratory, New Mexico, U.S.A.
Dr.J.Růžička, Technical University of Denmark, Lyngby, Denmark
Dr.E.Sawicki, Taft Sanitary Engineering Centre, Cincinnati, U.S.A.
Professor W.Simon, Eidg. Technische Hochschule, Zürich, Switzerland
Dr.A.A.Smales, A.E.R.E., Harwell, England
Professor G.Frederick Smith, University of Illinois, Urbana, U.S.A.
Professor E.Stahl, University of Saarland, Saarbrücken, German Federal Republic
Dr.G.Svehla, Queen's University, Belfast, Northern Ireland
Dr.G.Tölg, Max Planck Institute, Stuttgart, Germany
Dr.E.Wänninen, Åbo Academy, Finland
Professor T.S.West, Imperial College, University of London, England
Professor Yu.A.Zolotov, Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, U.

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 defini contributions to the subject: they must be new publications. Papers may be written in English, Fre or German; all papers have abstracts in these three languages and also in Russian. Special importa is attached to work dealing with the principles of analytical chemistry in which experimental materia 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 pa short communications and reviews are refereed in the normal manner. Preliminary communications refereed urgently and accorded priority in publication. Correspondence of interest to analytical che is welcomed by the Editor-in-Chief, at whose discretion it is published. A new feature is Annotatio 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
Polymer Science USSR
Society of Cosmetic Chemists Journal
Spectrochimica Acta, Part A: Molecular Spectro
Spectrochimica Acta, Part B: Atomic Spectrosco
Tetrahedron
Tetrahedron Letters
Water Research

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

Talanta, 1971, Vol. 18, pp. 557 to 567. Pergamon Press. Printed in Northern Ireland

PROPERTIES AND ANALYTICAL APPLICATIONS OF THE HETEROPOLYMOLYBDATES OF PHOSPHORUS, ARSENIC, SILICON AND GERMANIUM—I

SPECTROPHOTOMETRIC EXAMINATION OF THE HETEROPOLY ACIDS

A. Halász and E. Pungor
Institute for Analytical Chemistry, University for Chemical Engineering,
Veszprém, Hungary

(*Received* 3 *March* 1970. *Accepted* 15 *November* 1970)

Summary—Spectrophotometric studies have been made of the heteropoly acids of phosphorus, arsenic, silicon and germanium, formed at molybdate concentrations of 10^{-1}–10^{-3} *M*. It was found that the heteropoly anion is quantitatively produced at a *Z*-value of 1·60 in the case of a quinquevalent central atom and 1·50 for a quadrivalent central atom, if the amount of the latter is not higher than 50% of the stoichiometric (*Z* is the number of moles of protons taken up by one mole of molybdenum.) On addition of further acid the anion takes up protons, but its absorbance remains unchanged if measured at a wavelength at which the isopolymolybdates show no absorption. At *Z*-values higher than 2·2–2·3, *i.e.*, in highly acidic media, a decomposition reaction starts; its products are octamolybdate and molybdenyl ions. The different molar absorptivities and other "irregularities" found in the various analytical procedures in the literature are due not to the heteropoly acids but to the isopolymolybdate formed together with the former.

The heteropoly acids of arsenic, phosphorus, silicon and germanium have long been used for colorimetric and spectrophotometric determination of the hetero-element. These compounds can be determined by means of the absorbance of their acidified aqueous solutions, or of their extracts in organic solvents, or of their blue reduction products. The conditions for the determinations can be varied so widely that the literature on them is very large and often contradictory. The authors generally remark that the absorbance of the heteropoly acids is highly dependent on the experimental conditions, and that reproducible results can be obtained only by strict adherence to standardized conditions. This indicates that the chemical and optical properties of these compounds, and the conditions for their formation and decomposition are not yet fully elucidated.[1]

The 12:1 mole-ratio of molybdenum to hetero-atom in the heteropolymolybdates has long been recognized and the composition corresponding to the formula $H_nX(Mo_3O_{10})_4$ can be regarded as generally accepted since the X-ray work of Keggin;[2] $n = 3$ if X is P(V) or As(V) and $n = 4$ if X is Si(IV) or Ge(IV). This composition has been verified by a number of authors.[3–6]

Compounds of a different composition produced under special conditions have also been described. For example, Souchay, Tchakirian and Faucherre[3,7] have observed the formation of compounds corresponding to the ratios Ge:Mo = 1:11 and P:Mo = 2:5. Phosphorus and arsenic compounds corresponding to the composition X:Mo = 2:18 have also been described.[8] However these compounds are of no analytical significance. According to Souchay and Tchakirian,[3] only silicon does not form compounds of different compositions. On the other hand, Kemula and Rosolowski[9,10] have claimed the formation of an Si:8Mo compound. Many of the contradictions encountered in the literature can be explained by the formation of various modifications. Strickland[11] showed that silicomolybdic acid may be formed in two modifications, depending on the acid and molybdate concentrations and the unstable (β) modification is slowly transformed spontaneously into the stable one (α). The two forms have different molar absorptivities and the absorbance measured is dependent on time unless the α-form is produced exclusively. Later, other authors presumed the other three compounds can also form various modifications.

The existence of various modifications is, however, not sufficient to explain all the observed phenomena. Consequently, some authors, such as Grasshoff and Hahn[12] have presumed hydrolytic equilibria to exist, while according to others[13] not all of the isopoly acids of molybdenum tend to form heteropoly acids. De Sesa and Rogers[14] have observed that the absorbance and the wavelength of the absorption maximum of silicomolybdic acid depend on the concentration of the acid and of molybdenum, but give no detailed explanation. The present series of papers is intended to assist in elucidating the chemistry of these four heteropoly acids.

EXPERIMENTAL

Reagents

Phosphate solution. Potassium dihydrogen phosphate of Sörensen buffer quality was used. The amount of hydrogen ion brought into the system by use of this salt was taken into consideration in calculating the degree of acidification.

Arsenate solution. Analytical grade disodium hydrogen arsenate was used, standardized by iodometric titration. The amount of hydrogen ions was also calculated.

Silicate solution. Made from crystalline sodium silicate, standardized gravitmetrically.

Germanate solution. Spectroscopically pure germanium dioxide was dissolved in the calculated amount of $0{\cdot}1M$ sodium hydroxide and the solution was diluted.

Molybdate solution. A $0{\cdot}2M$ solution of analytical grade sodium molybdate was prepared and diluted to the appropriate degree.

Perchloric acid. Analytical grade 70% perchloric acid was diluted to the appropriate degree, and standardized by titration.

Apparatus

A Unicam SP 700 spectrophotometer and a Radiometer pH meter type 4 were used.

Formation of the heteropoly acids

A fixed volume of molybdate solution was acidified with various amounts of perchloric acid and then an amount of hetero-atom solution was added that corresponded to the stoichiometric amount for formation of the 12-molybdate or to 50 or 25% of that amount. The solutions were left for some time if necessary, and the absorption spectra of the solutions were recorded with solutions of identical acid and molybdenum concentration or, in some cases, water as reference. The absorbances at various wavelengths and the wavelength corresponding to the absorption maximum were determined and the pH of the solutions was measured, in order to calculate the proton uptake (Z) values, as in our earlier work.[15,16] Z is the number of protons taken up per molybdenum atom, and is obtained from the difference between the amount of acid added and the amount of free hydrogen ions from the pH measurements. The experiments were carried out at 10^{-1}, 10^{-2} and $10^{-3}M$ molybdenum concentration.

RESULTS

On addition of increasing amounts of acid to the solution, setting in of the reaction is indicated by appearance of an absorption maximum at 303–333 nm. There appears to be no other significant point in the spectrum. It is, however, not only the amount of heteropoly acid present that determines the position of the peak and the absorbance and consequently it was found preferable to use also a wavelength on the slope of the peak where there was practically no absorption by any isopolymolybdate. For the phospho-, silico-, and germano-heteropoly acids this wavelength was 400 nm and for arsenomolybdic acid 385 nm.

The absorbances at the peak and at the selected wavelength and the values of Z for a molybdenum concentration of 10^{-1} and $10^{-2}M$ and a central atom concentration corresponding to 50% stoichiometry are plotted in Figs. 1–8 against the ratio of acid added to molybdenum taken and in Figs. 9 and 10 for $10^{-3}M$ molybdenum, except for the absorbances at 400 and 385 nm, which were much too low to be measured satisfactorily. The results show that the reaction starts already at pH > 5 and with increasing acidification the absorbance increases rapidly and then sharply becomes constant. The Z-value corresponding to the break-point can be determined either from the absorbance curve or from the slope of Z *vs.* $[H^+]/[Mo]$ added. The values are listed in Table I. The first part of the germanium curve in Fig. 8 is shown enlarged in Fig. 11.

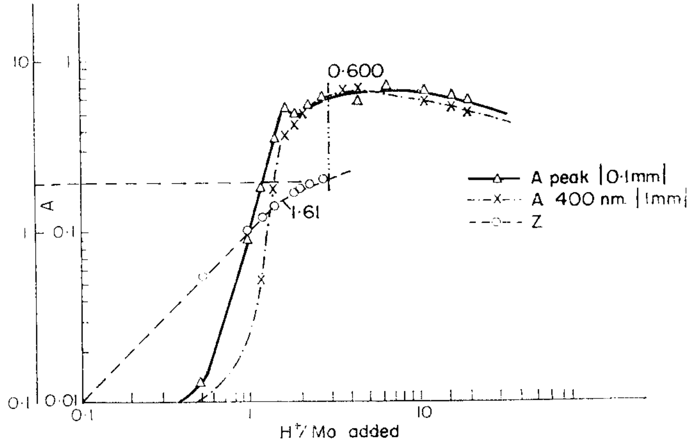


Fig. 1.—Absorption and Z-values of phosphomolybdic acid, plotted against the amount of acid added.

$C_{Mo} = 10^{-1}M$, C_P = 50% of the stoichiometric amount.

Curvette path-length in brackets.

Polymerization of molybdate in the presence of the heteropoly acids

When the Z-values at the break-points are known, the state of polymerization of the excess of molybdate can be estimated. If the formation of the heteropoly acids is

Table I.—Z-values of heteropoly acid formation, 100% excess of molybdate

	Z			
	Mo $10^{-3}M$	Mo $10^{-2}M$	Mo $10^{-1}M$	Mean
P	1·60	1·60	1·61	1·60
As	1·62	1·62	1·58	1·61
Si	1·49	1·45	1·50	1·48
Ge	1·55	1·51	1·51	1·52

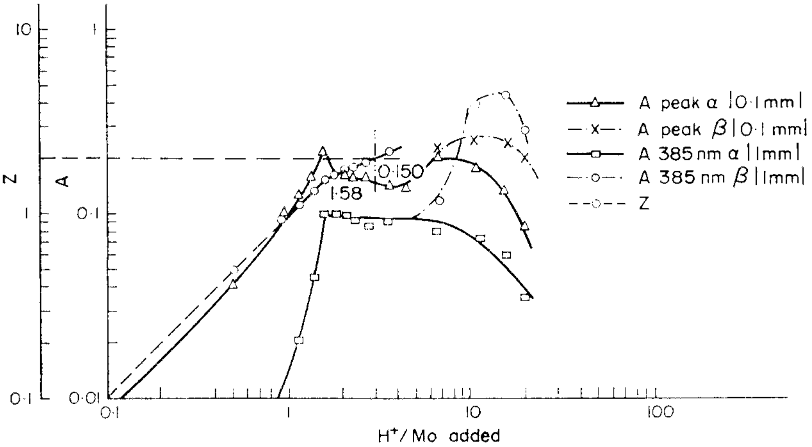


FIG. 2.—Absorption and Z-values of α- and β-arsenomolybdic acid, plotted against the amount of acid added.

$C_{Mo} = 10^{-1}M$, $C_{As} = 50\%$ of the stoichiometric amount.

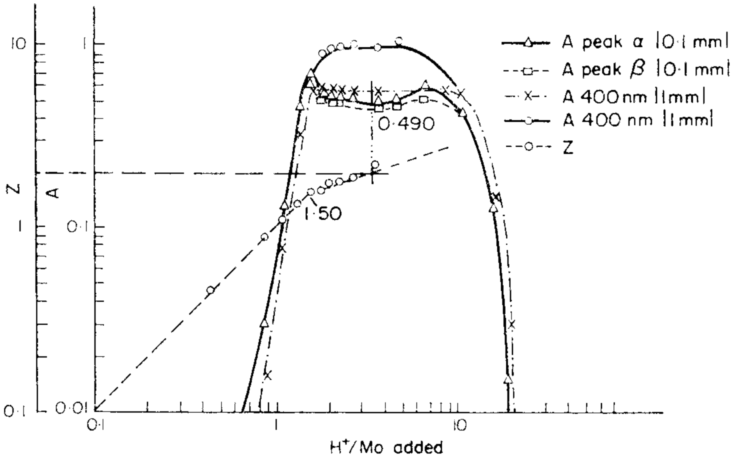


FIG. 3.—Absorption and Z-values of α- and β-silicomolybdic acid, plotted against the amount of acid added.

$C_{Mo} = 10^{-1}M$, $C_{Si} = 50\%$ of the stoichiometric amount.

considered, for simplicity, to start from monomeric molybdate and hetero-species, then for phosphorus a value of $Z = 24/12 = 2{\cdot}00$ is obtained from

$$PO_4^{3-} + 12MoO_4^{2-} + 24H^+ = [P(Mo_3O_{10})_4]^{3-} + 12H_2O \qquad (1)$$

whereas for silicon we have

$$SiO_3^{2-} + 12MoO_4^{2-} + 22H^+ = [Si(Mo_3O_{10})_4]^{4-} + 11H_2O \qquad (2)$$

and the value obtained for Z is $22/12 = 1{\cdot}83$.

The assumption that the heteropoly acid is practically quantitatively formed with a molybdate excess of 100% seems to be justified by the fact that experiments with varying hetero-atom concentrations indicated that after the break-point the Lambert-Beer law always holds if the molybdate excess is $>100\%$. The initial 45° slope of the

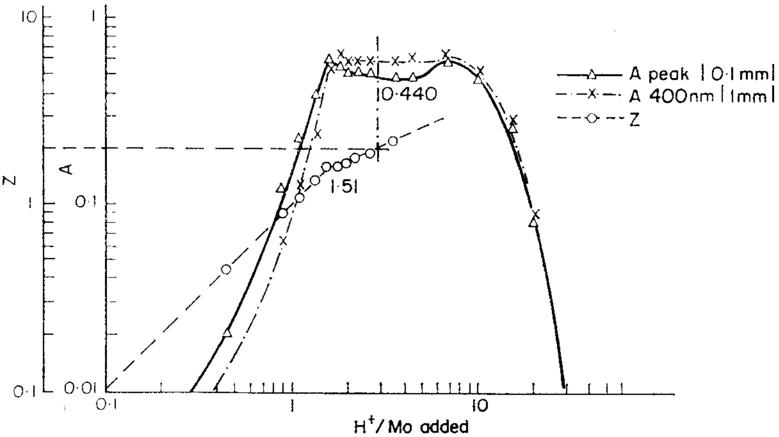


FIG. 4.—Absorption and Z-values of α-germanomolybdic acid, plotted against the amount of acid added.

$C_{Mo} = 10^{-1}M$, $C_{Ge} = 50\%$ of the stoichiometric amount.

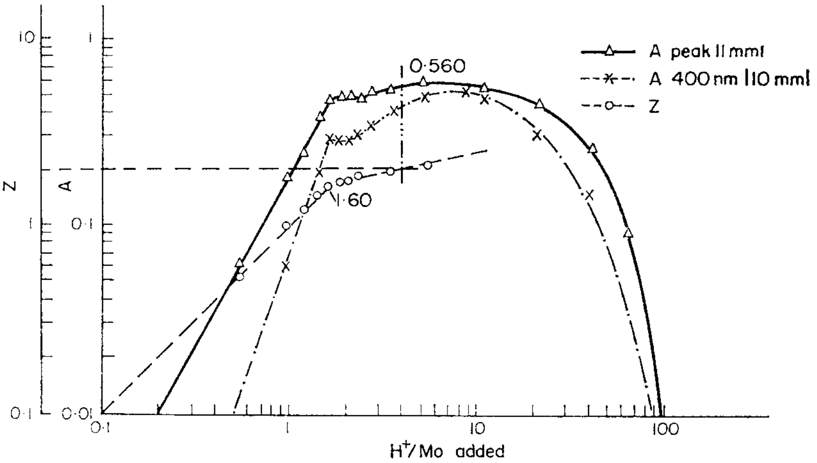


FIG. 5.—Absorption and Z-values of phosphomolybdic acid, plotted against the amount of acid added.

$C_{Mo} = 10^{-2}M$, $C_P = 50\%$ of the stoichiometric amount.

Z curve indicates that heteropoly acid formation takes up practically all of the protons added. It is only after the break in the Z curve that some protons are left over.

It is apparent from Table I that in the case of phosphorus and arsenic the reaction is complete at $Z = 1{\cdot}60$. Since the amount of hetero-element present corresponds to 50% stoichiometry; 1·00 of this value is related to the heteropoly acid, and the remaining 0·6 is related to the excess of molybdenum. This means that the Z-value corresponding to the isopoly condensation of the excess of reagent is $Z = 0{\cdot}6/0{\cdot}5 = 1{\cdot}20$, which indicates that it is heptamolybdate which is present. Similarly, in the case of silicon and germanium we have $1{\cdot}50 - 1{\cdot}83/2 = 0{\cdot}59$ and $0{\cdot}59/0{\cdot}50 = 1{\cdot}18$, *i.e.*, the conditions are very much the same.

However, in the comparison solution, containing molybdenum and acid in the same concentrations as in the test solution, $Z > 1{\cdot}43$, which indicates a condensation

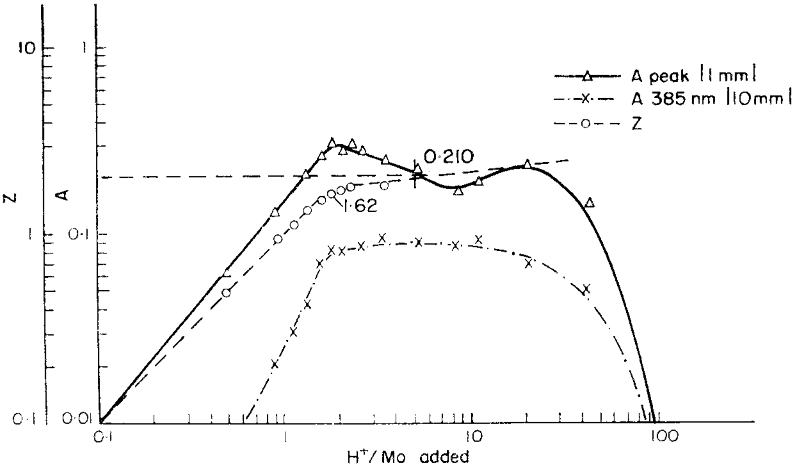


FIG. 6.—Absorption and Z-values of arsenomolybdic acid, plotted against the amount of acid added.

$C_{Mo} = 10^{-2}M$, $C_{As} = 50\%$ of the stoichiometric amount.

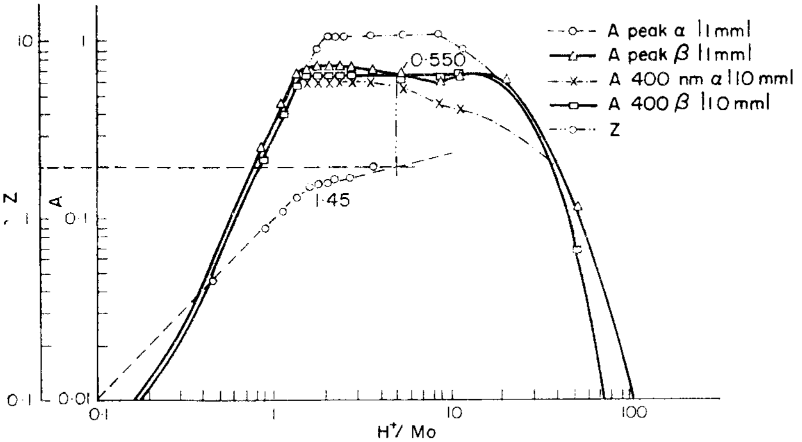


FIG. 7.—Absorption and Z-values of α- and β-silicomolybdic acid, plotted against the amount of acid added.

$C_{Mo} = 10^{-2}M$, $C_{Si} = 50\%$ of the stoichiometric amount.

higher than that corresponding to heptamolybdate. The comparison solutions made in this way are therefore identical to the test solutions neither in composition, nor in optical properties, although they were intended to be. Accordingly, the recorded spectrum is to be regarded as a "difference-spectrum". From our earlier work[15,16] it is evident that after the break-point at $Z = 1{\cdot}43$, the course of the reaction is not independent of the molybdenum concentration: octamolybdate is formed in dilute solutions, whereas in more concentrated solutions molybdenyl cations are also produced. The absorptivities of these species differ at the wavelength of the absorption peak of the heteropoly acid. Our experiments showed that the Lambert–Beer law holds in the 10^{-2}–$10^{-1}M$ concentration range for measurements made at the

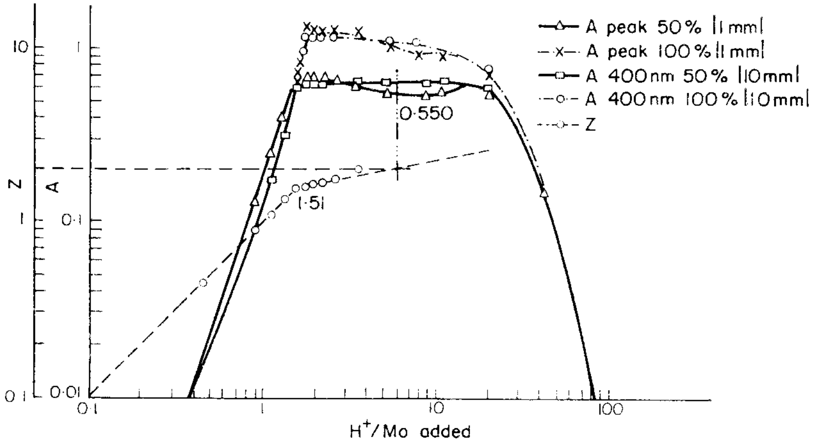


FIG. 8.—Absorption and Z-values of α-germanomolybdic acid, plotted against the amount of acid added.

$C_{Mo} = 10^{-2}M$, $C_{Ge} = 50\%$ and 100% of the stoichiometric amount.

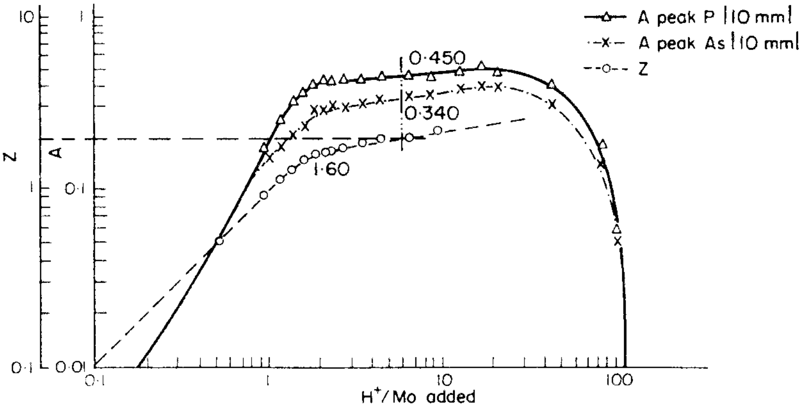


FIG. 9.—Absorption and Z-values of the absorption maximum of phospho- and arsenomolybdic acids plotted against the amount of acid added.

$C_{Mo} = 10^{-3}M$, C_P and $C_{As} = 50\%$ of the stoichiometric amount.

longer wavelength where isopolymolybdates do not absorb, but not at the wavelength of the absorption peak. It is clear that this is due to the nature of the isopoly acids and not to that of the heteropoly acids (*cf.* Table II).

Decomposition of the heteropoly acids

We have seen in Figs. 1–8 that the behaviour of the heteropoly acids can be characterized by the curves for absorbance at 385 and 400 nm. It can be seen from the curves (leaving aside the α and β modifications for the moment, which is why the behaviour of phosphomolybdic acid will not be discussed at first) that after the breakpoints horizontal straight lines are obtained for which the Lambert–Beer relation holds. At the same time, however, the Z curve continues to rise. There is no other possible explanation for this than proton uptake by the ions formed, according to

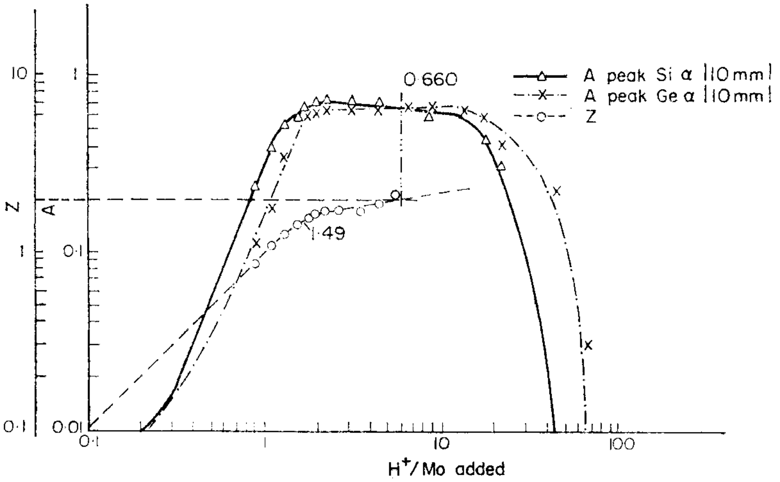


FIG. 10.—Absorption and Z-values of the absorption maximum of silico- and germanomolybdic acids, plotted against the amount of acid added.

$C_{Mo} = 10^{-3}M$, C_{Si} and $C_{Ge} = 50\%$ of the stoichiometric amount.

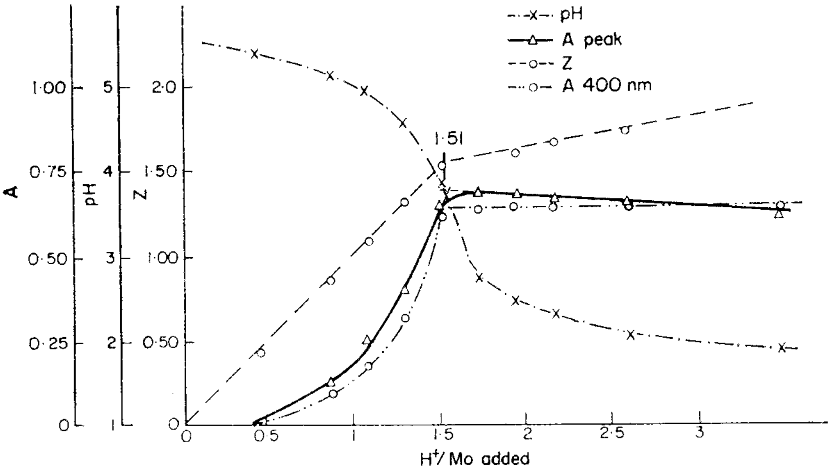


FIG. 11.—Absorption, Z and pH-values of germanomolybdic acid in the stages of formation.

$C_{Ge} = 50\%$ of the stoichiometric amount.

equations (1) and (2). It is regrettable that Z values higher than 2 can only be estimated, on account of the limitations of pH measurement. Even so it is apparent that decrease in absorbance, which may be equated with decomposition of the heteropoly acid, occurs with all four compounds at values very close to each other (2.2–2.3). In the case of phosphorus and arsenic the value $Z = 27/12 = 2{\cdot}25$ corresponds to formation of the compound $H_3PMo_{12}O_{40}$, whereas in the case of silicon and germanium we have $Z = 26/12 = 2{\cdot}17$, corresponding to the formula $H_4SiMo_{12}O_{40}$ on addition of further acid. Accordingly, the heteropoly anions take up protons after their formation. At acidities above this limiting value, heteropoly acid is formed partially, or not at all, or the compound already formed is decomposed by the action of the acid. The rate of this decomposition can be very different, depending on the compound and on the concentration. These results allow conclusions to be drawn about the mechanism of the decomposition, since the reactions must be in accordance with the following conditions.

1. The downward branches of the curve are rather steep; the decomposition must therefore be brought about by a relatively small amount of protons.
2. The reaction must be brought about only by protons and must result in liberation of water.
3. Because the Z-value is higher than 2, molybdic acid and molybdenyl ions must be present simultaneously. This is also proved by the fact that the absorption peaks at 219 and 246 nm appear in the spectrum.[16]
4. The absorption spectrum after decomposition is identical with that of a pure molybdate solution acidified to the same degree, and consequently no heteropoly acid of different composition is formed.

These conditions are satisfied by the following reactions:

$$H_3PMo_{12}O_{40} + 8H^+ = H_4Mo_8O_{26} + 4MoO_2^{2+} + H_3PO_4 + 2H_2O \qquad (3)$$

and

$$H_4SiMo_{12}O_{40} + 8H^+ = H_4Mo_8O_{26} + 4MoO_2^{2+} + H_4SiO_4 + 2H_2O \qquad (4)$$

The Z-value pertaining to these reactions is $8/12 = 0{\cdot}67$. Accordingly, the Z-values of the system in the final stage are $2{\cdot}25 + 0{\cdot}67 = 2{\cdot}92$, and $2{\cdot}17 + 0{\cdot}67 = 2{\cdot}87$ for the phosphorus and silicon compounds respectively. These values correspond roughly to the values which can be obtained from the diagrams by extrapolation. According to this, it is always the $[H^+]/]Mo]$ ratio and not the absolute acid concentration which governs formation and decomposition of the compounds.

Further observations pertaining to the absorption maximum

When, in order to elucidate the properties of the absorption maxima, the curves marked A_{peak} in Figs. 1–10 (the values given indicate the absorption at the maxima, independent of wavelength) are studied, it can be seen that the curves indicate different absorbances at different concentrations and show different, and—at first sight—irregular shapes. This pheomenon was mentioned in the introduction in connection with the various analytical procedures. This means that, as opposed to the situation just dealt with, a uniform evaluation which is independent of concentration is not possible.

It is difficult to find some characteristic point on these curves which could be a basis of comparison. It was, however, mentioned above that the cause of the irregularity lies not with the heteropoly acids but with the isopoly acids. Accordingly it was found preferable to study the point on the curves pertaining to $Z = 2$. This would seem an arbitrary method, but—as is apparent from our previous paper[15,16]—this is the point where a well-defined state is reached, *i.e.*, it is the maximum of octamolybdate formation. The absorbances at this point are summarized in Table II. (For simplicity, only the α-compounds were taken into consideration.) It is seen from the Table that the absorbance apparently decreases as the molybdenum concentration increases (the product of concentration and path-length is a constant) except for the phosphorus compound; this last is attributed to a change in form and for the time being will be neglected.

TABLE II.—ABSORBANCES AT THE ABSORPTION MAXIMA AT VARIOUS Mo CONCENTRATIONS AND AT $Z = 2$; 50% STOICHIOMETRY

Hetero-atom	Mo 10^{-3}M*	Mo $10^{-2}M$†	Mo $10^{-1}M$‡
P	0·450	0·550	0·600
As	0·340	0·210	0·150
Si	0·660	0·550	0·490
Ge	0·660	0·550	0·490

* Path-length 10 mm.
† Path-length 1 mm.
‡ Path-length 0·1 mm.

This decrease in absorbance can be attributed to the presence of a higher amount of molybdenyl ions in the comparison solution at higher concentrations and the fact that the absorbance of these ions at the wavelength of determination is higher than that of a corresponding amount of octamolybdate. It also explains the change in the wavelength of the absorption maximum. The slope of the downward branch of the spectrum depends on the state of polymerization, and with variations in the latter, the maximum difference between the two spectra, *i.e.*, the peak of the difference-spectrum, is found in different places. This variation is not too large at a given molybdenum concentration. At a molybdenum concentration of $10^{-2}M$ and stoichiometries of 0–50%, the position of the peak varies in the range 313–328 nm. It is apparent from this that in other spectrophotometric determinations a maximum concentration can generally be defined up to which the calibration curve is linear, while in this particular case the practically linear region extends over a few orders of magnitude, but always within rather narrow concentration limits. This fact was found to be of paramount importance in formulation of analytical procedures.

The absorbances at the maxima for a molybdenum concentration of $10^{-3}M$ increase a little with increase of amount of acid brought into the system (except for silicomolybdic acid, of which an unstable modification is formed). The reason for this is formation of octamolybdate, as proved by our previous investigations (Figs. 9 and 10). A flat minimum is observed at a molybdenum concentration of $10^{-2}M$, on account of simultaneous formation of octamolybdate and molybdenyl ions (Figs. 5–9). In place of the break-point, a peak is observed with a molybdate concentration of $10^{-1}M$ (Figs. 1–4) because intensive formation of molybdenyl cations after the break-point corresponding to the isopolymolybdates at $Z = 1{\cdot}43$ greatly increases the absorbance of the comparison solution.

Experiments carried out at stoichiometries of 25 and 100% furnished no new results. The Lambert–Beer law holds—in optimum cases—up to a stoichiometry of 80–90%. The curves for 100% stoichiometry are shown in Fig. 8; the plots are similar in the other cases.

Summing up, it can be stated that the diagrams do not indicate the formation of compounds of different compositions. A possibility for this to occur seems to exist only in the formation or in the decomposition stage, within very narrow acid concentration limits. Accordingly, it is of no consequence as far as analytical applications are concerned. The "irregularities" of the diagrams, as described by previous authors, are to be attributed to the properties of the isopolymolybdates.

Zusammenfassung—Die Heteropolysäuren von Phosphor, Arsen, Silicium und Germanium wurden bei Molybdatkonzentrationen von 10^{-1}–$10^{-3}M$ spektrophotometrisch untersucht. Mit einem fünfwertigen Zentralatom wird das Heteropolyanion bei einem Z-Wert von 1,60 quantitativ gebildet, mit einem vierwertigen Zentralatom bei $Z = 1{,}50$, sofern die Konzentration des Zentralatoms nicht größer ist als 50% der stöchiometrischen (Z ist die Anzahl der von einem Mol Molybdän aufgenommenen Mole Protonen). Bei Zugabe weiterer Säure nimmt das Anion Protonen auf; jedoch bleibt seine Extinktion unverändert, sofern man bei einer Wellenlänge mißt, bei der die Isopolymolybdate nicht absorbieren. Bei Z-Werten über 2,2–2,3, d.h. in stark sauren Medien, beginnt eine Zersetzungsreaktion; ihre Produkte sind Oktamolybdat- und Molybdänylionen. Die verschiedenen molaren Extinktionskoeffizienten und andere bei den verschiedenen in der Literatur angegebenen analytischen Vorschriften auftretenden "Unregelmäßigkeiten" liegen nicht an den Heteropolysäuren, sondern an dem gleichzeitig gebildeten Isopolymolybdat.

Résumé—On a effectué des études spectrophotométriques sur les hétéropolyacides du phosphore, de l'arsenic, du silicium et du germanium, formés à des concentrations en molybdate de 10^{-1}–$10^{-3}M$. On a trouvé que l'hétéropolyanion est produit quantitativement pour une valeur de Z de 1,60 dans le cas d'un atome central pentavalent et 1,50 pour un atome central tétravalent, si la quantité de ce dernier n'excède pas 50% de la valeur stoechiométrique (Z est le nombre de moles de protons fixés par une mole de molybdène). Par addition de plus d'acide l'anion fixe des protons, mais son absorption reste inchanée si elle est mesurée à une longueur d'onde pour laquelle les isopolymolybdates n'offrent pas d'absorption. A des valeurs de Z plus élevées que 2,2–2,3, c'est-à-dire en milieux hautement acides, une réaction de décomposition se déclenche; ses produits sont des ions octamolybdate et molybdényle. Les différents coefficients d'absorption molaire et autres "irrégularités" trouvé dans les diverses techniques analytiques de la littérature sont dûs non aux hétéropolyacides mais à l'isopolymolybdate formé conjointement à eux.

REFERENCES

1. O. G. Koch and G. A. Koch-Dedic, *Handbuch der Spurenanalyse*, Springer-Verlag, Berlin, 1964.
2. J. F. Keggin, *Proc. Roy. Soc.*, 1934, **144A**, 75.
3. P. Souchay and A. Tchakirian, *Ann. Chim.*, 1946, **1**, 249.
4. C. Ferrari and N. Nanni, *Gazz. Chim. Ital.*, 1939, **69**, 301.
5. R. Ripan and C. Liteanu, *Compt. Rend.*, 1947, **224**, 196.
6. T. Dupuis and C. Duval, *ibid.*, 1949, **229**, 51.
7. P. Souchay and A. Faucherre, *Bull. Soc. Chim. France*, 1951, 335.
8. P. Pascal, *Nouveau traité de chimie minerale, Tome XIV*, Masson, Paris, 1959.
9. W. Kemula and S. Rosolowski, *Roczniki Chem.*, 1960, **34**, 3.
10. *Idem*, *Bull. Acad. Polon. Sci. Ser. Chim. Geogr.*, 1959, **5**, 351.
11. J. D. H. Strickland, *J. Am. Chem. Soc.*, 1952, **74**, 862.
12. K. Grasshoff and H. Hahn, *Z. Anal. Chem.*, 1959, **168**, 246.
13. K. Schriever and W. Leetsch, *Naturwiss.* 1962, **17**, 392.
14. M. A. De Sesa and L. B. Rogers, *Anal. Chem.*, 1954, **26**, 1278.
15. A. Halász and E. Pungor, *Magy. Kém. Folyóirat*, 1968, **74**, 545.
16. E. Pungor and A. Halász, *J. Inorg. Nucl. Chem.*, 1970, **32**, 1187.

Talanta, 1971, Vol. 18, pp. 569 to 575. Pergamon Press. Printed in Northern Ireland

PROPERTIES AND ANALYTICAL APPLICATIONS OF THE HETEROPOLYMOLYBDATES OF PHOSPHORUS, ARSENIC, SILICON AND GERMANIUM—II*

MODIFICATIONS OF THE HETEROPOLY ACIDS

A. HALÁSZ and E. PUNGOR
Institute for Analytical Chemistry, University of Chemical Engineering, Veszprém, Hungary

(*Received* 3 *March* 1970. *Accepted* 15 *November* 1970)

Summary—Phospho-, arseno-, silico- and germanomolybdic acids may all exist in an α- and a β-modification. α-Silicomolybdic acid is formed if the degree of acidification is below $[H^+]/[Mo] = 1{\cdot}5$. At higher acid concentrations the β-modification is formed, and spontaneously transformed into the α-form. Germanomolybdic acid behaves similarly, but the transformation is much faster. Arsenomolybdic acid is always formed as the α-modification and is transformed into the β-modification only later and in a very slow reaction if the pH of the solution is below 1. Formation of the two modifications is also dependent on acid concentration in the case of phosphomolybdic acid, but both modifications are stable and no spontaneous transformation occurs. Compounds similar to the β-modifications but showing different molar absorptivities are formed in acetone-containing solution.

IT HAS LONG been known that the absorbance of silicomolybdic acid changes as a function of time. Strickland[1] has explained this in terms of two modifications of silicomolybdic acid, the stable α-form produced at low, the β-modification at higher acid concentrations (the ratio $[H^+]/[Mo] > 1{\cdot}5$). The β-form is slowly but spontaneously transformed into the α-form. He also found that the composition of the two modifications is identical and the Si:Mo ratio is 1:12 for both. He stated that so-called α, β and γ species may occur in acidified molybdate solutions; of these, α and β lead to formation of the corresponding silicomolybdic acids, whereas the γ-form does not react with silicic acid. He did not define the α-form and assumed the β-form to be tetramolybdate and the γ-form to be the molybdenyl ion.

According to Armand and Bertoux[2] the α-modification is produced if the $[H^+]/[Mo]$ ratio is lower than 1·5, whereas the β-form is produced if the ratio is higher than 3. In intermediate cases, a mixture of the two is formed. The quinoline salt of both compounds was prepared and the molybdenum and silicon content determined gravimetrically and found to be identical. Chalmers and Sinclair[3] have dealt with the structure of the two compounds, and have proposed an explanation of the differences on the basis of the Keggin-structure[4] with changes in position of three of the molybdenum atoms, which means only a slight difference in the structure of the compound. Ringbom and his co-workers[5] have accepted the theory of Lindqvist[6–9] on the isopoly acids of molybdenum and found it probable that the α-compound is formed from heptamolybdate and the β-compound from octamolybdate. On the other hand Chalmers and Sinclair claim the α-compound to be derived from octamolybdate and the β-compound from deca- or dodecamolybdate.

---

* Part I—See Reference 16.

Some authors doubt even the 1:12 Si:Mo ratio. Kemula and Rosolowski[10,11] have a ratio of 1:8 for the α- and β-modifications and claim that the 1:12 compound is formed only on warming. They call this the γ-modification.

Much less information is available about modifications of the other three compounds. Krumholtz[12] has observed that the colour of germanomolybdic acid changes with time, and Boltz and Mellon[13] consider this compound unsuitable for determination of germanium on account of the necessity for rigorous standardization of the conditions. Ferrari first commented[14,15] on the "colourless" and "yellow" varieties of phosphomolybdic acid. When reduced, these two forms show different behaviour. Chalmers and Sinclair have "titrated" phosphomolybdic acid with acid and observed a break-point and an increase in absorbance at a value of $[H^+]/[Mo] = 1{\cdot}8$. For the arsenic compound they observed the break-point at a higher acid concentration, with a decrease in absorbance. Certain corrections had to be applied in interpretation on account of the light-absorption characteristics of the isopolymolybdates present (*cf.* Part I[16]).

EXPERIMENTAL

Aqueous media

We found that at a molybdenum concentration of 10^{-1}–$10^{-2}M$ and a medium acid concentration the maximum absorbance of silicomolybdic acid can be observed after 4–5 min, and after 15 min a slow decrease starts which is complete after about 48 hr. It is evident that the β-modification, initially formed, is transformed into the α-modification. The transformation takes place in 30 min if the solution is kept in a boiling water-bath, but a precipitate may occur in more concentrated solutions. The α-modification is produced if the $[H^+]/[Mo]$ ratio is lower than 1·5. It is difficult to identify the modification in molybdate solutions more dilute than $10^{-3}M$, not only because of the low reaction rate but also because the absorbance at 400 nm cannot be determined at this dilution. There is one fact, however, which suggests that there are certain differences even in such dilute solutions: the maximum absorbance decreases with increasing acid concentration. This is explained by the molar absorptivity of the β-compound being lower than that of the α at the absorption maximum (*cf.* Figs. 3, 7 and 10 in Part I[16]). Total formation of the β-modification occurs at a ratio $[H^+]/[Mo] = 2$; at ratios between 1·5 and 2, a mixture of the two modifications is present.

The spectra of the two modifications, recorded with water as reference, are shown in Fig. 1. They are very similar and closely resemble the spectra of heptamolybdate and octamolybdate.

There is only one significant difference in the spectra and this is the cause of the maximum at 303–333 nm obtained in the difference spectrum recorded with molybdate as reference. It is apparent from the curves that the maximum occurs at a different wavelength for the two modifications, at 314 nm for the α-form and 321 nm for the β ($10^{-2}M$ molybdate, 50% stoichiometry, Fig. 2). The wavelength of the maximum varies with the experimental conditions, as discussed previously.[16] It is evident from Figs. 1 and 2 that the absorptivity of the α-modification is higher at the maximum, and the β-modification has the higher absorptivity, so often referred to in the literature, only at longer wavelengths. If the spectrum of the β-modification is recorded against the α-modification as reference, a sharp peak is obtained at 375 nm. We did not observe the presence of a third modification in any of our experiments.

Changes in modification of germanomolybdic acid cannot be followed, on account of the rapid transformation. Qualitatively, however, it could be observed that two modifications exist. The conditions of formation and the spectra are similar to those for the silicon compounds, the only difference being that transformation at room temperature is complete within 2 hr. Germanomolybdic acid is quite suitable for spectrophotometric determination of germanium provided measurements are made after transformation into the α-modification is complete and not immediately after the reaction.

Modifications of arsenomolybdic acid show a totally different picture. No indication of modification can be observed at molybdenum concentrations of 10^{-3} and $10^{-2}M$ (*cf.* Figs. 6 and 9 of Part I[16]). Once the compound has been formed the absorbance at 385 nm is independent of the amount of acid added. The same holds for $10^{-1}M$ molybdate; accordingly, in aqueous solution it is always the "colourless" modification that is formed. This is the first significant difference from the silicon and germanium compounds. However, with $0{\cdot}1M$ molybdenum and an acid concentration $>0{\cdot}5N$ a slow increase in absorbance occurs with time, the maximum being reached at an acid concentration of 1–1·5*N* (*cf.* Fig. 2 of Part I[16]). The solution then appears to be yellow. The reaction is

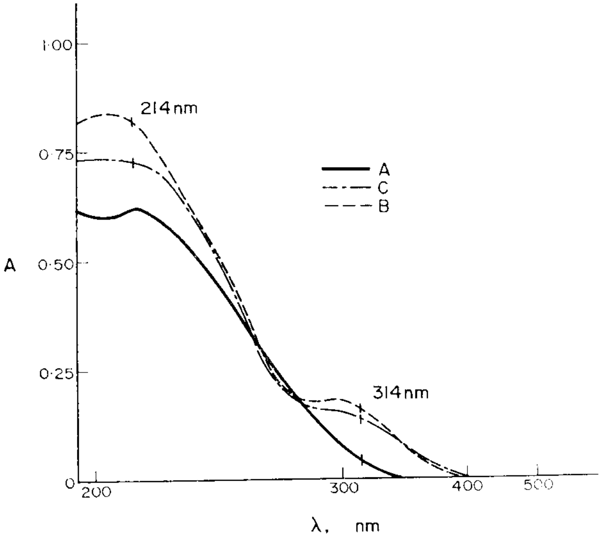


FIG. 1.—Absorption spectrum of silicomolybdic acid, recorded against water as reference.

A—Solution not containing silicon; Mo and acid concentration equal to that of silicomolybdic acid.
B—α-modification.
C—β-modification.

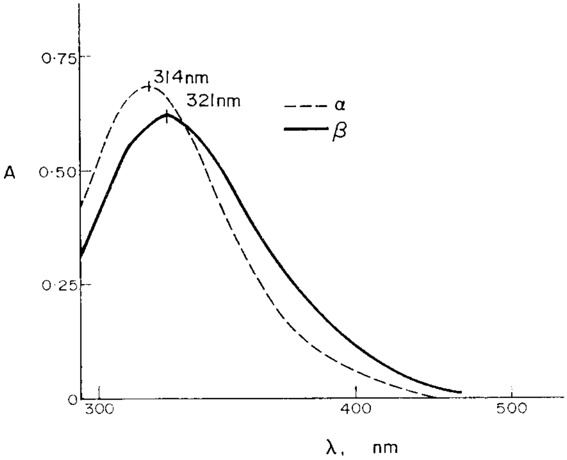


FIG. 2.—Difference spectrum of silicomolybdic acid recorded against a reference solution of identical acid and Mo concentration ($C_{Mo} = 10^{-2}M$).

very slow, however, the first detectable change occurring after 30 min and a slow increase still being observable even after three days. (The values shown in the figure were measured after this waiting period.) The process can be made faster by warming, but a precipitate may form, so this modification change cannot be utilized for analytical purposes.

The difference spectra of the two modifications (0·1*M* molybdenum, 50% stoichiometry, recorded *vs.* reagent blank) are shown in Fig. 3. The maxima are at 321 and 327 nm. If the compound with the higher absorptivity at longer wavelength is called the β-form, a significant difference is found from the silicon and germanium compounds. At appropriate acid concentrations it is the β-form which is

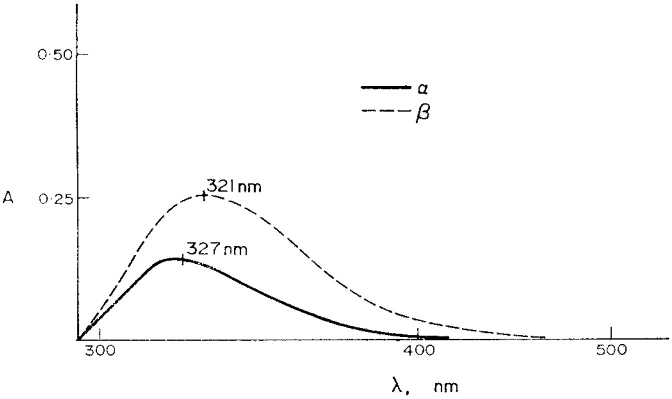


FIG. 3.—Difference spectrum of arsenomolybdic acid recorded against a reference solution of identical acid and Mo concentration ($C_{Mo} = 10^{-1}M$).

the stable one, which is in accordance with the results of Chalmers and Sinclair. There is an appreciable difference also in the spectra, the β-form always having a higher absorptivity.

For phosphomolybdic acid the picture is different again. No change in modification can be observed at a molybdenum concentration of $10^{-3}M$ (*cf.* Fig. 9 in Part I[16]). Both the E_{400} and E_{max} values show a short horizontal portion for a molybdenum concentration of $10^{-2}M$ after the break-point at $Z = 1{\cdot}60$. After this horizontal part a slow rise follows—a difference from the other three compounds—and continues until decomposition of the compound starts (*cf.* Fig. 5 in our previous paper[16]). The colour of the solution is intensified, and a change in modification occurs.

The slow rise starts immediately after the break-point if the molybdenum concentration is $10^{-1}M$, and only a slight shift in the absorbance curve indicates that an α-compound is also formed, within narrow acid concentration limits (Fig. 1 in Part I[16]). It is noteworthy that—as opposed to all the other compounds—a change in absorbance cannot be observed even after two or three days' standing. Apparently both forms are stable.

Figure 4 shows the difference spectrum of the two modifications at an acid concentration corresponding to the horizontal on the curve at $[H^+]/[Mo] = 1{\cdot}7$. and that for maximum absorbance at $[H^+]/[Mo] = 11$. The point of intersection is, in contrast to that for silicomolybdic acid, before the maximum, so the absorbance of the β-form is higher at the maximum and in the downward branch

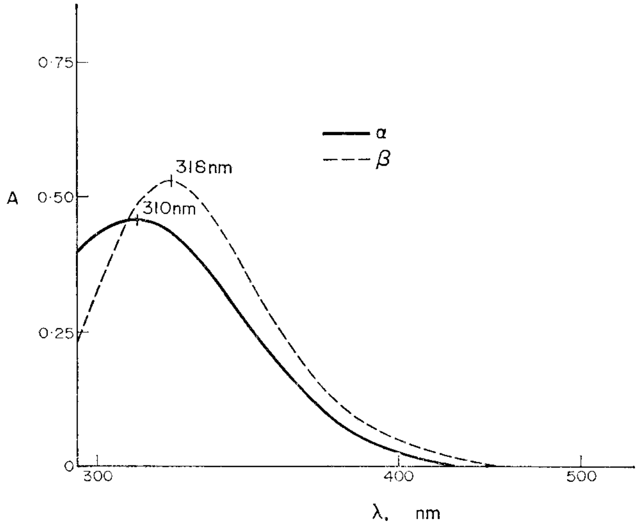


FIG. 4.—Difference spectrum of phosphomolybdic acid recorded against a reference solution of identical concentration ($C_{Mo} = 10^{-2}M$).

too. The stability and lability of both the α- and β-forms explain why the rules concerning changes in the absorption maxima described in our previous paper[16] do not hold for phosphomolybdic acid.

It is very difficult to decide unambiguously on the connection between the heteropoly acid modifications and the forms of the isopolymolybdates. In our opinion, Ringbom[5] is correct in saying that for the silicon and germanium compounds the α-modification is produced from heptamolybdate, and the β from octamolybdate. Formation of the β-modification occurs at a Z-value higher than 1·5, whereas formation of octamolybdate starts at $Z = 1{\cdot}43$, *i.e.*, a certain concentration of octamolybdate is necessary for the formation of the β-modification.

With phosphomolybdic acid, formation of the β-form starts only in more concentrated solutions, and at different Z-values if the molybdenum concentration is different. In the case of arsenic it is always the α-form which is produced first and the slow transformation starts only in concentrated and strongly acidic solutions. The case of phosphorus may be similar, but the transition is so fast that it cannot be followed photometrically. Formation of modifications may be connected with the pH of the solution. The critical value is about pH = 2 for phosphorus and pH < 1 for the arsenic compound. With $10^{-3}M$ molybdenum and phosphorus, and 10^{-2} or $10^{-3}M$ molybdenum and arsenic, the required pH values cannot be reached without decomposition of the compound. This may well explain why no modification changes are observed in dilute solutions.

Acetone-containing media

It is known that the heteropoly acids can be extracted at suitable molybdenum and acid concentrations with a few oxygen-containing organic solvents, such as ethers, esters, ketones or higher alcohols. The conditions of the extraction and the differences in the behaviour of the four compounds have been dealt with in some detail by Wadelin and Mellon,[17] who explained the extraction by the assumption that under certain circumstances the hydration sheath of the heteropoly acid may be replaced by organic molecules. Chalmers and Sinclair[3] have used this fact to explain why some water-miscible organic solvents have an effect on the heteropoly acids. They mention as a characteristic example that the absorbance of the compounds increases in acetone–water medium. According to them solvation has a stabilizing effect on the β-forms. Analytically the phenomenon is of importance first of all in the case of arsenic, since the absorbance of the α-modification in aqueous media is very low at wavelengths where the molybdates show no light absorption, and the β-modification can be produced only very slowly. At a molybdenum concentration of $10^{-2}M$ it is always the α-form, *i.e.*, the colourless modification, that is obtained in aqueous solutions. If, on the other hand, the reaction is carried out in the presence of acetone, the solution is a vivid yellow.

We examined the effect of various amounts of acetone at a molybdenum concentration of $10^{-2}M$ and arsenic corresponding to 25 and 50% stoichiometry, the absorbance being measured at 400 nm.

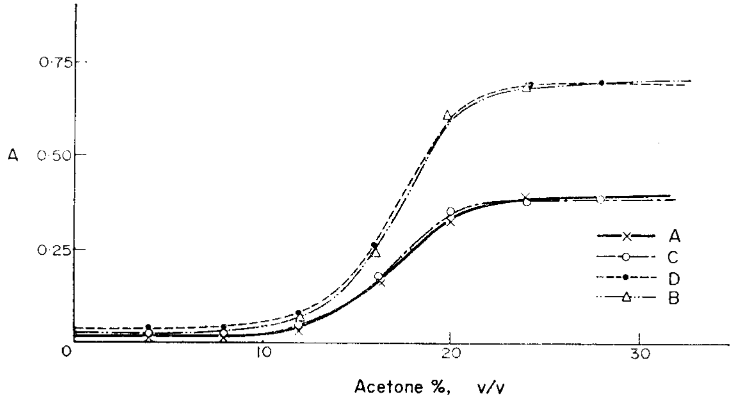


FIG. 5.—Extinction of arsenomolybdic acid at 400 nm plotted against amount of acetone.

A—$C_{Mo} = 1 \times 10^{-2}M$; 25% stoichiometry

B—$C_{Mo} = 4 \times 10^{-2}M$; 25% stoichiometry

C—$C_{Mo} = 1 \times 10^{-2}M$; 50% stoichiometry

D—$C_{Mo} = 4 \times 10^{-2}M$; 50% stoichiometry

The results are illustrated in Fig. 5. Acetone concentrations up to 10% v/v had no effect, but concentrations >25% v/v gave increased and constant absorbance (curves *A* and *C*). Repetition with the same arsenic concentration and $4 \times 10^{-2}M$ molybdenum gave identical results (curves *B* and *D*). Accordingly, the degree of saturation is independent of both the arsenic and the molybdenum concentrations and depends only on the amount of acetone added. Consequently formation of a compound of fixed composition cannot be assumed and the results can be explained by solvent action. It seems, that by addition of acetone the β-form is stabilized, but the absorbance values are considerably higher, then in aqueous medium.

Experiments with the other three compounds showed that again the absorbances are higher in acetone-containing solution. The silicon and germanium compounds are even more similar to each other in acetone media. A slow modification is observed, with roughly the same rate of transformation, the absorbance of both compounds decreasing by 1% in about 30 min after formation.

At high acetone concentrations (about 50% v/v or more) and a molybdenum concentration of $4 \times 10^{-2}M$ the molybdenum solution itself becomes yellow. This phenomenon will not be discussed here but is mentioned because it may give rise to erroneous analytical results.

Zusammenfassung—Phospho-, Arseno-, Silico- und Germanomolybdänsäuren können alle in einer α- und einer β-Modifikation auftreten. α-Silicomolybdänsäure bildet sich, wenn der Säuregrad kleiner ist als $[H^+]/[Mo] = 1{,}5$. Bei höheren Säurekonzentrationen bildet sich die β-Modifikation und wandelt sich spontan in die α-Form um. Germanomolybdänsäure verhält sich ähnlich, nur geht die Umwandlung viel schneller. Arsenomolybdänsäure bildet sich stets in der α-Modifikation und wandelt sich erst später in einer sehr langsamen Reaktion in die β-Modifikation um, wenn der pH der Lösung unter 1 liegt. Die Bildung der beiden Modifikationen hängt auch im Fall der Phosphomolybdänsäure von der Säurekonzentration ab, aber beide Modifikationen sind stabil und es findet keine spontane Umwandlung statt. Ähnliche Verbindungen wie die β-Modifikationen bilden sich in acetonhaltiger Lösung, haben aber andere molare Extinktionskoeffizienten.

Résumé—Les acides phospho-, arséno-, silico- et germanomolybdiques peuvent tous exister dans une α- et une β-modification. L'acide α-silicomolybdique est formé si le degré d'acidification est en-dessous de $[H^+]/[Mo] = 1{,}5$. A des concentrations acides plus élevées, la modification β est formée et spontanément transformée en la forme α. L'acide germanomolybdique se comporte de manière similaire, mais la transformation est beaucoup plus rapide. L'acide arsénomolybdique est toujours formé dans la modification α et est transformé en la modification β seulement ultérieurement et dans une réaction très lente si le pH de la solution est inférieur à 1. La formation des deux modifications dépend aussi de la concentration en acide dans le cas de l'acide phosphomolybdique, mais les deux modifications sont stables et il ne se produit pas de transformation spontanée. Des composés similaires aux modifications β mais montrant des coefficients d'absorption molaire différents se forment en solution contenant de l'acétone.

REFERENCES

1. J. D. H. Strickland, *J. Am. Chem. Soc.*, 1952, **74**, 862.
2. M. Armand and J. Bertoux, *Anal. Chim. Acta*, 1953, **8**, 510.
3. R. A. Chalmers and A. G. Sinclair, *ibid.*, 1965, **33**, 384; 1966, **34**, 412.
4. J. F. Keggin, *Proc. Roy. Soc.*, 1934, **144A**, 75.
5. A. Ringbom, P. E. Ahlers and S. Siitonen, *Anal. Chim. Acta*, 1969, **20**, 78.
6. I. Lindqvist, *Arkiv Kemi*, 1950, **2**, 325.
7. *Idem*, *ibid.*, 1950, **2**, 349.
8. *Idem*, *Nova Acta Regiae Soc. Sci. Upps.*, 1950, **1**, 15.
9. *Idem*, *Acta. Chim. Scand.* 1951, **5**, 568.
10. W. Kemula and S. Rosolowski, *Roczniki Chem.*, 1960, **3**, 34.

11. *Idem, Bull. Acad. Polon. Sci. Ser. Chim. Geogr.*, 1959, **5**, 351.
12. P. Krumholtz, *Z. Anorg. Allgem. Chem.* 1933, **212**, 91.
13. D. F. Boltz and M. G. Mellon, *Anal. Chem.*, 1951, **19**, 872.
14. C. Ferrari, *Gazz. Chim. Ital.*, 1951, **81**, 795.
15. *Idem, Mikrochim. Acta*, 1956, 551.
16. A. Halász and E. Pungor, *Talanta*, 1971, **18**, 557.
17. C. Wadelin and M. G. Mellon, *Anal. Chem.*, 1953, **25**, 1668.

Talanta, 1971, Vol. 18, pp. 577 to 586. Pergamon Press. Printed in Northern Ireland

PROPERTIES AND ANALYTICAL APPLICATIONS OF THE HETEROPOLYMOLYBDATES OF PHOSPHORUS, ARSENIC, SILICON AND GERMANIUM—III*

EXAMINATION OF TWO- AND THREE-COMPONENT SYSTEMS WITHOUT SEPARATION

A. HALÁSZ, E. PUNGOR and K. POLYÁK
Institute for Analytical Chemistry, University for Chemical Engineering,
Veszprém, Hungary

(*Received* 3 *March* 1970, *Accepted* 15 *November* 1970)

Summary—By taking advantage of the possible variations in acid and molybdenum concentration, wavelength of measurement, α- and β-modifications, and media, P, As, Si and Ge can be determined spectrophotometrically as the heteropolymolybdates without separation. Rapid procedures are proposed for the analysis of two- and three-component mixtures of these elements.

SEVERAL procedures have been described in the literature for the individual spectrophotometric determination of phosphorus, arsenic, silicon and germanium as their heteropolymolybdates. For analysis of systems containing more than one of these elements, however, separation procedures are usually proposed because the four compounds are very similar to each other. Such separations usually involve distillation of the volatile halides or selective extraction of the heteropoly acids.[1]

Determination without separation has been proposed by a few authors for phosphorus and silicon, or arsenic and silicon, an auxiliary complexing agent being used to decompose the arseno- or phosphomolybdic acid, whereas the silicomolybdic acid remains unchanged. Tartaric, citric and oxalic acids or their salts are proposed as complexing agents. However, the authors themselves remark that these methods are not totally selective.

A method for the analysis of three-component heteropoly acid systems was first proposed by Alekseyev;[2] first phosphomolybdic acid is extracted with n-butanol–chloroform mixture, then arsenomolybdic acid with a mixture of n-butanol, ethyl acetate and chloroform, and finally the silicon compound with pure butanol. The acid concentrations had to be varied during the procedure. This method was applied by Filippova and Kuznetsova to the determination of impurities in copper and nickel alloys.[3] In the methods proposed by Paul,[4–6] formation of silicomolybdic acid is prevented by use of strongly acidic solution, the phosphorus compound is extracted with butyl acetate, and arsenic is determined in the remaining aqueous phase. Silicon is determined in another aliquot in which the phosphorus and arsenic compounds are decomposed with citric acid. For a ternary mixture containing phosphorus, arsenic and germanium, first phosphomolybdic acid is extracted with isobutyl acetate, and then germanomolybdic acid at a different pH. Arsenic remains in the aqueous phase. These procedures are rather cumbersome and the multiple extraction operations may cause considerable error.

According to the results presented in Parts I and II,[7,8] in spite of the many similar characteristics of the four compounds there are some differences in their properties

---

* Part II—See Reference 8.

which allow their determination without separation. Thus the light-absorption of α-arsenomolybdic acid is practically zero at 427 nm whereas that of the other three compounds is considerable. Another difference is that at a molybdenum concentration of $10^{-1}M$, as we have seen, phosphomolybdic acid and arsenomolybdic acid are, even at higher acid concentrations, more stable than the corresponding silicon and germanium compounds. A further possibility is utilization of differences between the α- and β-modifications, in aqueous solution primarily in the case of silicon, and in aqueous acetone solution in the case of arsenic and germanium.

By combination of these variables we have succeeded in solving the problem of determination without separation in five of the six possible variations of two-component mixtures. In some cases, more than one method could be found. The basic principle is to choose conditions under which a single component can be determined in one aliquot, and the sum of the components in another. Sometimes methods can be found for independent determination of the two components.

If silicon and germanium occur together, measurement of the heteropoly acids will not suffice because the two compounds are too much alike. Only the sum of the two can be measured; one of them must be determined by some other method *e.g.*, germanium by the phenylfluorone method. Provided silicon and germanium are not both present, three-component systems can also be analysed.

EXPERIMENTAL

The amount of sample taken is governed by the fact that neither the Lambert–Beer law nor the principle of additivity can be regarded as valid at concentrations of hetero-atom higher than that corresponding to 50% stoichiometry. Calibration curves must be established for all the wavelengths and optical path-lengths quoted, with reference solutions of similar composition. The Lambert–Beer law holds for the isopoly acids only over a narrow range, and measurement made for one path-length cannot be calculated to another. Similarly, the methods are very sensitive to acid concentration, and it is preferable to start with neutral and unbuffered solutions.

Concentrations or path-lengths different from those given should not be used, unless the validity of the Lambert–Beer law and the principle of additivity has been established for the new conditions. The molar absorptivities given in the Tables are the mean of three parallel determinations and refer to the conditions quoted in the procedures.

The methods proposed are considerably simpler than the distillation or extraction procedures. Once the calibration curves have been established all that is needed is to mix the solutions and to measure the absorbances. The waiting time is generally not more than a few minutes, except for the aqueous silicon and germanium systems where 48 and 2-hr waiting periods respectively are necessary for formation of the α-modifications.

Reagents

Sodium molybdate solution, 0·2*M*.

Perchloric acid. Concentrated (70%) and a fourfold dilution. (~2*M*)

Reagents and sample are added in the order given in the procedures.

Determination of phosphorus and arsenic

In aqueous solution. α-Arsenomolybdic acid does not interfere with the determination of the other three compounds, if a suitable wavelength is used. Under conditions chosen to ensure formation of the α-form, in one measurement phosphorus can be determined independently of any arsenic present, and in a second measurement the sum phosphorus + arsenic is determined. The molar absorptivities are grossly different at the two wavelengths used, so cells of different path-lengths have to be used.

To 10·0 ml of 0·2*M* molybdate in a 50-ml volumetric flask add 4·0 ml of dilute perchloric acid and the appropriate amount of sample solution, dilute with distilled water to the mark, mix, and immediately measure phosphorus at 427 nm in a 20-mm cell and phosphorus + arsenic at 370 nm in a 10 or 5-mm cell.

Typical results are given in Table I. The relative error for phosphorus is about 1%, that for arsenic is higher (<6%) because the measurement is by difference and the molar absorptivity of arsenic at 370 nm is much lower than that of phosphorus.

TABLE I.—DETERMINATION OF PHOSPHORUS AND ARSENIC IN THE PRESENCE OF EACH OTHER IN AQUEOUS SOLUTION

$\varepsilon_{P_{427}} = 66{\cdot}5\ l.mole^{-1}.mm^{-1}$; $\varepsilon_{P_{370}} = 375\ l.mole^{-1}.mm^{-1}$; $\varepsilon_{As_{370}} = 200\ l.mole^{-1}.mm^{-1}$

P taken, *μg/ml*	P found, *μg/ml*	Error %	As taken *μg/ml*	As found *μg/ml*	Error %
2·60	2·60	0·0	18·7	18·2	−2·7
2·60	2·65	+1·9	37·4	38·9	+4·0
2·60	2·70	+3·8	62·4	64·3	+3·0
2·60	2·75	+5·8	87·4	86·3	−1·3
5·20	5·25	+1·0	18·7	17·6	−5·9
5·20	5·20	0·0	37·4	37·7	+0·8
5·20	5·30	+2·0	62·4	61·4	−1·6
5·20	5·25	+1·0	87·4	87·3	−0·1
7·70	7·80	+1·3	18·7	18·2	−2·7
7·70	7·70	0·0	37·4	38·4	+4·0
7·70	7·65	−0·6	62·4	66·0	+5·8
7·70	7·65	−0·6	87·4	85·9	−1·7
10·30	10·35	+0·5	18·7	17·8	−4·8
10·30	10·25	−0·5	37·4	37·4	0·0
10·30	10·30	0·0	62·4	64·0	+3·0
10·30	10·25	−0·5	87·4	88·2	+0·9
12·90	13·10	+1·5	18·7	19·1	+2·1
12·90	12·85	−0·4	37·4	38·9	+4·0
12·90	12·85	−0·4	62·4	64·3	+3·0
12·90	12·85	−0·4	87·4	84·0	−4·1
15·20	15·45	−0·3	18·7	19·1	+2·1
15·50	15·40	−0·6	37·4	38·9	+4·0
15·50	15·50	0·0	62·4	61·6	−1·3
20·60	20·60	0·0	18·7	17·8	−4·8
20·60	20·60	0·0	37·4	38·1	+1·9

In acetone-containing solution. In acetone-containing solution arsenomolybdic acid is formed as a vivid yellow compound; the molar absorptivity of this compound is considerably higher than in aqueous solution and its absorption spectrum is very similar to that of the corresponding phosphorus compounds. Phosphorus is therefore determined in acetone-free medium by a method similar to that just described; it is preferable to use a higher molybdenum and acid concentration to avoid interference from any silicon present. The sum of the two components is determined in another aliquot in the presence of acetone.

Add 25·0 ml of 0·2*M* molybdate, 10·0 ml of concentrated perchloric acid and x ml of sample ($x \leq 10$) to a 50-ml volumetric flask and dilute to the mark. Measure the absorbance at 427 nm in a 20-mm cell within not more than 20 min to avoid formation of the β-form of arsenomolibdic acid. Take 10·0 ml of 0·2*M* molybdate, 10·0 ml of concentrated perchloric acid, 20·0 ml of acetone and again x ml of sample in a 50-ml volumetric flask and dilute to the mark with water. Measure phosphorus + arsenic at 345 nm after a waiting period of 5–15 min.

The molar absorptivities of phospho- and arsenomolybdic acid scarcely differ from each other in acetone-containing solution. Consequently, this method is more accurate for arsenic, especially at low concentrations (Table II).

Determination of silicon and arsenic

β-Silicomolybdic acid method, in aqueous solution. The conditions are chosen so that β-silicomolybdic acid and α-arsenomolybdic acid are formed. Arsenic does not interfere with the measurement of silicon at 427 nm. The sum of the two is measured at 370 nm. The β-silicomolybdic acid is formed rather quickly and transforms into the α-form but so slowly as not to affect the measurements.

Add 10·0 ml of 0·2*M* molybdate, 4·0 ml of dilute perchloric acid and the sample to a 50-ml volumetric flask and dilute to the mark with water. After 5–15 min, measure silicon at 427 nm in a 20-mm cell and the sum at 370 nm in a 5-mm cell. The method gives good results, especially for low silicon contents (Table III).

α-Silicomolybdic acid method, in aqueous solution. If the solutions prepared as just described are left to stand at room temperature for at least 48 hr, the β-silicomolybdic acid is completely transformed

TABLE II.—DETERMINATION OF PHOSPHORUS AND ARSENIC (ACETONE-CONTAINING SOLUTION)

$\varepsilon_{P_{427}} = 69{\cdot}0\ l.mole^{-1}.mm^{-1}$; $\varepsilon_{P_{345}} = 1{\cdot}19 \times 10^{3}\ l.mole^{-1}.mm^{-1}$; $\varepsilon_{As_{345}} = 1{\cdot}04 \times 10^{3}\ l.mole^{-1}.mm^{-1}$

P taken, *μg/ml*	P found, *μg/ml*	Error %	As taken, *μg/ml*	As found *μg/ml*	Error %
2·60	2·55	−1·9	6·3	6·1	−2·4
2·60	2·55	−1·9	18·8	18·2	−3·3
2·60	2·53	−2·6	31·2	30·9	−1·0
2·60	2·53	−2·6	43·7	43·8	+0·2
7·70	7·45	−3·2	6·3	6·2	−1·6
7·70	7·70	0·0	18·8	19·1	+1·6
7·70	7·60	−1·3	31·2	31·8	+1·9
12·90	12·75	−1·2	6·3	6·5	+3·2
12·90	12·50	−3·1	18·8	19·1	+1·6
18·10	17·90	−1·1	6·3	6·1	−3·2

TABLE III.—DETERMINATION OF SILICON AND ARSENIC (β-SILICOMOLYBDIC ACID IN AQUEOUS SOLUTION)

$\varepsilon_{Si_{427}} = 985\ l.mole^{-1}.mm^{-1}$; $\varepsilon_{Si_{370}} = 515\ l.mole^{-1}.mm^{-1}$; $\varepsilon_{As_{370}} = 200\ l.mole^{-1}.mm^{-1}$

Si taken, *μg/ml*	Si found, *μg/ml*	Error %	As taken *μg/ml*	As found, *μg/ml*	Error %
2·40	2·35	−2·1	18·7	18·0	−2·9
2·40	2·40	0·0	37·4	36·6	−2·1
2·40	2·40	0·0	62·4	60·0	−3·8
2·40	2·50	+4·2	87·4	84·0	−3·9
4·70	4·55	−3·2	18·7	19·2	+2·7
4·70	4·65	−1·1	37·4	36·0	−3·7
4·70	4·65	−1·1	62·4	60·6	−2·9
4·70	4·65	−1·1	87·4	85·2	−2·5
7·10	7·05	−0·7	18·7	18·6	−0·5
7·10	7·10	0·0	37·4	36·6	−2·1
7·10	7·10	0·0	62·4	61·0	−2·2
7·10	7·20	+1·4	87·4	84·6	−3·2
9·40	9·40	0·0	18·7	19·0	+1·6
9·40	9·40	0·0	62·4	64·0	+2·6
9·40	9·40	0·0	62·4	64·0	−1·1
9·40	9·45	+0·5	87·4	86·4	−1·1
11·80	11·70	−0.8	18·7	19·0	+1·6
11·80	11·70	−0·8	37·4	37·6	+0·5
11·80	11·70	−0·8	62·4	60·4	−3·8
11·80	11·70	−0·8	87.4	87.4	0·0

into the stable α-modification. The α-arsenomolybdic acid remains unchanged. This method is preferable if higher amounts of silicon are present (Table IV).

Measurement in acetone-containing solution. The silicon is measured as either the α- or the β-form in aqueous solution as before, independently of the arsenic content. A strongly acidic medium is used for a second aliquot, in which case no silicomolybdic acid is formed and the amount of arsenic can be determined in acetone-containing solution. The procedure for silicon is as already described. For arsenic, take 10·0 ml of 0·2*M* molybdate, 10·0 ml of concentrated perchloric acid, 20·0 ml of acetone and the sample in a 50-ml volumetric flask and dilute to the mark. After 5–15 min measure at 370 or 345 nm in a cell with path-length suited to the expected arsenic content.

This method is the quickest and, since the two measurements are totally independent, the most accurate (Table V).

TABLE IV.—DETERMINATION OF SILICON AND ARSENIC (α-SILICOMOLYBDIC ACID IN AQUEOUS SOLUTION)

$\varepsilon_{\mathrm{Si}_{427}} = 39·5$ *l.mole*$^{-1}$.*mm*$^{-1}$;		$\varepsilon_{\mathrm{Si}_{370}} = 336$ *l.mole*$^{-1}$.*mm*$^{-1}$;		$\varepsilon_{\mathrm{As}_{370}} = 200$ *l.mole*$^{-1}$.*mm*$^{-1}$	
Si taken, *μg/ml*	Si found, *μg/ml*	Error %	As taken, *μg/ml*	As found, *μg/ml*	Error %
2·40	2·42	+0·8	18·7	18·0	−3·7
2·40	2·35	−2·1	37·4	37·5	+0·3
2·40	2·25	−6·2	62·4	65·2	+4·5
2·40	2·35	−2·1	87·4	88·8	+1·6
4·70	4·70	0·0	18·7	19·6	+4·8
4·70	4·60	−2·1	37·4	39·4	+5·3
4·70	4·80	+2·1	62·4	63·0	+1·0
4·70	4·95	+5·3	87·4	84·2	−3·7
7·10	7·10	0·0	18·7	18·0	−3·7
7·10	7·18	+1·1	37·4	36·0	−3·7
7·10	7·25	+2·1	62·4	59·3	−4·9
7·10	7·25	+2·1	87·4	84·8	−3·0
9·40	9·40	0·0	18·7	18·2	−2·7
9·40	9·48	+0·9	37·4	35·8	−5·1
9.40	9·40	0·0	62·.4	62·4	0·0
9·40	9·57	+1·8	87·4	84·7	−3·1
11·80	11·50	−2·1	18·7	18·2	−2·7
11·80	11·80	0·0	37·4	37·6	+0·5
11·80	11·80	0·0	62·4	62·4	0·0
11·80	11·80	0·0	87·4	88·0	+0·7
14·10	14·05	−0·4	18·7	18·2	−2·7
14·10	14·05	−0.4	37·4	36·8	−2·1
14·10	14·17	+0·5	62·4	62·6	+0·3
18·80	18·77	−0·2	18·7	18·5	−1·1
18·80	18·90	+0·5	37·4	35·5	−5·1

TABLE V.—INDEPENDENT DETERMINATION OF ARSENIC IN PRESENCE OF SILICON

$\varepsilon_{\mathrm{Si}_{427}} = 98·5$ *l.mole*$^{-1}$.*mm*$^{-1}$;		$\varepsilon_{\mathrm{As}_{370}} = 440$ *l.mole*$^{-1}$.*mm*$^{-1}$	
As taken, *μg/ml*	Si added, *μg/ml*	As found, *μg/ml*	Error %
6·3	11·8	6·2	−1·4
6·3	18·8	6·4	+1·4
18·7	11·8	18·9	+1·1
31·2	11·8	31·4	+0·6

Determination of germanium and arsenic

In aqueous solution. Germanomolybdic acid behaves very like silicomolybdic acid except that transformation of the β-form into the α is much faster. Consequently, the β-form cannot be used analytically unless it is stabilized in some way (*cf.* Chalmers and Sinclair[9]); the time of measurement must be fixed within 30 sec, if reproducible results are to be obtained, which is very inconvenient for practical purposes. However, the transformation is quantitative within 2 hr and the stable α-modification can easily be measured. The procedure is identical to the α-silicomolybdic acid method just described, except that only 2 instead of 48 hr standing is required (Table VI.)

In acetone-containing solution. The transformation time of germanomolybdic acid in acetone-containing solution is similar to that of silicomolybdic acid. The procedure is the same as that described above for silicon and arsenic, except that the germanium *must* be determined in the α-form (Table VII).

TABLE VI.—DETERMINATION OF GERMANIUM AND ARSENIC, IN AQUEOUS SOLUTION

$\varepsilon_{Ge_{427}} = 41·0$ *l.mole*$^{-1}$.*mm*$^{-1}$;		$\varepsilon_{Ge_{370}} = 350$ *l.mole*$^{-1}$.*mm*$^{-1}$;		$\varepsilon_{As_{370}} = 200$ *l.mole*$^{-1}$.*mm*$^{-1}$	
Ge taken, *µg/ml*	Ge found, *µg/ml*	Error %	As taken, *µg/ml*	As found, *µg/ml*	Error %
6·0	5·9	−1·6	18·7	19·3	+3·2
6·0	5·9	−1·6	37·4	37·4	0·0
6·0	6·2	+3·3	62·4	60·2	−2·9
6·0	6·2	+3·3	87·4	84·0	−3·9
12·1	11·9	−1·6	18·7	18·9	+1·1
12·1	12·1	0·0	37·4	37·0	−1·1
12·1	12·3	+1·7	62·4	60·0	−3·8
12·1	12·5	+3·3	87·4	82·0	−6·2
18·1	18·1	0·0	18·7	19·0	+1·7
18·1	18·1	0·0	37·4	37·5	+0·3
18·1	18·7	+3·3	62·4	59·2	−5·1
18·1	18·9	+4·4	87·7	86·6	−0·9
24·2	23·7	−2·1	18·7	19·0	+1·7
24·2	24·4	+0·8	37·4	36·0	−3·7
24·2	24·4	+0·8	62·4	63·5	+1·4
24·2	24·8	+2·5	87·4	88·0	+0·5
30·2	30·2	0·0	18·7	17·9	−4·3
30·2	30·2	0·0	37·4	36·0	−3·7
30·2	30·3	+0·3	62·4	62·9	+0·8
30·2	30·7	+1·7	87·0	89·6	+2·5
36·2	36·4	+0·5	18·7	17·9	−4·3
36·2	36·5	+0·8	37·4	35·5	−5·1
36·2	36·5	+0·8	62·4	59·2	−5·1

TABLE VII.—DETERMINATION OF GERMANIUM AND ARSENIC IN ACETONE-CONTAINING SOLUTION

$\varepsilon_{Ge_{427}} = 41·0$ *l.mole*$^{-1}$.*mm*$^{-1}$;		$\varepsilon_{As_{370}} = 440$ *l.mole*$^{-1}$.*mm*$^{-1}$	
As taken, *µg/ml*	Ge added, *µg/ml*	As found, *µg/ml*	Error %
6·3	30·2	6·5	+3·2
6·3	48·3	6·6	+4·8
18·8	30·2	19·0	+1·1
31·2	30·2	31·6	+1·3

Determination of phosphorus and silicon

In aqueous solution. Both measurements are made at the same wavelength and optical path-length, and only the molybdenum and acid concentrations are varied. Silicomolybdic acid is not formed in strongly acidic medium, and phosphorus can be measured independently of any silicon present. At lower acid and molybdenum concentrations the sum of the two compounds is measured. The wavelength used is 427 nm so that any arsenic present does not interfere. A different wavelength can be used if arsenic is quite certainly absent. Theoretically, both α- and β-silicomolybdic acid could be used, but the former offers no advantage.

Take 25·0 ml of 0·2*M* molybdate, 10·0 ml of concentrated perchloric acid and the sample in a 50-ml volumetric flask, and dilute to the mark with water. Measure phosphorus at 427 nm in a 20-mm cell. No waiting period is necessary.

Take 10·0 ml of 0·2*M* molybdate, 4·0 ml of dilute perchloric acid and the sample in a 50-ml volumetric flask, dilute to the mark, and measure phosphorus + silicon at 427 nm in a 20-mm cell after 5–15 min (Table VIII).

TABLE VIII.—DETERMINATION OF PHOSPHORUS AND SILICON IN AQUEOUS SOLUTION

$\varepsilon_{P_{427}} = 69{\cdot}0\ l.mole^{-1}.mm^{-1}$ (high acidity); 66·0 (low acidity); $\varepsilon_{Si_{427}} = 98{\cdot}0\ l.mole^{-1}.mm^{-1}$

P taken, *μg/ml*	P found, *μg/ml*	Error %	Si taken, *μg/ml*	Si found, *μg/ml*	Error %
5·20	5·30	+1·9	4·70	4·48	−4·7
5·20	5·30	+1·9	9·40	9·27	−1·4
5·20	5·30	+1·9	14·10	14·00	−0·7
10·30	10·35	+0·5	4·70	4·58	−2·6
10·30	10·45	+1·5	9·40	9·35	−0·5
10·30	10·55	+2·5	14·10	14·12	+0·1
15·50	15·30	−1·6	4·70	4·70	0·0
15·50	15·40	−0·8	9·40	9·60	+2·1
15·50	15·40	−0·8	14·10	14·65	+3·9

In acetone-containing solution. Take 10·0 ml of 0·2*M* molybdate, 10·0 ml of concentrated perchloric acid, 20·0 ml of acetone and the sample in a 50-ml volumetric flask, dilute with water to the mark, and after 5–15 min measure phosphorus at 345 or 370 nm in a cell with path-length suited to the amount expected.

Take 10·0 ml of 0·2*M* molybdate, 4·0 ml of dilute perchloric acid, 10·0 ml of acetone and the sample in a 50-ml volumetric flask, dilute with water to the mark, and measure the sum P + Si at 345 or 370 nm, after 5–15 min (Table IX).

Determination of phosphorus and germanium

In aqueous solution. The method is that described for phosphorus and silicon except that *β*-germanomolybdic acid cannot be measured and a 2-hr waiting period is necessary before measurement of the sum of the phsophorus and germanium (Table X).

In acetone-containing solution. The method is identical to that for phosphorus and silicon (Table XI).

Determination of silicon and germanium

Germanium must be determined by some other method, *e.g.*, phenylfluorene, and it is only the sum of the two components that is measured by means of the heteropoly acids. The difference in transformation time of the two α-acids, 2 hr for germanomolybdic, 48 hr for silicomolybdic, and the

TABLE IX.—DETERMINATION OF PHOSPHORUS AND SILICON IN ACETONE-CONTAINING SOLUTION

$\varepsilon_{P_{370}} = 610\ l.mole^{-1}.mm^{-1}$ (high acidity); 440 (low acidity); $\varepsilon_{Si_{370}} = 520\ l.mole^{-1}.mm^{-1}$

P taken, *μg/ml*	P found, *μg/ml*	Error %	Si taken, *μg/ml*	Si found, *μg/ml*	Error %
2·60	2·62	+0·8	2·40	2·45	+2·1
2·60	2·55	−1·9	7·10	6·95	−2·1
2·60	2·70	+3·8	11·80	12·10	+2·5
2·60	2·70	+3·8	18·80	19·30	+2·7
7·70	7·75	+0·6	2·40	2·40	0·0
7·70	7·80	+1·2	7·10	7·40	+4.1
7·70	7·80	+1·2	11·80	11·90	+0·8
12·90	12·90	0·0	2·40	2·60	+0·3
12·90	12·90	0·0	7·10	7·45	+4·9
12·90	12·90	0·0	11·80	12·10	+2·5

TABLE X.—DETERMINATION OF PHOSPHORUS AND GERMANIUM IN AQUEOUS SOLUTION

$\varepsilon_{P_{427}} = 69{\cdot}0\ l.mole^{-1}.mm^{-1}$ (high acidity); 66·0 (low acidity); $\varepsilon_{Ge_{427}} = 39{\cdot}0\ l.mole^{-1}.mm^{-1}$

P taken, *μg/ml*	P found, *μg/ml*	Error %	Ge taken, *μg/ml*	Ge found, *μg/ml*	Error %
5·20	5·25	+1·2	12·1	11·4	−5·8
5·20	5·35	+3·4	24·2	24·5	+1·2
5·20	5·35	+3·4	36·2	36·8	+1·7
10·30	10·35	+0·5	12·1	11·6	−4·1
10·30	10·45	+1·5	24·2	23·5	−2·9
10·30	10·55	+2·5	36·2	36·1	−0·3
15·50	15·30	−1·2	12·1	11·6	−4·1
15·50	15·30	−2·2	24·2	24·5	+1·2
15·50	15·50	0·0	36·2	36·5	+0.8

TABLE XI.—DETERMINATION OF PHOSPHORUS AND GERMANIUM IN ACETONE-CONTAINING SOLUTION

$\varepsilon_{P_{370}} = 610\ l.mole^{-1}.mm^{-1}$ (high acidity); 440 (low acidity); $\varepsilon_{Ge_{370}} = 510\ l.mole^{-1}.mm^{-1}$

P taken, *μg/ml*	P found, *μg/ml*	Error %	Ge taken, *μg/ml*	Ge found, *μg/ml*	Error %
2·60	2·55	−2·0	6·0	6·1	+1·7
2·60	2·55	−2·0	18·1	18·5	+2·2
2·60	2·70	+4·0	30·2	31·5	+4·3
2·60	2·70	+4·0	48·3	50·0	+2·7
7·70	7·75	+0·6	6·0	5·8	−3·4
7·70	7·80	+1·2	18·1	18·7	+3·3
7·70	7·80	+1·2	30·2	31·5	+4·3
12·90	12·90	0·0	6·0	6·3	+5·1
12·90	12·90	0·0	18·1	19·6	+2·8
12·90	12·90	0·0	30·2	31·5	+4·3

instability of β-germanomolybdic acid in aqueous medium, make it preferable to use the acetone method.

Take 10·0 ml of 0·2*M* molybdate, 4·0 ml of dilute perchloric acid, 10·0 ml of acetone and the sample in a 50-ml volumetric flask, dilute with water to the mark, and measure at 370 nm in a 5-mm cell after 5–15 min.

In constructing Table XII, the amount of germanium was assumed to be known and only the silicon results are given.

Determination of phosphorus, arsenic and silicon

Silicomolybdic acid is not formed in strongly acidic medium and then does not interfere in the determination of phosphorus. Arsenomolybdic acid does not interfere either, if it is present as the α-modification and the appropriate wavelength is chosen. In this way, phosphorus can be measured independently of the other two components. With a second sample the sum of phospho- and β-silicomolybdic acids is measured at the same wavelength but a lower acid and molybdenum concentration. In a third sample, the sum of phosphorus and arsenic is measured in a strongly acidic acetone-containing solution.

Take 25·0 ml of 0·2*M* molybdate, 10·0 ml of concentrated perchloric acid, and the sample in a 50-ml volumetric flask, dilute with water to the mark, and measure phosphorus at 427 nm in a 20-mm cell within 20 min so as to avoid β-arsenomolybdic acid formation.

Take 10·0 ml of 0·2*M* molybdate, 4·0 ml of dilute perchloric acid and the same size of sample aliquot as before in a 50-ml volumetric flask, dilute to the mark with water, and measure phosphorus + silicon in a 20-mm cell at 427 nm after 5–15 min.

TABLE XII.—DETERMINATION OF SILICON AND GERMANIUM IN ACETONE-CONTAINING SOLUTION

$\varepsilon_{Ge_{370}} = 510$ *l.mole*$^{-1}$.*mm*$^{-1}$; $\varepsilon_{Si_{370}} = 520$ *l.mole*$^{-1}$.*mm*$^{-1}$

Si taken, *μg/ml*	Ge added, *μg/ml*	Si found, *μg/ml*	Error %
2·40	6·0	2·40	0·0
2·40	18.1	2·50	+4·2
2·40	30·2	2·35	−2·1
2·40	48·3	2·35	−2·1
7·10	6·0	7·00	−1·4
7·10	18·1	7·20	+1·4
7·10	30·2	7·35	+3·5
11·80	6·0	11·90	+0·8
11·80	18·1	11·80	0·0
11·80	30·2	11·50	−2·5
18·80	6·0	18·90	+0·5

TABLE XIII.—DETERMINATION OF PHOSPHORUS, SILICON AND ARSENIC

P taken, *μg/ml*	P found, *μg/ml*	Error %	Si taken, *μg/ml*	Si found, *μg/ml*	Error %	As taken, *μg/ml*	As found, *μg/ml*	Error %
7·70	7·70	0·0	7·10	7·08	−0·3	18·8	19·1	+1·6
12·90	12·50	−3·1	2·40	2·42	+0·8	18·8	19·1	+1·6
12·90	12·75	−1·2	7·10	7·08	−0·3	6·3	6·5	+3·2
2·60	2·53	−2·7	7·10	7·00	−1·4	31·2	30·9	−1·0
7·70	7·60	−1·3	2·40	2·47	+2·9	31·2	31·8	+1·9
2·60	2·55	−1·9	11·80	11·70	−0·8	18·8	18·2	−3·3
7·70	7·45	−3·2	11·80	11·78	−0·2	6·3	6·2	−1·6
2·60	2·45	−5·8	16·50	16·45	−0·3	6·3	6·1	−2·4
18·10	17·90	−1·6	2·40	2·45	+2·9	6·3	6·1	−2·4
2·60	2·53	−2·7	2·40	2·40	0·0	43·6	43·7	+0·2

TABLE XIV.—DETERMINATION OF PHOSPHORUS, GERMANIUM AND ARSENIC

P taken, *μg/ml*	P found, *μg/ml*	Error %	Ge taken, *μg/ml*	Ge found, *μg/ml*	Error %	As taken, *μg/ml*	As found, *μg/ml*	Error %
7·70	7·72	+0·3	18·1	18·3	+1·1	18·8	19·0	+1·1
12·90	12·80	−0·8	6·0	5·8	−3·1	18·8	18·8	0·0
12·90	13·00	+0·8	18·1	17·2	−4·9	6·3	6·2	−1·6
2·60	2·60	0·0	18·1	18·3	+1·1	31·2	30·7	−1·6
7·70	7·70	0·0	6·0	6·0	0·0	31·2	31·9	+2·2
2·60	2·55	−1·9	30·2	30·2	0·0	18·8	18·3	−2·7
7·70	7·70	0·0	30·2	29·9	−1·0	6·3	6·3	0·0
2·60	2·65	+1·9	42·3	42·1	−0·5	6·3	5·9	−6·3
18·10	17·90	−1·0	6·0	6·0	0·0	6·3	6·6	+4·8
2·60	2·55	−1·9	6·0	6·2	+3·3	43·6	44·2	+1·4

Take 10·0 ml of 0·2*M* molybdate, 10·0 ml of concentrated perchloric acid, 20·0 ml of acetone and the same-sized aliquot of sample as before in a 50-ml volumetric flask, dilute with water to the mark, and measure phosphorus + arsenic in a 1-mm cell at 345 nm after 5–15 min (Table XIII).

Determination of phosphorus, arsenic and germanium

The method is that just described for phosphorus, arsenic and silicon except that a waiting period of 2 hr is necessary before the second measurement (Table XIV).

Zusammenfassung—Mit hilfe von Änderungen in Säure- und Molybdänkonzentration, Meßwellenlänge, α- und β-Modifikationen und im Medium kann man P, As, Si und Ge spektrophotometrisch ohne Trennung als Heteropolymolybdate bestimmen. Schnell ausführbare Vorschriften für die Analyse von Gemischen dieser Elemente mit zwei oder drei Komponenten werden vorgeschlagen.

Résumé—En prenant avantage des variations possibles dans la concentration en acide et molybdène, la longueur d'onde de la mesure, les modifications α et β, et les milieux, on peut doser spectrophotométriquement P, As, Si et Ge sous forme d'hétéropolymolybdates sans séparation. On propose des techniques rapides pour l'analyse de mélanges à deux ou trois composants de ces éléments.

REFERENCES

1. O. G. Koch and G. A. Koch-Dedic, *Handbuch der Spurenanalyse*, Springer-Verlag, Berlin, 1964.
2. R. I. Alekseyev, *Zavodsk. Lab.*, 1945, **11**, 123.
3. N. A. Filippova and L. G. Kuznetsova, *ibid.*, 1950, **16**, 536.
4. J. Paul, *Anal. Chim. Acta*, 1966, **35**, 200.
5. *Idem*, *Mikrochim. Acta*, 1965, 830.
6. *Idem*, *ibid.*, 1965, 836.
7. A. Halász and E. Pungor, *Talanta*, 1971, **18**, 557.
8. *Idem*, *ibid.*, 1971, **18**, 569.
9. R. A. Chalmers and A. G. Sinclair, *Anal. Chim. Acta*, 1965, **33**, 384; 1966, **34**, 412.

Talanta, 1971, Vol. 18, pp. 587 to 601. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF NOBLE METALS BY NEUTRON-ACTIVATION ANALYSIS

R. GIJBELS
Institute of Nuclear Chemistry, State University of Ghent, Belgium

(*Received* 22 *June* 1970. *Accepted* 16 *September* 1970)

Summary—The scope and limitations of neutron-activation analysis in the field of the platinum metals are discussed. Special attention is given to interferences that occur in determination of noble metals in platinum metals and in natural samples. The problem of standards, carriers and chemical yield determination is emphasised. A recommendation is given of modern techniques for counting radionuclides formed by neutron activation of the platinum metals.

FOR SIMPLICITY, we will discuss separately the two cases of trace determination of noble metals in other noble metals and in an arbitrary matrix, because different nuclear problems and interferences may occur. The discussion will be limited to activation with thermal and epithermal neutrons, *i.e.*, *via* (n, γ) reactions. Special attention will be given to recommended radiation detectors.

Neutron cross-section data, half-lives and precise gamma-transition energies of analytically important radionuclides, produced by (n, γ) reactions on the noble metals, are shown in Table Ia; energy data for K X-rays are presented in Table Ib. Data are taken from Lederer *et al.*,[1] Holden and Walker,[2] Drake[3] and Adams and Dams.[4]

TRACE DETERMINATION OF NOBLE METALS IN OTHER NOBLE METALS

If noble metals are to be determined in other noble metals, techniques other than neutron activation, such as spectrophotometric methods, may be sensitive enough, since the impurity concentration will be rarely smaller than *ca.* 1 ppm, even for "spectrographically standardized" samples. In the case of specially purified samples, such as osmium distilled from sulphuric acid–hydrogen peroxide mixtures, neutron activation is superior, since it can deal with much smaller concentrations, provided that irradiation is performed at a sufficiently high neutron flux. Even if the radionuclide of interest must be separated from very large accompanying activities (from the matrix or other constituents), it is possible to obtain a radiochemically pure final fraction by a combination of chemical separations. These need not be quantitative, since carrier can be added and the chemical yield determined. The latter feature, which is also characteristic for isotope dilution–mass spectrometry, offers a larger choice of possible separation methods than classical analysis. It must be borne in mind, however, that nuclear interferences from the matrix can limit the sensitivity, *e.g.*, second-order interference, primary interference of the type (n, p) and (n, α), and others.

Second-order interference

Determination of iridium *via* the reaction ^{191}Ir(n, γ)^{192}Ir is very sensitive and amounts of 10^{-10} g are easily measured. When iridium is determined in osmium,

TABLE Ia.—RADIONUCLIDES PRODUCED BY IRRADIATION OF THE NOBLE METALS WITH THERMAL OR EPITHERMAL NEUTRONS

Radionuclide ($t_{1/2}$)[1]	Production	σ_{th},[2] *barns*	I[3] *barns**	Main gamma-transition energies, *keV* (relative intensity)[4]	Other energies,[4] *keV*
^{97}Ru(2·9 day)	^{96}Ru(n, γ)	0·21	5·51	215·8(100); 325·1(9)	569; Tc X-rays
^{103}Ru(39·6 day)	^{102}Ru(n, γ)	1·3	4·16	497·0(100); 610·2(8)	295; 558
^{105}Ru(4·44 hr)	^{104}Ru(n, γ)	0·5	4·6	130·0(100); 263·2(5); 317·1(10); 469·6(17); 676·0(10); 724·3(40) 876·0(3); 969·9(2)	150; 317; 326; 350; 394; 414; 575; 676; 908
^{104m}Rh(4·41 min)	^{103}Rh(n, γ)	11	1060 (m + g)	51·4(100); 77·6(5); 97·2(5); 555·8	768; 1239; others; Rh X-rays
^{104}Rh(43 sec)	^{103}Rh(n, γ)	137	—	555·8	Ru X-rays
^{105}Rh(35·9 hr)	^{104}Ru(n, γ, β^-)	0·5	4·6	306·2(27); 319·1(100)	280; 443
^{109m}Pd(4·7 min)	^{108}Pd(n, γ)	0·19	—	188·9	Pd X-rays
^{109}Pd(13·47 hr)	^{108}Pd(n, γ)	11	—	311·5(10); 88·0(100)	Ag X-rays
^{111m}Pd(5·5 hr)	^{110}Pd(n, γ)	0·02	—	172·1	Pd X-rays
^{111}Pd(22 min)	^{110}Pd(n, γ)	0·42	—	376·5(75); 580·0(100); 1388·1(60); 1458·9(60)	290; 509; 623; 836; 1120; others
^{108}Ag(2·42 min)	^{107}Ag(n, γ)	36·6	87·2	433·8(30); 632·9(100)	619; β^+; Pd X-rays
^{109m}Ag(40 sec)	^{108}Pd(n, γ, β^-)	11·19	—	88·0	Ag X-rays
^{110m}Ag(253 day)	^{109}Ag(n, γ)	4	47·5 (m)	657·8(100); 677·9(10); 706·4(20); 763·9(24); 818·0(8); 884·5(74); 937·2(33); 1384·0(22)	434; 447; 620; 687; 744; 1476; 1504; 1563
^{111}Ag(7·5 day)	^{110}Pd(n, γ, β^-)	0·42	—	245·4(10); 341·9(100)	97
^{185}Os(94 day)	^{184}Os(n, γ)	3000	1320	162·6(1); 645·8(100); 717·1(6); 874·8(9); 880·0(10)	126; 234; 592; Re X-rays
^{190m}Os(9·9 min)	^{189}Os(n, γ)	0·26 mb	—	186·7(80); 361·2(100); 616·4(100)	503; 510; Os X-rays
^{191}Os(15 day)	^{190}Os(n, γ)	13	28	129·4	Ir X-rays
^{193}Os(31 hr)	^{192}Os(n, γ)	2·0	5·4	139·0(80); 280·3(35); 321·5(80); 387·5(35); 460·4(100); 557·7(50)	107; 181; 219; 251; 289; 298; 362; 484; 533
^{192m}Ir(1·4 min)	^{191}Ir(n, γ)	520	3500	56·8	Ir *L* X-rays
^{192}Ir(74·2 day)	^{191}Ir(n, γ)	436	(m + g)	295·8(35); 308·4(35); 316·5(100); 467·9(65); 588·3(8); 604·2(15); 612·3(10)	206; 374; 416; 484; 785; 884; Os X-rays; Pt X-rays
^{194}Ir(17·4 hr)	^{193}Ir(n, γ)	110	1370	328·0(100); 644·6(28); 938·4(10); 293·6(20)	621; 1149; 1183; 1209; 1469; 1512; 1623
^{191}Pt(3·0 day)	^{190}Pt(n, γ)	90	—	172·4(25); 178·9(25); 219·4(4); 269·3(12); 350·7(60); 359·7(60); 409·1(50); 456·0(12); 539·0(100)	130; 190; 602; 624; Ir X-rays
^{195m}Pt(4·1 day)	^{194}Pt(n, γ)	0·09	—	99·0	130; Pt X-rays
^{197m}Pt(80 min)	^{196}Pt(n, γ)	0·05	—	346·3	Pt X-rays
^{197}Pt(18 hr)	^{196}Pt(n, γ)	0·9	—	77·7(100); 191·4(10)	269; Au X-rays
^{199}Pt(30 min)	^{198}Pt(n, γ)	4·0	—	185·9; 246·5; 316·9; 493·5; 542·8; 714·3	475; 791: 968; Au X-rays
^{198}Au(2·70 day)	^{197}Au(n, γ)	98·8	1558	411·8(100); 675·9(1)	1088
^{199}Au(3-15 day)	^{198}Pt(n, γ, β^-)	4.0	—	158·3(100); 208·2(25)	Hg X-rays

* Includes the $1/v$ contribution to the resonance integral; (m) refers to the resonance integral for an excited state, (m + g) to the sum of the integrals for the excited and ground states.

TABLE Ib.—*K* X-RAYS: APPROXIMATE ENERGIES AND RELATIVE INTENSITIES[1]

	K_{α_2}	K_{α_1}	K_{β_1}	K_{β_2}
Tc	18·25(50)	18·37(100)	20·6(24)	21·0(4·2)
Ru	19·15(50)	19·28(100)	21·7(24)	22·1(4·4)
Rh	20·07(50)	20·22(100)	22·7(25)	23·2(4·6)
Pd	21·02(50)	21·18(100)	23·8(25)	24·3(4·8)
Ag	21·99(51)	22·16(100)	24·9(25)	25·5(5)
Re	59·72(54)	61·14(100)	69·2(34)	71·2(8)
Os	61·49(54)	63·00(100)	71·3(34)	73·4(9)
Ir	63·29(54)	64·90(100)	73·5(34)	75·6(9)
Pt	65·12(55)	66·83(100)	75·7(34)	77·8(9)
Au	66·99(55)	68·81(100)	77·9(35)	80·1(9)
Hg	68·89(55)	70·82(100)	80·2(35)	82·5(10)

the sensitivity will be ultimately limited by the reaction ^{190}Os(n, γ)^{191}Os(β$^-$)^{191}Ir (n,γ)-^{192}Ir, which yields the same radionuclide. From Table II it appears that, for instance, an apparent iridium concentration of 215 ppb will be found after an irradiation time of 2·67 days at a thermal neutron flux of 5 × 10^{10} n.mm^{-2}.sec^{-1}, when ^{192}Ir is measured. Similar examples are summarized in Table II, taken from a compilation by Op de Beeck.[5] The general formulae used to calculate this interference can be found, for instance, in an article by Ricci and Dyer.[6]

TABLE II.—CALCULATED SECOND-ORDER INTERFERENCES[5]
(φ_{th} = 5 × 10^{10} n.mm^{-2}.sec^{-1}; φ_e = 5 × 10^{8} n.mm^{-2}.sec^{-1})

(1)	^{102}Ru(n, γ)^{103}Ru(β$^-$)^{103}Rh(n, γ)^{104m}Rh			(Rh in Ru)
	t_b = 0·110	1·76	28·13	225·1 min
	ppb = 0·3 × 10^{-8}	0·8 × 10^{-6}	0·4 × 10^{-3}	0·35 × 10^{-1}
(2)	^{102}Pd(n, γ)^{103}Pd(E.C.)Rh^{103}(n, γ)^{104m}Rh			(Rh in Pd)
	t_b = 0·110	1·76	28·13	225·1 min
	ppb = 0·8 × 10^{-9}	0·2 × 10^{-6}	0·1 × 10^{-3}	0·95 × 10^{-2}
(3)	^{108}Pd(n, γ)^{109}Pd(β$^-$)Ag^{109}(n, γ)^{110m}(Ag)			(Ag in Pd)
	t_b = 0·021	0·333	5·33	21·33 days
	ppb = 0·27	62	5982	30120
(4)	^{107}Ag(n, γ)^{108}Ag(β$^+$, E.C.)^{108}Pd(n, γ)^{109}Pd			(Pd in Ag)
	t_b = 0·338	5·40	86·47	345·8 hr
	ppb = 3·8	87	2133	10240
(5)	^{190}Os(n, γ)^{191}Os(β$^-$)^{191}Ir(n, γ)^{192}Ir			(Ir in Os)
	t_b = 0·021	0·167	2·67	10·67 days
	ppb = 0·013	0·86	215	3216
(6)	^{192}Os(n, γ)^{193}Os(β$^-$)^{193}Ir(n, γ)^{194}Ir			(Ir in Os)
	t_b = 0·475	7·59	60·77	243·0 hr
	ppb = 0·033	8·6	603	6879
(7)	^{191}Ir(n, γ)^{192}Ir(E.C.)^{192}Os(n, γ)^{193}Os			(Os in Ir)
	t_b = 0·801	12·81	102·5	410·0 hr
	ppb = 0·026	7·19	660	15650
(8)	^{193}Ir(n, γ)^{194}Ir(β$^-$)^{194}Pt(n, γ)^{195m}Pt			(Pt in Ir)
	t_b = 0·102	0·819	3·27	13·10 days
	ppb = 155	8820	10120	79420
(9)	^{190}Pt(n, γ)^{191}Pt(E.C.)^{191}Ir(n, γ)^{192}Ir			(Ir in Pt)
	t_b = 0·021	0·167	1·33	10·67 days
	ppb = 0·36 × 10^{-3}	0·023	1·40	58·67
(10)	^{196}Pt(n, γ)^{197}Pt(β$^-$)^{197}Au(n, γ)^{198}Au			(Au in Pt)
	t_b = 1·62	6·48	25·93	103·7 hr
	ppb = 0·135	2·095	30·17	345·4

t_b = irradiation time.

It can be shown that this interference increases proportionally with the neutron flux. It is also strongly dependent on irradiation time. Reactions 5 and 10 have been studied experimentally.[7,8] Neutron flux and irradiation time can be chosen in order to minimize the interference: when platinum is irradiated for 6·48 hr at 5×10^{10} $n.mm^{-2}.sec^{-1}$, the apparent gold content from the second-order reaction will be only 2·1 ppb (ppb = 1 in 10^9, or $10^{-7}\%$). If the sample contains 1 ppm of Au, the systematic error is thus quite small, but perhaps the analyst wishes to increase the precision and sensitivity of the gold analysis by increasing the integrated neutron flux by a factor of 10. If he chooses an irradiation position where the flux is 5×10^{11} $n.mm^{-2}.sec^{-1}$, the second-order interference will give an apparent gold content of 21 ppb for the same irradiation time: this is still quite low. But if the irradiation is carried out for 64·8 hr at a flux of 5×10^{10} $n.mm^{-2}.sec^{-1}$ [which gives the same sensitivity for the reaction $^{197}Au(n, \gamma)^{198}Au$], the second-order interference will be *ca.* 160 ppb. It is thus better to increase the nominal flux than the irradiation time.

Primary interference

If, as a result of radiative capture, a nuclide ^{M+1}Z is formed on neutron irradiation of a nuclide ^{M}Z, then this nuclide may also be produced by the following (n, p) and (n, α) reactions:

$$^{M+1}(Z+1)(n, p)^{M+1}Z$$

$$^{M+4}(Z+2)(n, \alpha)^{M+1}Z$$

Hence the presence of elements $(Z + 1)$ or $(Z + 2)$ *can* interfere with the determination of element Z.

The interference will obviously be more or less serious, depending on the relative concentrations of the target nuclides in the sample, on the ratio fast/thermal flux and on the ratio of the cross-sections involved. Fortunately, the cross-sections for (n, p) and (n, α) reactions are generally quite low compared to the (n, p) cross-sections, so that these reactions normally cause serious interference only in the presence of macroquantities of the interfering elements, *i.e.*, if the interfering element is the matrix, or if the element to be determined is present in extremely low concentration and the interfering element is a minor constituent. This interference will, of course, be less important or even negligible if the irradiation is carried out with a well thermalized neutron spectrum.

The importance of a primary interference can be estimated from the following equation, assuming equal weights:

$$\text{Interf.} = \frac{\theta' A'}{\theta A} \cdot \frac{\bar{\sigma}}{\sigma_{n,\gamma}} \cdot \frac{\bar{\varphi}_f}{\varphi_{th}}$$

where: θ = isotopic abundance of nuclide which gives the (n, γ) reaction product of interest;

A = atomic weight of the element to be determined;

θ' = isotopic abundance of nuclide which gives (n, p) or (n, α) reaction;

A' = atomic weight of interfering element;

$\sigma_{n,\gamma}$ = activation cross-section for (n, γ) reaction, including both thermal and resonance activation $\left[\text{reaction rate for (n, }\gamma\text{) reaction} = \varphi_{th}\sigma_{n,\gamma} = \varphi_{th}\left(\sigma_{th} + \frac{\varphi_f}{\varphi_{th}} I\right)\text{, where } I = \text{total resonance activation integral}\right]$;

$\bar{\sigma}$ = average cross-section for (n, p) or (n, α) reaction in an equivalent fission-neutron spectrum (flux $\bar{\varphi}_f$).

The possible cases in the field of the noble metals are presented in Table III, assuming a $\bar{\varphi}_f/\varphi_{th}$ ratio of 1/10. The most serious interference occurs for the determination of ruthenium in rhodium, 37 ppm apparent concentration in the assumed experimental conditions. This reaction has also been studied experimentally.[9] Primary interference is independent of the irradiation time. It will be minimized, however, in a well thermalized neutron spectrum, *i.e.*, at a low $\bar{\varphi}_f/\varphi_{th}$ ratio. An alternative is to use another nuclear reaction, *e.g.*, ^{96}Ru(n, γ)^{97}Ru instead of ^{102}Ru(n, γ)^{103}Ru, *i.e.*, to analyse by counting another radionuclide which is not subject to

TABLE III.—PRIMARY INTERFERENCE REACTIONS OF THE TYPE (n, p) AND (n, α)

	Activation reaction of interest; isotopic abundance and cross-section for thermal neutrons[1,2]	Interfering reaction; isotopic abundance and cross-section for fission neutrons[59]	Interference if $\bar{\varphi}_f/\varphi_{th}$ = 0·1, *ppm*	Element determined and matrix
(1)	^{102}Ru(n, γ)^{103}Ru 31·35%; 1·3 b	^{103}Rh(n, p)^{103}Ru 100%; 0·093 mb[9]	37	Ru in Rh
(2)	^{102}Ru(n, γ)^{103}Ru 31·35%; 1·3 b	^{106}Pd(n, α)^{103}Ru 27·3%; 2·7 μb	0·19	Ru in Pd
(3)	^{104}Ru(n, γ)^{105}Ru 18·6%; 0·5 b	^{108}Pd(n, α)^{105}Ru 26·75%; 0·9 μb	0·27	Ru in Pd
(4)	^{103}Rh(n, γ)$^{104(m)}$Rh 100%; 11(+137) b	^{104}Pd(n, p)$^{104(m)}$Rh 10·97%; 0·23 mb	0·017	Rh in Pd
(5)	^{108}Pd(n, γ)$^{109(m)}$Pd 26·75%; 0·19(+11) b	^{109}Ag(n, p)$^{109(m)}$Pd 48·65%; 0·2 mb	3·3	Pd in Ag
(6)	^{103}Rh(n, γ)$^{104(m)}$Rh 100%; 11(+137) b	^{107}Ag(n, α)^{104}(^{m})Rh 51·35%; 21 μb	0·008	Rh in Ag
(7)	^{190}Os(n, γ)$^{191(m)}$Os 26·4%; 10 + 3 b	^{191}Ir(n, p)$^{191(m)}$Os 38·5%; 0·02 mb	0·23	Os in Ir
(8)	^{192}Os(n, γ)^{193}Os 41·0%; 2·0 b	^{193}Ir(n, p)^{193}Os 61·5%; 5 μb	4×10^{-4}	Os in Ir
(9)	^{191}Ir(n, γ)$^{192(m)}$Ir 38·5%; 520 + 436 b	^{192}Pt(n, p)$^{192(m)}$Ir 0·78%; 0·02 mb	4×10^{-5}	Ir in Pt
(10)	^{193}Ir(n, γ)^{194}Ir 61·5%; 110 b	^{194}Pt(n, p)^{194}Ir 32·9%; 8 μb	4×10^{-3}	Ir in Pt
(11)	^{190}Os(n, γ)$^{191(m)}$Os 26·4%; 10 + 3 b	^{194}Pt(n, α)$^{191(m)}$Os 32·9%; <0·1 μb	$<10^{-3}$	Os in Pt
(12)	^{192}Os(n, γ)^{193}Os 41·0%; 2·0 b	^{196}Pt(n, α)^{193}Os 25·2%; <0·1 μb	$<3 \times 10^{-5}$	Os in Pt
(13)	^{196}Pt(n, γ)$^{197(m)}$Pt 25·2%; 0·05 + 0·9 b	^{197}Au(n, p)$^{197(m)}$Pt 100%; 7 μb	2·95	Pt in Au
(14)	^{193}Ir(n, γ)^{194}Ir 61·5%; 110 b	^{197}Au(n, α)^{194}Ir 100%; 0·1 μb	$1·5 \times 10^{-4}$	Ir in Au

this kind of error. It is, however, not easy to count ^{97}Ru in the presence of large ^{103}Ru activities, hence a thermalized neutron spectrum is recommended.

Other interferences

Other interferences must be considered, which cannot be eliminated by chemical separation. For example: in determination of gold in platinum, the gold fraction, in which ^{198}Au must be counted, will contain very high ^{199}Au activities, formed by the reaction ^{198}Pt(n, γ)^{199}Pt(β^-)^{199}Au. Integral gamma- or beta-counting is, of course, not allowed; discrimination is possible by the use of lead or aluminium absorbers, combined with gamma or beta spectrometry, since beta and gamma energies of ^{199}Au are lower than for ^{198}Au. A similar situation arises in determination of silver in palladium: the silver fraction, in which ^{110m}Ag must be measured, will also contain ^{111}Ag from the reaction ^{110}Pd(n, γ)^{111}Pd(β^-)^{111}Ag. Again, 57-min ^{103m}Rh will be present in neutron-irradiated ruthenium and palladium, from the decay of ^{103}Ru(β^-) and ^{103}Pd (E.C.) respectively, and can contribute to the $^{104(m)}$Rh activity from the rhodium impurity to be measured. Discrimination is, however, very easily achieved, owing to the very low-energy radiation from ^{103m}Rh (mostly Rh X-rays, *ca.* 20 keV).

Note that, so far, no impurities have been determined in iridium by using neutron activation analysis. This is due to the extreme activation of the matrix, which requires special shielding and care to avoid contamination, the more so as ^{192}Ir has a half-life of 74·2 days.

TRACE DETERMINATION OF PLATINUM METALS IN OTHER MATERIALS

In some materials, such as sulphide ores and meteorites, platinum metals may be present in the ppm range, hence several classical analytical techniques may be sensitive enough to deal with the direct analysis. In other samples, such as silicate rocks, pure metals, and organic material, most techniques are not sensitive enough. Even when spectrography, spectrophotometry, or atomic absorption are combined with the fire assay, Pt, Pd and Rh cannot always be detected in the resulting lead button or silver bead. Riley *et al.*[10,11] obtained sensitivities of 10 ppb Pt, 4 ppb Pd and 5 ppb Rh in silicate rocks by a combination of fire assay and spectrographic analysis of the dissolved gold bead. Fire assay is not safe for preconcentrating Os and Ru. Neutron-activation analysis is sensitive enough, so that preconcentration is, in principle, not required. Simon and Millard combined fire assay, neutron-activation of the lead button, addition of silver and cupellation after irradiation, followed by instrumental counting of ^{198}Au without further separations.[12] This technique was used not because neutron-activation analysis was not sensitive enough, but because the analysis became less time-consuming, and simpler for routine work (also the sample is more likely to be representative, 30 g instead of 0·1–1 g).

Nevertheless one must be aware of some limitations of neutron-activation analysis. Natural terrestrial samples, and others, frequently contain uranium concentrations well in excess of those of the noble metals, so that reactions such as ^{235}U(n, f)^{103}Ru and ^{235}U(n, f)^{109}Pd, having a high fission yield, can directly interfere with the determination of Ru and Pd *via* ^{103}Ru and ^{109}Pd. Other ruthenium and palladium radioisotopes are formed by fission of ^{235}U, namely 4·44-hr ^{105}Ru, 22-sec ^{107m}Pd, 22-min ^{111}Pd and 5·5-hr ^{111m}Pd. The degree of interference on the same reaction product,

TABLE IV.—INTERFERENCE FROM THE FISSION OF ^{235}U WITH THERMAL NEUTRONS

Activation reaction of interest; isotopic abundance and cross-section for thermal neutrons	$t_{1/2}$	Fission yield (total chain yield) %	Calculated interference from equal amount of natural U, %	Element determined
^{102}Ru(n, γ)^{103}Ru 31·35%; 1·3 b	39·6 day	2·9	13*	Ru
^{104}Ru(n, γ)^{105}Ru 18·6%; 0·5 b	4·44 hr	0·85	16	Ru
^{106}Pd(n, γ)^{107m}Pd 27·25%; 0·013 b	22 sec	0·18	95	Pd
^{108}Pd(n, γ)$^{109(m)}$Pd 26·75%; 0·19 + 11 b	13·47 hr	0·04	0·025	Pd
^{110}Pd(n, γ)$^{111(m)}$Pd 12%; 0·02 + 0·4 b	22 min 55 hr(m)	0·015	0·55	Pd

* This means that in a sample containing 1 ppm of U (natural), an apparent Ru content of 0·13 ppb will be found, if the analysis is based on ^{103}Ru.

formed by (n, γ) reaction, is indicated in Table IV, and is calculated from the formula

$$\frac{4\cdot18yA}{238\cdot0\,\theta\sigma_{n,\gamma}}\left(=0\cdot01756\,\frac{yA}{\theta\sigma_{n,\gamma}}\right)$$

where 238·0 = atomic weight of uranium

4·18 = cross-section for fission of ^{235}U in natural uranium [= $(\sigma_f)_{235}\theta_{235}$]

A = atomic weight of Ru, Pd, *etc*

θ = isotopic abundance of nuclide giving rise to the (n, γ) reaction product measured

$\sigma_{n,\gamma}$ = cross-section for (n, γ) reaction of interest

y = the yield.

Apart from direct nuclear interference by fission, yielding the same radionuclide as the (n, γ) reaction, other fission products may be present in the Pd or Ru fractions, namely 21-hr ^{112}Pd (y = 0·013%) and 1-yr ^{106}Ru (y = 0·38%). Owing to the long half-life of the latter radioisotope, its activity will be much smaller than that of ^{103}Ru and ^{105}Ru, shortly after irradiation.

Palladium is usually determined *via* 13·47-hr ^{109}Pd. Correction for fission-produced ^{109}Pd and ^{112}Pd is necessary in the case of beta-counting (G.M. tube) and is suggested to be 13% for counts taken 20 hr after a 16-hr irradiation in the case of U.S.G.S. standard rock G-1.[13,14] Although the ^{112}Pd beta-energy is relatively low (280 keV max) as compared to ^{109}Pd (1·03 MeV max, >99·9%), discrimination is not possible by simple beta-counting, since 21-hr ^{112}Pd decays to 3·2-hr ^{112}Ag, which is a high-energy beta-emitter (3·94 MeV max, 54%, and others). If ^{109}Pd can be counted selectively, *e.g.*, *via* the 88·0-keV photo peak, by using a 1 or 2 mm thick NaI(Tl) detector, or a Ge(Li) semiconductor detector, correction should only be required for fission-produced ^{109}Pd; the correction is then independent of irradiation and waiting times.

In the case of ruthenium, 2·9-day ^{97}Ru can be measured instead of ^{103}Ru; the former isotope is not produced by fission ("shielded nuclide"). Crocket *et al.*[14] observed, however, only radiation from ^{103}Ru and ^{105}Ru in the Ru-fraction of irradiated G-1 and W-1 standard rocks: no ^{97}Ru component could be identified from gamma-spectra or beta-decay curves. Owing to the high U/Ru ratio (10^3–10^5), fission-product Ru (mostly ^{103}Ru and ^{105}Ru, ^{106}Ru being practically negligible) constitutes most of the induced Ru activity. This factor, together with the relatively low production rate of ^{97}Ru, prevents the direct determination of Ru in G-1 and W-1, and in many other natural samples. It is perhaps possible to increase the specificity of the ^{97}Ru measurement by observing the Tc *K* X-rays from its E.C. decay (18·25; 18·37 keV) with a high resolution Ge(Li) or Si(Li) detector (FWHM $\leq$ 0·3 keV), which can resolve these X-rays from the Rh *K* X-rays (20·07; 20·22 keV) produced by decay of ^{103}Ru(^{103m}Rh) and ^{105}Ru(^{105m}Rh). The Tc *K* X-rays from the E.C. decay of ^{97}Ru could probably also be measured, with a low-energy photon spectrometer, in coincidence with the 215·8-keV gamma transition. The separation of ^{97}Ru from ^{103}Ru and ^{105}Ru by means of an isotope separator is another possible approach. No experimental results with such techniques have been described, however. In general, very few direct Ru analyses of terrestrial or moon samples are available. The situation is more favourable in the case of meteorites.[15]

For low U/Ru ratios, the Ru determination *via* ^{103}Ru poses no special problem: in the case of a U/Ru ratio of 1, the error made by simply measuring ^{103}Ru is *ca.* 12% (Table IV). It is thus necessary to know the U content; the latter may be obtained from isotope-dilution mass spectrometry or from the fission track technique,[16] for instance. Some results for samples with a low U/Ru ratio are shown below.

	Total apparent Ru, *ppb*	U, *ppb*	Apparent Ru from fission *ppb*	Ru nett, *ppb*
Peridotite standard rock (PCC-1)	11·8	4·8	0·6	11·2
Chromite (Bushveld, S. Africa)	534	3	0·3	534
Plagioclase (Bushveld, S. Africa)	36·3	29	3·1	33·2
Orthopyroxene (Bushveld, S. Africa)	7·9	34·6	3·6	4·3

In other cases, a preseparation before activation will be required. Since fire assay is not recommended in the case of ruthenium, distillation and co-precipitation procedures can probably be suggested.

A third element that is difficult to determine by neutron-activation analysis is rhodium, although its activation cross-section is very high. This is due to the short half-life of the (n, γ) activation products ^{104m}Rh and ^{104}Rh (4·41 min and 43 sec respectively). Schindewolf and Wahlgren[17] have described a fast radiochemical separation procedure that can be applied in the case of meteorites. No direct results have been obtained so far to the author's knowledge for samples containing Rh in the ppb range.

SIMULTANEOUS DETERMINATION OF SEVERAL NOBLE METALS

Crocket *et al.*[14] have described the simultaneous determination of Pd, Os, Ir, Pt and Au (+ Ru if the U-interference is not too prohibitive) in geological materials. Rh was not determined, because of its short half-life.

Such a simultaneous analysis may become difficult, particularly if a series of say 4 or more samples must be analysed: Os, Ru, Ir and Au pose no special problem in this respect, but Pt and Pd may, because of the relatively short half-life of the radionuclides of interest.

For practical reasons the isotopes might be dealt with in two groups: the "long-lived" (Os, Ru, Ir and Au) and the "short-lived" (Pt, Pd and Au). Rh must be considered as a special case, requiring work near to the reactor.

In the case of Rh, a preseparation may even become desirable, owing to the relatively short half-life of the product radionuclides. This can be done by a spontaneous deposition from dilute acid solution on copper powder, followed by irradiation of copper. Apart from the fact that copper becomes quite active, two major advantages of activation analysis can be lost by such a procedure, namely the risk of losing a part of the element to be determined (unless the yield of the preseparation is determined by adding a carrier-free radioisotope before the treatment) and the possibility of contamination from reagents, especially copper. Copper often contains gold in ppm concentration.

Spontaneous deposition on copper from dilute hydrochloric acid solution before activation is described by Park *et al.*[18] for the determination of Pt, Pd and Rh in industrial concentrates, such as lead foam and raw lead; concentrations down to 10 ppm of Pt, 25 ppm of Pd and 0·5 ppm of Rh were observed.

A combination of fire assay and irradiation of the lead button could perhaps also simplify the analysis, and make the sample size more representative. The short-lived ^{110}Ag ($t_{1/2}$ = 24 sec) and ^{108}Ag ($t_{1/2}$ = 2·41 min) produced from silver, will interfere with the instrumental determination of rhodium *via* ^{104}Rh ($t_{1/2}$ = 43 sec) or ^{104m}Rh ($t_{1/2}$ = 4·4 min); thus, if the latter element is to be determined, and if a preseparation is required, silver should be absent. Schnepfe and Grimaldi[19] proposed a procedure in which rhodium, along with palladium and platinum, is collected in a tellurium precipitate formed by the reduction of tellurite with tin(II) chloride, followed by atomic-absorption determination. Such a method could perhaps also be used for neutron-activation analysis of rhodium at the ppb level. Since sensitivity itself is not the problem, it is more correct to describe the process as preseparation rather than preconcentration.

It should be emphasized again that preseparation is not required in the case of Pd and Pt if the samples are processed within a few days after irradiation: it may, however, simplify the separations, and speed up the procedure.

STANDARDS

Neutron-activation analysis is usually performed by means of a relative method, *i.e.*, by the simultaneous irradiation of a standard of known concentration. Systematic errors are possible, if the neutron absorption is not the same in samples and standards. A comprehensive account of thermal and resonance neutron shielding in activation analysis is given by Høgdahl;[20] the theory was applied to the determination of gold in solid silver spheres. Self-shielding for the determination of iridium in rhodium powder is discussed by Gijbels and Hoste.[21] Because of the large absorption cross-section of rhodium, flux depressions of *ca.* 10% may occur in samples of only 10 mg. On the other hand, at least 2·5 g of osmium sponge may be irradiated before a reduction of 10% in specific activity induced by thermal neutrons is caused.

Self-shielding of thermal neutrons in solid samples (slabs, spheres, cylinders) can be computed with reasonable accuracy.[22] A powdered sample is treated in terms of an equivalent sphere:

$$f = 1 - \tfrac{3}{4} n \sigma r$$

where: f = "attenuation factor" = average flux within sample divided by flux if sample were absent;
n = atom density (atoms/mm^3), based on the apparent density of the powder;
σ = thermal absorption cross-section (mm^2);
r = radius of equivalent sphere (mm).

The best practical way to avoid such errors is the addition method of analysis. This approach has been systematically followed by Morris *et al.*[23–32] and by Gijbels and Hoste[21,34–37] for the determination of impurities in platinum, palladium, osmium, ruthenium and rhodium, where self-absorption in the matrix may occur. The standards were prepared by adding a known and sufficient amount of the element to be determined to the matrix and evaporating to dryness. It is even possible to dissolve the samples (with and without addition) in small sealed silica tubes and irradiate in solution: this ensures a homogeneous distribution of the added element. The addition method of analysis yields the best results if the amount added is at least equal to the amount present in the sample. The added amounts should not be too high, since this might give rise to activities which are too high to be counted without introducing counter dead-time problems (in the same geometry). Moreover, this increases the contamination risk.

In analysis of, for instance, a geological material, neutron shielding in the sample usually appears to be negligible. Self-absorption might, however, occur in the standards, if these were, for example, a weighed amount of metal (a few mg of Au, Ir or Rh). Here also, addition of a standard solution to the finely powdered sample is recommended. Some authors have used spectrographically standardized silica, alumina or magnesia, for "diluting" the standard solutions. It should be emphasized, however, that "very pure" samples are more likely to contain relatively high noble metal concentrations than simple natural materials, since they are often purified by methods using crucibles made of Pt-Ir alloys or the like. Hence the noble metal content of the materials should be determined (blank).

Special care is required when evaporating osmium standards in dilute acid solution. Losses are minimized (<1–2%) if the temperature is kept below 35° and if a large excess of Fe(II) is present. An interesting alternative is to make the solution alkaline, which results in the formation of iron hydroxide, and no loss of Os at all.[38]

Standard solutions are usually prepared from spectrographically standardized grade Au, Ag, Pd, Pt, $(NH_4)_2OsCl_6$, $(NH_4)_2IrCl_6$ and $(NH_4)_2[Ru(H_2O)Cl_5]$. The use of the latter three salts avoids the need to fuse Os, Ir and Ru with sodium peroxide before preparing the standard solution, and eliminates the introduction of impurities such as Na, Ni or Zr, although this poses no special problem if separations are carried out after the irradiation. If several metals are determined simultaneously, composite standards can be prepared.

CARRIERS AND CHEMICAL YIELD

The chemical yield of the separation of the activity of interest can be determined *via* classical techniques, such as spectrophotometry, atomic absorption or gravimetry, of which a sufficient choice is available. Weighing as the metal after reduction is the most popular way. Reactivation in the reactor is an interesting alternative if a large number of samples are analysed, but it requires many irradiation positions having the same neutron flux, such as the "lazy Susan" in a TRIGA reactor.

It is always very important to ensure isotopic exchange between the added carrier and the corresponding radionuclides. This is most easily obtained by a peroxide fusion, although the latter cannot be used for all applications. Ru, Pd, Ir, Pt and Au carriers are usually made up in $\sim 3M$ hydrochloric acid. Weights of 5–20 mg are usually transferred by pipette into zirconium crucibles and evaporated to dryness, preferably on a layer of sodium hydroxide, prior to the addition of the activated sample and sodium peroxide. Direct weighing of Os, Ru and Ir carriers (metals or salts) is perhaps even faster, and, in the special case of Os, avoids losses by volatilization.

Kimberlin *et al.*[39] have shown that complete exchange between Ir carrier and radioactivity can be obtained by prolonged heating (*ca.* 150 min) of acidic mixtures used to dissolve metallic samples.

When dealing with very low ^{103}Ru activities, special care must be taken in the selection of the carrier: many recent ruthenium samples are, indeed, contaminated with fission-product ^{106}Ru ($t_{1/2} = 1$ yr); the contamination may be as high as 1000 disintegrations/min/g of Ru, *i.e.*, 10 dpm per 10 mg of carrier. This activity will be negligible in bottles that have been stored for at least a few years.

Problems of isotopic exchange can be avoided, if only simple quantitative separation methods are used, such as distillation and liquid-liquid extraction (so that no chemical-yield determination is required), and if the activity of interest can be counted in solution. (No precipitate can, of course, be obtained without the addition of carrier, although co-precipitation is another possibility for separation, if it is quantitative.)

RECOMMENDED RADIATION DETECTORS FOR NEUTRON ACTIVATION ANALYSIS OF NOBLE METALS

Osmium

Osmium is usually determined *via* the reaction ^{190}Os(n, γ)^{191}Os (see Table 1). This radionuclide is easily counted with a normal NaI(Tl) scintillation detector, *e.g.*, 75 × 75 mm.[34,37,40,41] The use of a thin NaI(Tl) crystal or wafer, *e.g.*, 75 × 1 or 2 mm, results in a more favourable signal-to-background ratio, since a wafer is less sensitive to high-energy gamma rays from possible contaminants.[34] A thin window, *e.g.*, 0·25 mm beryllium, is recommended for minimum absorption of the low-energy radiation. The prominent peak in the ^{191}Os gamma-ray spectrum is the I.r. K_α X-ray (65 keV). This is thus the most sensitive peak. In order to minimize interference from the fluorescent lead K X-rays at 75 and 86 keV, the lead shield should be carefully lined with cadmium and copper, as described by Heath.[42] ^{191}Os can also be measured with a Ge(Li) detector.[43] Beta-counting is possible too, in the case of radiochemically pure osmium fractions.[14,24,43] The decay curve should reveal the presence of 15-day ^{191}Os and 31-hr ^{193}Os.

Additional information is obtained when counting ^{185}Os from the reaction ^{184}Os(n, γ) ($t_{1/2} = 94$ day, $E_\gamma = 645{\cdot}8$ keV + others, Re X-rays) by using an ordinary NaI(Tl) detector 75 × 75 mm,[40,44] or a Ge(Li) detector.[43] More specific measurement is possible by X-ray/γ-ray coincidence counting: the Re K_α X-ray (61 keV) from the electron capture decay is best measured with a NaI(Tl) wafer, in coincidence with a 75 × 75 mm NaI(Tl) detector, from which the complex 645-keV photo peak is selected.[43,44]

Ruthenium

Ruthenium is usually determined *via* the reaction ^{102}Ru(n, γ)^{103}Ru (see Table I) and counted with a 75 × 75 mm NaI(Tl) crystal.[14,35,37,40,41] The most intense photopeak at 497 keV cannot easily be distinguished from the 511-keV annihilation radiation of possible contaminants. It should also be noted that the ^{103}Ru gamma spectrum, as observed with a NaI(Tl) crystal, is quite similar to that of ^{106}Ru (fission product). Identification is easier with a Ge(Li) detector,[43] but the source must be sufficiently active because the detection efficiency of semiconductor detectors is much lower. No coincidence countings are possible since the ^{103m}Rh half-life is too long (57 min). For radiochemically pure sources, G.M. counting (preferably with a low background, 1·5–2 cpm) is feasible.[14,28,43]

Some remarks concerning the measurement of ^{97}Ru activity were made earlier in this paper.

Iridium

Iridium is generally determined *via* the reaction ^{191}Ir(n, γ)^{192}Ir; the latter radionuclide is counted with a solid (or well-type) NaI(Tl) scintillator.[14,24,25,35–39,43–51] Iridium is often separated from the irradiated sample by absorption on an anion-exchange resin from dilute hydrochloric acid medium. It may then be contaminated with gold (which can be eluted with thiourea, or allowed to decay) or with some chromium present as chromate; since ^{51}Cr emits gamma-rays of 320 keV, interference in the complex ^{192}Ir photo peak at $\sim$320 keV is possible. This can easily be checked by calculating the iridium content from the intensity of the 468-keV and the complex 610-keV photo peaks as well: the results must agree with that from the complex 317-keV peak. Additional control is obtained from beta counting (^{51}Cr decays by E.C.) and especially from Ge(Li) gamma-ray spectra which allow many photo peaks to be used for the analysis (see Table I).[43] Very specific γ-γ coincidence measurements are possible,[43,51,52] as appears from the decay scheme of ^{192}Ir.[1] This even allows instrumental determination of iridium in meteorites, by using NaI(Tl) detectors.[51,52]

Rhodium

Although rhodium can be determined with gamma-ray detectors,[18,53] the sensitivity can be considerably increased with beta-counting, *e.g.*, with a G.M. tube[54] or a plastic scintillator,[18] but at the cost of specificity. The largest activation cross-section is, indeed, for the production of 43-sec ^{104}Rh (137 barns), 98% of which beta-decays ($E_{\max} = 2{\cdot}22$ MeV) to stable ^{104}Pd (only 2% of the disintegrations give rise to a gamma transition, of energy 555·5 keV). The decay of 43-sec ^{104}Rh should then be followed by using a multiscaler, operated in steps of *ca.* 4 sec.[18]

Palladium

Palladium is usually determined *via* 13·47-hr ^{109}Pd, which beta-decays ($E_{\max} =$ 1·03 MeV; 99·97%) to 40-sec ^{109m}Ag. Radiochemically pure samples can be counted with a G.M. tube; the purity should be checked by following the decay.[13,14,27,33,43,55]

The internal transition energy of ^{109m}Ag is 87·7 keV, with an internal conversion coefficient of *ca.* 11, which means that the Ag X-radiation will dominate the gamma-spectrum ($\sim$22 keV). For such low energy photons, a NaI(Tl) wafer with a thin Be window is recommended. Great care must be taken to ensure the same source thickness for samples and standards in order to avoid differences in absorption. If the 87·7-keV photo peak is counted, the lead shield must be carefully lined with cadmium and copper, to minimize interference from the fluorescent Pb *K* X-rays (75 and 86 keV).

Platinum

Platinum is generally determined *via* 18-hr ^{197}Pt; the maximum beta-energy is 0·670 MeV, so a G.M. tube can easily be used.[33] The gamma-ray spectrum is dominated by low energy radiation namely 77·7 and 191·4 keV, and especially Au X-rays (*ca.* 68 keV): these can be measured with a normal or thin NaI(Tl) detector,[18] or a Ge(Li) detector.[18]

Platinum can also be determined *via* the reaction $^{198}Pt(n, \gamma)^{199}Pt(\beta^-)^{199}Au(\gamma$: 158·4 and 208·2 keV + Hg X-rays).[47] If gold is present in the sample, ^{198}Au will also be present in the gold fraction, plus ^{199}Au from the reaction $^{197}Au(n, \gamma)^{198}Au(n, \gamma)^{199}Au$, especially after long irradiations in a high neutron flux.

TRACER STUDIES

Other nuclear techniques, especially radioactive tracer studies, may be very helpful in the field of the noble metals, since it is then so much easier to investigate their behaviour during chemical separations such as distillation, ion-exchange and liquid-liquid extraction. Most of these tracers are commercially available, or may be prepared as follows: 39·6-day ^{103}Ru, 17-day ^{103}Pd, 254-day ^{110m}Ag, 15-day ^{191}Os, 74·2-day ^{192}Ir, 4-day ^{195m}Pt (+ ^{193m}Pt) and 2·70-day ^{198}Au: by reactor neutron irradiation of ruthenium, palladium, silver, osmium, iridium, platinum and gold.

Chemical purification of irradiated platinum from ^{199}Au (by extraction into ethyl acetate) and of irradiated palladium from ^{111}Ag (by precipitation as chloride) is required. ^{199}Au can be used as carrier-free tracer, if extracted with ethyl acetate. A procedure for the chelating ion-exchange separation of carrier-free ^{111}Ag from neutron irradiated palladium is described by Lyle and Maghzian.[56]

Tracer studies are best carried out with a gamma-ray spectrometer, in order to avoid misinterpretations which can arise from the presence of small ^{192}Ir impurities in all the above tracers.

Carrier-free rhodium tracer can be prepared from reactor irradiated ruthenium, *via* the reaction $^{104}Ru(n, \gamma)^{105}Ru(\beta^-)^{105}Rh$ (Table I).[57]

Since the latter isotope has a half-life of only 35·9 hr, it is more convenient to prepare carrier-free $^{102,102m}Rh$ (^{102}Rh: $t_{1/2} = 206$ days; ^{102m}Rh: $t_{1/2} = 2{\cdot}9$ yr) by proton or deuteron bombardment of ruthenium foil in a cyclotron. A procedure is described by François *et al.*[58] with a detailed description of the gamma-ray spectrum.

CONCLUSIONS

Although some limitations of neutron-activation analysis must be borne in mind when determining noble metals in other noble metals (some nuclear interferences), or in an arbitrary matrix (interference from uranium fission products in the determination of Pd and Ru) it is certainly a powerful analytical tool, particularly because of its high sensitivity, allowing analyses at the sub-ppb level. A peculiarity of the technique arises from the relatively short half-life of the analytically most interesting radionuclides produced from Pd and Pt, *viz.*, the need to process the irradiated samples within a day after the irradiation. Rhodium is a special case, since it produces only very short-lived radionuclides ($t_{1/2} = 4{\cdot}41$ min max.) on neutron activation, hence instrumental analysis, fast radiochemical separations, or separations prior to irradiation are required; the analysis must always be done in the reactor building itself.

Zusammenfassung—Anwendungsbereich und Grenzen der Neutronenaktivierungsanalyse auf dem Gebiet der Platinmetalle werden diskutiert. Besonderes Augenmerk wird auf Störungen gerichtet, die bei der Bestimmung von Edelmetallen in Platinmetallen und in natürlichen Proben workommen. Nachdruck wird auf die Behandlung von Standards, Trägern und Bestimmung der chemischen Ausbeute gelegt. Moderne Arbeitsweisen bei der Zählung von durch Neutronenaktivierung der Platinmetalle gebildeten Radionuklide werden empfohlen.

Résumé—On discute du cadre et des limitations de l'analyse par activation de neutrons dans le domaine de métaux du platine. On porte une attention particulière aux interférences qui se manifestent dans la détermination de métaux nobles dans les métaux du platine et dans des échantillons naturels. On souligne le problème des étalons, des porteurs et de la détermination du rendement chimique. On donne une recommandation de techniques modernes pour le comptage de radionucléides formés par activation de neutrons des métaux du platine.

REFERENCES

1. C. M. Lederer, J. M. Hollander and I. Perlman, *Table of Isotopes*, 6th Ed., Wiley, New York, 1968.
2. N. E. Holden and F. M. Walker, *Chart of the Nuclides*, 10th Ed., General Electric Co., Schenectady, N.Y. 12305, U.S.A., Dec. 1968.
3. M. K. Drake, *Nucleonics*, 1966, **24**, (8) 108.
4. F. Adams and R. Dams, *J. Radioanal. Chem.*, 1969, **3**, 99.
5. J. P. Op de Beeck, *ibid.*, 1969, **3**, 431; 1970, **4**, 137.
6. E. Ricci and F. F. Dyer, *Nucleonics*, 1964, **22**, (6) 45.
7. R. Gijbels and J. Hoste, *Proc. 2nd Intern. Conf. Modern Trends in Act. Anal.*, College Station, Texas, 1965, p. 129.
8. R. Gijbels, M. De Vos, R. De Neve and J. Hoste, *Radiochem. Radioanalyt. Letters*, **5**, 145.
9. J. P. François, D. De Soete and J. Hoste, *Radiochim. Acta*, 1967, **8**, 192.
10. J. Haffty and L. B. Riley, *Talanta*, 1968, **15**, 111.
11. N. J. Page, L. B. Riley and J. Haffty, *U.S. Geol. Surv. Circ.* 624, 1969.
12. F. O. Simon and H. T. Millard, Jr., *Anal. Chem.*, 1968, **40**, 1150.
13. J. H. Crocket and G. B. Skippen, *Geochim. Cosmochim. Acta*, 1966, **30**, 129.
14. J. H. Crocket, R. R. Keays and S. Hsieh, *J. Radioanal. Chem.*, 1968, **1**, 487.
15. J. H. Crocket, *Platinum Metals*, in *Handbook of Geochemistry*, ed. K. H. Wedepohl, Springer-Verlag, Berlin, 1969.
16. D. E. Fischer, *Anal. Chem.*, 1970, **42**, 414.
17. U. Schindewolf and M. Wahlgren, *Geochim. Cosmochim. Acta*, 1960, **18**, 36.
18. K. S. Park, R. Gijbels and J. Hoste, *J. Radioanal. Chem.*, 1970, **5**, 31.
19. M. M. Schnepfe and F. S. Grimaldi, *Talanta*, 1969, **16**, 1461.
20. O. T. Høgdahl, *Proc. Symp. Radiochemical Methods of Analysis* (Salzburg, 19–23 Oct. 1964), Vol. I, p. 23, I.A.E.A., Vienna, 1965
21. R. Gijbels and J. Hoste, *Anal. Chim. Acta*, 1967, **39**, 89.
22. P. F. Zweifel, *Nucleonics*, 1960, **18**, (11), 174.
23. D. F. C. Morris and R A. Killick, *Talanta*, 1959, **3**, 34.

24. *Idem, ibid.*, 1961, **8,** 129.
25. *Idem, ibid.*, 1961, **8,** 373.
26. *Idem, ibid.*, 1961, **8,** 793.
27. R. A. Killick and D. F. C. Morris, *Talanta*, 1961, **8,** 601.
28. *Idem, ibid.*, 1962, **9,** 349.
29. *Idem, ibid.*, 1962, **9,** 879.
30. *Idem, ibid.*, 1963, **10,** 279.
31. *Idem, ibid.*, 1963, **10,** 987.
32. *Idem, ibid.*, 1963, **10,** 1153.
33. D. F. C. Morris, *Mikrochim. Acta*, 1963, 962.
34. R. Gijbels and J. Hoste, *Anal. Chim. Acta*, 1963, **29,** 289.
35. *Idem, ibid.*, 1965, **32,** 17.
36. *Idem, ibid.*, 1967, **39,** 132.
37. *Idem, ibid.*, 1968, **41,** 419.
38. K. S. Chung and F. E. Beamish, *ibid.*, 1968, **43,** 357.
39. J. Kimberlin, C. Charoonratana and J. T. Wasson, *Radiochim. Acta*, 1968, **10,** 69.
40. G. L. Bate and G. Huizenga, *Geochim. Cosmochim. Acta*, 1963, **27,** 345.
41. K. S. Chung and F. E. Beamish, *Anal. Chim. Acta*, 1968, **43,** 357.
42. R. L. Heath, *U.S. At. Energy Comm. Rept.*, IDO-16408 (July **1**, 1957).
43. R. Gijbels, H. T. Millard, Jr., G. A. Desborough and A. Bartel, *American Geophysical Union, Annual Meeting*, April 1970, Washington D.C., Paper V 87.
44. J. L. Barker and E. Anders, *Geochim. Cosmochim. Acta*, 1968, **32,** 627.
45. L. S. Jowanowitz, F. B. McNatt, R. E. McCarley and D. S. Martin, Jr., *Anal. Chem.*, 1960, **32,** 1271.
46. P. R. Rushbrook and W. D. Ehmann, *Geochim. Cosmochim. Acta*, 1962, **26,** 649.
47. P. A. Baedecker and W. D. Ehmann, *ibid.*, 1965, **29,** 329.
48. R. Gijbels and J. Hoste, *Anal. Chim. Acta*, 1967, **39,** 132.
49. R. C. Harris, J. H. Crocket and M. Stainton, *Geochim. Cosmochim. Acta*, 1968, **32,** 1049.
50. L. G. Cilindro and D. S. Martin, Jr., *J. Radioanal. Chem.*, 1969, **3,** 195.
51. W. D. Ehman, P. A. Baedecker and D. M. McKown, *Geochim. Cosmochim. Acta*, 1970, **34,** 493.
52. W. D. Ehmann and D. M. McKown, *Modern Trends in Activation Aanalysis*, *Natl. Bur. Std. U.S. Spec. Publ.* 312, Vol. I, p. 308 (Wash. D.C., 1969).
53. M. Wahlgren, *Univ. Michigan, Dept. of Chem., Prog. Rept.*, 1958, **7,** 59.
54. U. Schindewolf and M. Wahlgren, *Geochim. Cosmochim. Acta*, 1960, **18,** 36.
55. E. A. Vincent and A. A. Smales, *ibid.*, 1956, **9,** 154.
56. S. J. Lyle and R. Maghzian, *Talanta*, 1968, **15,** 712.
57. D. F. C. Morris and M. A. Khan, *Radiochim. Acta*, 1966, **6,** 110.
58. J. P. François, R. Gijbels and J. Hoste, *J. Radioanal. Chem.*, 1970, **5,** 251.
59. J. C. Roy and J. J. Hawton, *At. Energy Can. Ltd.*, AECL-1181, 1960.

Talanta, 1971, Vol. 18, pp. 603 to 613. Pergamon Press. Printed in Northern Ireland

A CONTRIBUTION TO THE USE OF CHELATING AGENTS IN ANODIC STRIPPING VOLTAMMETRY

LUDMILA ZIEGLEROVÁ, KAREL ŠTULÍK and JAN DOLEŽAL
Department of Analytical Chemistry, Charles University,
Prague, Czechoslovakia

(*Received* 16 *June* 1970. *Accepted* 30 *September* 1970)

Summary—The $E_{p/2}$ values of the ions Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, Tl^{+} were determined by means of cyclic voltammetry in solutions of acetate and Britton–Robinson buffers and in solutions containing EDTA and DCTA. DCTA was then utilized in the determination of small amounts of bismuth, down to $10^{-7}M$, in the presence of 10^{4} times as much lead, and of traces of thallium down to $5 \times 10^{-9}M$ in the presence of 2×10^{5} times as much cadmium by anodic stripping voltammetry. The precision was good. Further, the trace copper concentration in analytical grade DCTA was determined. A new flow-through vessel for stripping analysis with solution exchange is also described and the reproducibility of results without solution exchange, with manual solution exchange, and with the flow-through vessel is evaluated for a model determination of thallium in a DCTA solution.

BECAUSE of its high sensitivity and simplicity, anodic stripping voltammetry is a very suitable method for the determination of traces of metals. The greatest disadvantage in many determinations is the relatively low selectivity of the method (insufficient peak separation). This disadvantage is a serious one, because in most determinations large excesses of interfering elements are present. The problem of determining trace metal concentrations in the presence of an extremely large amount of interfering elements has been tackled in several different ways.

1. By preliminary separation of interfering elements. Such an operation is frequently very tedious and often introduces considerable errors.
2. By use of thin-layer electrodes with which narrower peaks are obtained owing to faster metal diffusion from mercury.[1] Sufficient separation of the peaks often cannot be achieved by this means alone.
3. If an interfering element is dissolved from its amalgam at a more negative potential than is required for the metal to be determined, it is possible to stop the potential scan at the maximum of the more negative peak, wait until the interfering element is oxidized, and then record the more positive peak.[2–4] This operation makes the determination longer and can fail at very high interfering element concentrations, owing to formation of too concentrated an amalgam.
4. The selective inhibition of the electrode reaction of an interfering element by surface active substances can also be used for increasing the selectivity.[5] This approach can sometimes be successful, especially if combined with masking of interfering elements.
5. The most frequently used method, which involves masking of interfering elements by complexing or chelating agents, has relatively the broadest range of application. The disadvantage of this process is often the insufficient purity of

masking agents, which themselves therefore introduce various metal ions into the solution.

Chelating agents can be used to shift the dissolution potentials of elements during the stripping process or to separate more widely the reduction potentials of the substances during the preliminary electrolysis. EDTA and related compounds are particularly suitable. Neeb used tartaric acid and EDTA in the determination of bismuth, lead, thallium and cadmium with a mercury-coated platinum electrode,[6] and EDTA in the determination of thallium with a mercury drop or a mercury-coated platinum electrode.[7] EDTA was used in the determination of copper in sea-water by Ariel, Eisner and Gottesfeld.[8] These authors replaced the base electrolyte after the preliminary electrolysis by one containing EDTA. Sinyakova and co-workers used EDTA for separating a lead peak from the peaks of cadmium and indium in the determination of impurities in indium metal and its salts.[4] Zaichko and Zakharov used NTA (nitrilotriacetic acid), EDTA, and DCTA (diaminocyclohexane-*N*,*N*,*N*′,-*N*′-tetra-acetic acid) for masking copper, tin, and lead in the determination of antimony in tin.[9] Zakharov *et al.* obtained well developed peaks of germanium in a solution of $0{\cdot}2M$ sodium carbonate and $0{\cdot}025M$ EDTA.[10] In the determination of thallium in pure indium, Mesiac and co-workers also used EDTA for masking indium, the main portion of which was separated beforehand by extraction with diethyl ether.[11] Neeb and Kiehnast listed some $E_{p/2}$ values of metals in an EDTA solution, for the mercury drop electrode.[12]

In the present paper, values of $E_{p/2}$ for Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+} and Tl^{+}, determined by cyclic voltammetry in solutions of EDTA and DCTA and at a pH of 4·6 and 9·5, are reported. On the basis of these values small amounts of bismuth were determined in the presence of large amounts of lead, and traces of thallium in cadmium were also determined. Because the DCTA used contained traces of copper, the method was also used for the determination of this metal in DCTA.

Because the purity of masking agents is very frequently insufficient for anodic stripping voltammetry, it is sometimes desirable to avoid preliminary electrolysis in the masking agent solution. This has been done by replacing the solution in which pre-electrolysis takes place, by the solution containing masking agent, in which the dissolution takes place.[8,13,14] In this paper a flow-through cell is described for such an exchange of solutions, and the reproducibility of results without solution exchange, with a manual solution exchange, and with the flow-through cell is determined for a model determination of Tl^{+} in a DCTA solution.

EXPERIMENTAL

Apparatus

The voltammetric and anodic stripping measurements were carried out with the LP-60 polorograph (Laboratorní přístroje, Czechoslovakia). The stationary mercury-drop electrode according to Kemula (Kemula Equipment E 69, Radiometer, Copenhagen) was used. In order to prevent solution penetration into the capillary of the electrode, the orifice and inner surface of the capillary were coated with a silicone layer: the capillary was washed through successively with 2% hydrofluoric acid, $6M$ hydrochloric acid and distilled water and dried by passing air through it; then a 6% solution of dimethyldichlorosilane (silicone oil OE 4018) in benzene was passed through, the capillary was dried for 1 hr in air and then heated in an oven to 240–260° for 4 hr. to prevent solution penetration into the capillary and to increase the drop stability in alkaline solutions, a stationary mercury-drop electrode with "sitting" drop (Mercury Drop Electrode Assembly 39016, Beckman Instruments) was used for cyclic voltammetry in alkaline media. A saturated calomel etectrode was used as reference in all measurements.

Depolarizer solutions were measured with a 0·5 ml micrometer syringe burette readable to 0·2 μl. Dissolved oxygen was removed from the solutions to be analysed, by passage of nitrogen purified by passing through a column containing a 0·2% w/v solution of sodium anthraquinone-2-sulphonate in 1*M* sodium hydroxide, and zinc amalgam.

All measurements, if not stated otherwise, were carried out at 22 ± 0·5°.

Reagents

The mercury used was of analytical-grade purity, further purified by distillation. Water was purified by re-distillation in a quartz apparatus.

Stock solutions ($10^{-2}M$) of depolarizers were prepared either by dissolving appropriate amounts of salts of analytical-grade purity in water [$Cd(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$, $TlNO_3$] or by dissolving metals (Cu, Bi), in dilute nitric acid, evaporating to dryness and dissolving the residue in water. From these stock solutions freshly diluted solutions were prepared daily.

Buffered solutions ($10^{-2}M$) of the disodium salt of ethylenediaminetetra-acetic acid (EDTA) and of 1,2-diaminecyclohexanetetra-acetic acid (DCTA) were prepared by dissolving appropriate amounts of analytical-grade purity preparations in acetate buffers of pH 4·6 and Britton-Robinson buffers of pH 9·5, both buffers[15] having ionic strength 0·1.

Acetic, boric and phosphoric acids, sodium hydroxide and potassium chloride solutions were prepared from analytical-grade chemicals. The sodium acetate solution was prepared from analytical-grade material which had been purified by repeated recrystallization.

Procedure

If not stated otherwise, the anodic stripping measurements were carried out in the following way: nitrogen was passed for 5–10 min through 15 ml of the solution to be studied. Then a mercury drop was formed at the capillary tip, stirring with a glass stirrer at 1140 rpm was begun, nitrogen was passed above the solution, and the solution was electrolysed for a predetermined time at a preset potential. After this time, the stirring and passage of nitrogen were discontinued and the electrolysis was continued for 1 min in the quiet solution. Then the potential was scanned from negative to positive potentials at a rate of 400 mV/min and dissolution peaks were recorded.

RESULTS

Determination of the $E_{p/2}$ *values by cyclic voltammetry*

The measurements on $10^{-4}M$ solutions of depolarizers were carried out at a scan rate of 400 mV/min in base electrolytes which were deaerated by passing nitrogen through them. Base electrolytes: acetate buffer, $\mu = 0{\cdot}1$, pH = 4·6; $10^{-2}M$ EDTA in acetate buffer of pH 4·6; $10^{-2}M$ DCTA in acetate buffer of pH 4·6; Kemula electrode: Britton-Robinson buffer, $\mu = 0{\cdot}1$, pH = 9·5; $10^{-2}M$ EDTA in Britton-Robinson buffer of pH 9·5; $10^{-2}M$ DCTA in Britton-Robinson buffer of pH 9·5; Beckman electrode.

The $E_{p/2}$ values are given in Table I. From them it is obvious that the alkaline media are less suitable for determinations than the acidic ones. In acidic media it would seem possible to determine bismuth and copper in lead, thallium or cadmium and lead or thallium in cadmium. A poorer separation would be achieved if bismuth and copper were both present in a solution.

Determination of small amounts of bismuth in the presence of large amounts of lead

On the basis of the results from the cyclic voltammetry (Table I) the determination of bismuth in the presence of lead in solutions of acetate buffer and DCTA was attempted. DCTA has already been used for masking in the polarographic determination of bismuth and copper in lead.[16] When tartrate was used to mask lead, the error in the bismuth determination was 15% with only a fivefold amount of lead.[6] NTA[17] and alkaline ethylenediamine[3,18] have also been used for masking lead in the determination of bismuth.

As follows from the $E_{p/2}$ values, the peaks of bismuth and lead are separated by

TABLE I.—THE VALUES OF $E_{p/2}$, V VS. SCE

pH 4·6

Ion	acetate buffer		EDTA		DCTA	
	cath.	an.	cath.	an.	cath.	an.
Pb^{2+}	−0·41	−0·41	—	−0·49	—	−0·50
Bi^{3+}	−0·11	−0·10	−0·55	−0·14	−0·71	−0·12
Cu^{2+}	+0·01	0·00	−0·27	−0·26	−0·37	−0·15
Cd^{2+}	−0·57	−0·58	—	−0·68	—	—
Tl^{+}	−0·46	−0·46	−0·46	−0·46	−0·46	−0·46

pH 9·5

Ion	Britton-Robinson buffer		EDTA		DCTA	
	cath.	an.	cath.	an.	cath.	an.
Pb^{2+}[a]	−0·63	−0·55	—	−0·58	—	−0·58
Bi^{3+}[a]	−0·45	−0·17	−0·74	−0·24	−0·73	−0·24
Cu^{2+}[a]	−0·13	−0·13	−0·48	−0·44	−0·55	−0·37
Cd^{2+}[a]	−0·67	−0·67	—	−0·72	—	−0·72
Tl^{+}	−0·47	−0·47	−0·63	−0·64	−0·53	−0·53

[a] hydrolysis occurs.

0·31 V in acetate medium at pH 4·6 and by 0·38 V in the presence of DCTA. These values are not sufficient for peak separation in the presence of large amounts of lead; there is, however, the possibility of using the fact that, in the DCTA medium, the $E_{p/2cath}$ of bismuth is −0·71 V and a cathodic lead peak does not appear at all. If a suitable pre-electrolysis potential were chosen, a much better separation factor could then be achieved. This was verified by determining the dependence of peak currents of bismuth and lead on the pre-electrolysis potential Fig. 1. It can be seen that the highest sensitivity for bismuth is obtained at pre-electrolysis potentials more negative than −1·6 V in both media 2 min pre-electrolysis. The current increases at these potentials owing to the stirring of the solution by evolving hydrogen. Bismuth concentrations as low as $10^{-7}M$ can be determined, and the calibration curves are linear up to $5 \times 10^{-6}M$. Unfortunately, the lead peak also has its maximum value at these potentials (see Fig. 1). Even a tenfold amount of lead causes a considerable error in the bismuth determination (see Table II,*a*,*b*). Moreover, the mercury drop is less stable at more negative potentials because of the low surface tension of mercury. If the pre-electrolysis potential in $10^{-2}M$ DCTA is decreased to −1·0 V, however, the sensitivity for bismuth decreases somewhat, but the lead peak does not appear at lead concentrations lower than $10^{-3}M$ (Fig. 1). Bismuth can then be determined down to $10^{-7}M$ even in the presence of 10^4 times the amount of lead with very good precision (see Table II*c*). Typical experimental curves are given in Fig. 2. The determination will be affected by higher concentrations of copper(II) ions because both the cathodic and anodic peaks of copper and bismuth are poorly separated in the media studied (for the dependence of the copper peak current on the pre-electrolysis potential in the DCTA solution, see Fig. 1).

Determination of traces of thallium in cadmium

A stripping voltammetric determination of thallium and cadmium has already been described by Nikelly and Cooke[19] who found that mixed peaks are obtained in

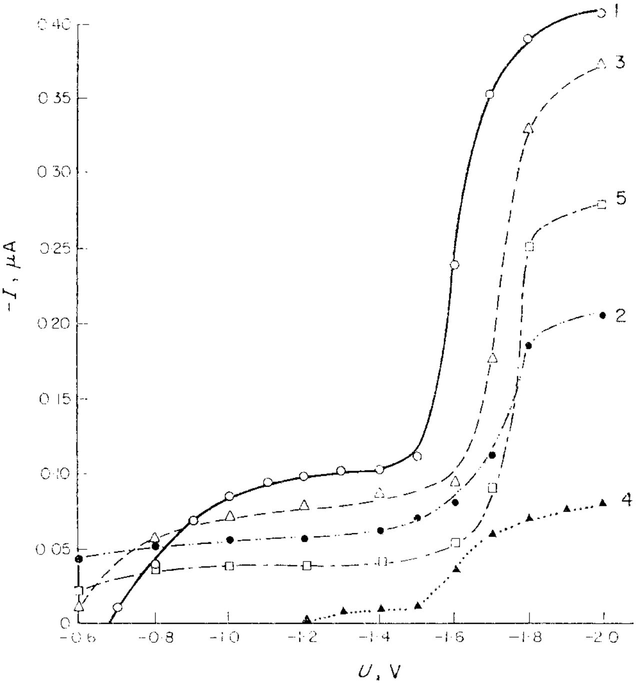


FIG. 1.—The dependence of the peak current on the pre-electrolysis potential (2 min pre-electrolysis)

1—$10^{-6}M$ Bi^{3+}, acetate buffer; *2*—$10^{-6}M$ Pb^{2+}, acetate buffer; *3*—$10^{-6}M$ Bi^{3+}, $10^{-2}M$ DCTA; *4*—$10^{-6}M$ Pb^{2+}, $10^{-2}M$ DCTA; 5—$10^{-6}M$ Cu^{2+}, $10^{-2}M$ DCTA.

0·1*M* potassium nitrate and the separation factor is increased if 0·05*M* ammonia + 0·05*M* ammonium chloride solution is used as a base electrolyte ($\Delta E_{p/2} = 0{\cdot}26$ V). Neeb[6] reported a good separation factor for EDTA solution. A number of polarographic determinations of thallium in cadmium have been described.[20]

From the values of $E_{p/2}$ in Table I it follows that the determination of thallium in the presence of cadmium in a DCTA solution should be accompanied by a high separation factor. This was also verified experimentally. In Fig. 3 is shown the dependence of the peak current of thallium on the pre-electrolysis potential in $10^{-2}M$ DCTA (2 min pre-electrolysis, pH 4·6). From Fig. 3 it follows that —0·9 V is a convenient value for the pre-electrolysis potential (the same consideration for potentials more negative than —1·6 V applies here as in the previous section). No cadmium peak appears in this potential range. A linear peak current dependence on the thallium concentration was found within the $1 \times 10^{-7}M$–$5 \times 10^{-6}M$ range. The results of the determination of thallium in the presence of various concentrations of cadmium are given in Table III*a*. Even a 10^4-fold amount of cadmium does not interfere. Concentrations of cadmium higher than $10^{-3}M$ interfere because the concentration of DCTA in the solution is limited by its solubility to $2 \times 10^{-2}M$. An increase in the DCTA concentration by converting the acid into the more soluble disodium salt by neutralization with sodium hydroxide[16] is not convenient because too many impurities are introduced into the solution. The separation factor is thus limited by the cadmium concentration and can be increased by lowering the concentration of thallium and using a longer pre-electrolysis time. If the pre-electrolysis

TABLE II.—THE DETERMINATION OF BISMUTH IN THE PRESENCE OF LEAD

$[Bi^{3+}]:[Pb^{2+}]$, M	$\bar{h}_{Bi}$, *mm*	Mean absolute error, *mm*	Mean relative error, %
(*a*) Acetate buffer, pH 4·6; pre-electrolysis potential −1·2 V			
$10^{-6}:0$	31·5	1·5	4·5
$10^{-6}:10^{-6}$	26·5	6·5	20
$10^{-6}:10^{-5}$	21·8	11·2	34
$10^{-6}:10^{-4}$	8·0	25·0	76
$10^{-6}:10^{-3}$	mixed peak Bi + Pb		
(*b*) $10^{-2}M$ DCTA, pH 4·6; pre-electrolysis potential −1·8 V			
$10^{-6}:0$	129·3	10·7	8
$10^{-6}:10^{-6}$	130·0	10·0	7
$10^{-6}:10^{-5}$	117·3	22·7	16
$10^{-6}:10^{-4}$	69·7	70·3	50
$10^{-6}:10^{-3}$	mixed peak Bi + Pb		
(*c*) $10^{-2}M$ DCTA, pH 4·6; pre-electrolysis potential −1·0 V			
$10^{-6}:0$	28·7	0·7	2·5
$10^{-6}:10^{-6}$	29·3	1·3	4·6
$10^{-6}:10^{-5}$	29·7	1·7	6·1
$10^{-6}:10^{-4}$	27·3	0·7	2·5
$10^{-6}:10^{-3}$	27·3	0·7	2·5
$10^{-7}:10^{-3}$	5·3	0·2	3·6
$10^{-7}:10^{-2}$	mixed peak Bi + Pb		

$\bar{h}$ = mean peak height; 10 mm corresponds to 24·8 nA.
Pre-electrolysis time 2 min.

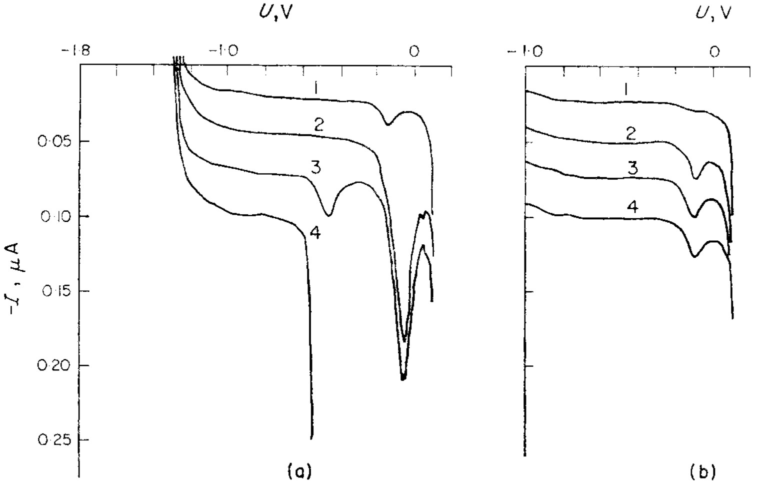


FIG. 2.—Typical stripping curves in the determination of Bi^{3+} in the presence of Pb^{2+}. Acetate buffer, pH 4·6, 2 min pre-electrolysis; (*a*) potential of −1·8 V, (*b*) potential of −1·0 V. *1*—$10^{-2}M$ DCTA, *2*—$10^{-2}M$ DCTA + $10^{-6}M$ Bi^{3+}, *3*—$10^{-2}M$ DCTA + $10^{-6}M$ Bi^{3+} + $10^{-6}M$ Pb^{2+}, *4*—$10^{-2}M$ DCTA + $10^{-6}M$ Bi^{3+} + $10^{-3}M$ Pb^{2+}.

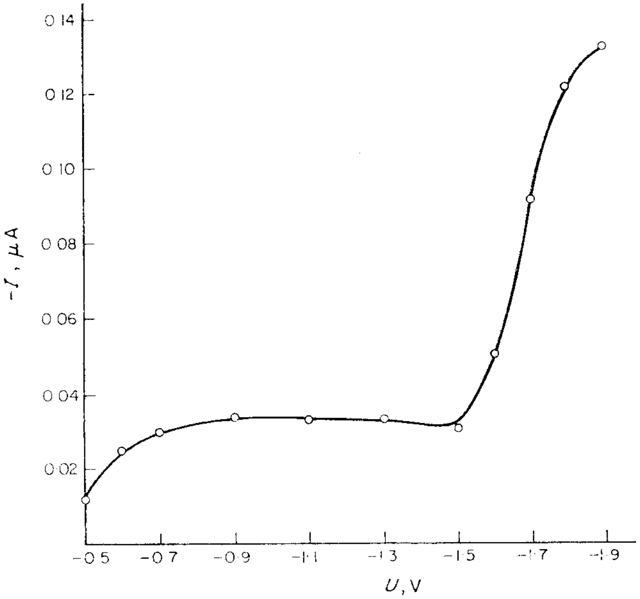


FIG. 3.—The dependence of the peak current of Tl^+ on the pre-electrolysis potential.
(2 min pre-electrolysis)
$10^{-6}M$ Tl^+ + $10^{-2}M$ DCTA in acetate buffer at pH 4·6.

at −0·9 V is prolonged from 2 to 10 min with 2 min of electrolysis in quiet solution, in the solution of $10^{-2}M$ DCTA, a linear dependence of the peak current on the thallium concentration is found within the range 5×10^{-9} to $1 \times 10^{-7}M$. It is then possible to increase the separation factor to 2×10^5 (see Table III*b*) with reasonable precision.

Determination of copper in DCTA

During the experiments described above it was found that the DCTA contained traces of copper. Stripping voltammetry was therefore used to determine this copper concentration. DCTA ($10^{-2}M$) in acetate buffer at pH 4·6 was deaerated and electrolysed for 5 min at −1·4 V. After 1 min of electrolysis in quiet solution the potential range was scanned and the copper peak recorded. The blank value was subtracted and the concentration determined by the method of standard addition, with a standard solution of $10^{-4}M$ $Cu(NO_3)_2$. The value obtained from four measurements was $6{\cdot}77 \pm 0{\cdot}82 \times 10^{-8}M$ which corresponds to $1{\cdot}25 \pm 0{\cdot}15 \times 10^{-4}\%$ of copper in DCTA (95% confidence limits).

Construction of a flow-through cell and comparison of the reproducibility of results with and without solution exchange

In most cases of analyses in solutions containing masking agents, both the pre-electrolysis and the stripping process are carried out in the same solution. Sometimes, however, it is desirable to avoid pre-electrolysis in media containing masking agents, because of impurities present in these substances. Up till now, the solutions used after the pre-electrolysis have been exchanged manually.[8,13,14] This is rather awkward and there are considerable losses of the substance to be determined, owing to aerial oxidation of the amalgam, unless the exchange is done very quickly. An electrolysis

TABLE III.—THE DETERMINATION OF Tl^+ IN THE PRESENCE OF Cd^{2+}

(*a*)
$10^{-2}M$ DCTA, pH 4·6; 2 min pre-electrolysis at −0·9 V;
h = 10 mm corresponds to 10·6 nA.

$[Tl^+]:[Cd^{2+}]$ *M*	$\bar{h}$ Tl, *mm*	Mean absolute error, *mm*	Mean relative error, %
$10^{-6}:0$	29·3	0·7	2·3
$10^{-6}:10^{-6}$	29·7	0·3	1·0
$10^{-6}:10^{-5}$	29·3	0·7	2·3
$10^{-6}:10^{-4}$	29·0	1·0	3·3
$10^{-6}:10^{-3}$	30·1	0·1	0·3
$10^{-6}:10^{-2}$	mixed peak Tl + Cd		
$10^{-6}:10^{-2}$*	15·3	14·7	49
$10^{-7}:10^{-3}$	3·2	0·2	7

(*b*)
$10^{-2}M$ DCTA, pH 4·6; 10 min pre-electrolysis at −0·9 V;
h = 10 mm corresponds to 3·54 nA

$[Tl^+]:[Cd^{2+}]$ *M*	$\bar{h}$ Tl, *mm*	Mean absolute error, *mm*	Mean relative error, %
$10^{-8}:10^{-3}$	8·5	0·5	6
$5 \times 10^{-9}:10^{-3}$	5·0	1·0	17

* $2 \times 10^{-2}M$ DCTA, pH 4·6

apparatus which makes possible the solution exchange under an inert atmosphere has been constructed[21] but the precision of measurement is no better than with the exchange in air, the error being 10–15%.

In order to avoid these disadvantages a flow-through cell, which makes possible fast solution exchange without opening the electric circuit, is described in this paper (Fig. 4). In **I**, the pre-electrolysis and the stripping process are carried out; **II** is a reservoir for the solution containing the masking agent. Solutions in both parts are deaerated and the pre-electrolysis is carried out in the non-chelating solution in **I**. After the electrolysis, stop-cocks *1* and *2* are simultaneously opened. The tube through which the chelating agent solution flows into the cell just touches the level of the solution in **I** and has a slightly larger diameter than that of the drain of **I**. By this method it is ensured that the drop electrode will not emerge during the solution exchange. The excess of the masking agent solution leaves through a siphon which keeps a constant solution volume in the cell (here 15 ml). It was found, by experiments with a coloured liquid, that a volume of the masking agent solution four times that of the liquid in **I** is necessary for complete exchange of solutions.

For the comparison of the reproducibility of results, three different concentrations of thallium ($5 \times 10^{-7}M$, $1 \times 10^{-6}M$, and $5 \times 10^{-6}M$) were determined, with use of 3 min pre-electrolysis at −0·9 V in solutions of:

(1) $10^{-2}M$ DCTA, pH 4·6

(2) acetate buffer, $\mu = 0{\cdot}1$, pH 4·6 with manual transfer to $10^{-2}M$ DCTA, pH 4·6 before the stripping process

(3) the same as (2) but using the flow-through cell for solution exchange.

In each case ten parallel determinations were made and standard deviations were calculated. The results are given in Table IV.

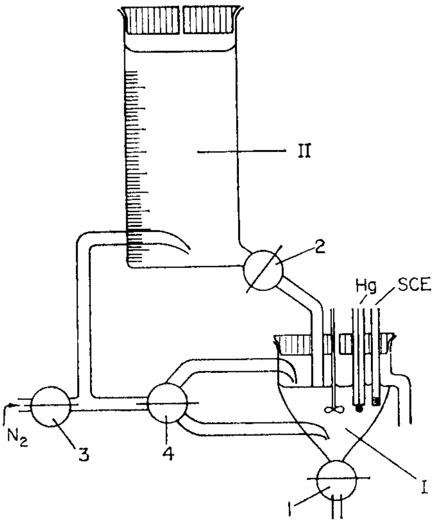


FIG. 4.—The flow-through cell.
I—electrolytic vessel, **II**—the chelating agent reservoir, *1*, *2*, *3*—stop-cocks, *4*—two-way stop-cock.

TABLE IV.—THE REPRODUCIBILITY OF THE DETERMINATION OF Tl^+
(h = 10 mm corresponds to 10·63 nA)

$[Tl^+]$, *M*		$\bar{h}$, *mm*	$\Delta\bar{h}$, *mm*	Relative deviation, %	Standard deviation, *mm*
5×10^{-7}	without exchange	16·7	0·4	2·5	0·4
	manual exchange	16·6	1·4	8·7	1·7
	flow-through cell	17·0	0·6	3·8	0·8
1×10^{-6}	without exchange	38·6	0·7	1·8	0·8
	manual exchange	36·9	4·0	10·8	4·6
	flow-through cell	37·3	1·3	3·4	1·5
5×10^{-6}	without exchange	182·0	5·3	2·9	6·9
	manual exchange	159·0	11·0	7·7	13·5
	flow-through cell	177·9	6·4	3·6	7·8

Measurements without solution transfer are the most precise and will be preferred in cases where sufficiently pure masking agents are used. If solution transfer is required, the use of the flow-through cell is more convenient and precise than manual transfer. A disadvantage is that more chelating agent is consumed than in manual solution exchange. The loss of substance by aerial oxidation, and consequently the error of determination with manual solution exchange depends on the time of the exposure of the drop to the air. The dependence of the peak current of Tl^+ on the time of drop exposure is given in Fig. 5.

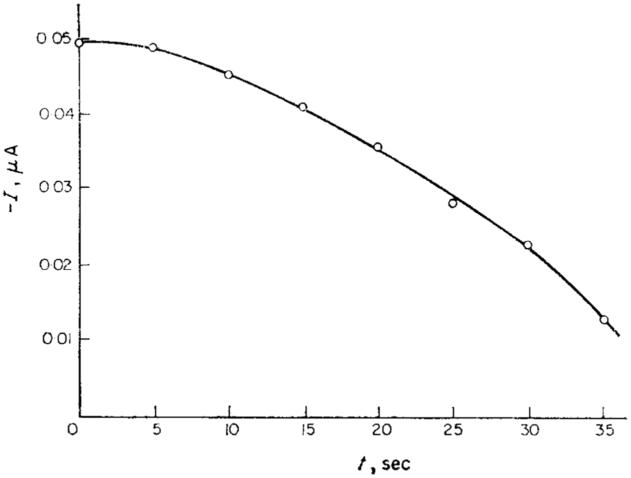


FIG. 5.—The dependence of the anodic dissolution current of Tl^+ on the time of exposure of the drop electrode to air during solution exchange.
$10^{-6}M$ Tl^+ + $10^{-2}M$ DCTA in acetate buffer at pH 4·6; 3 min pre-electrolysis in acetate buffer at pH 4·6 at a potential of −0·9 V.

If solution exchange is used, it is necessary to take into account that sometimes the separation factor can be decreased. For example, in the determination of thallium in cadmium there is no cadmium peak if both the pre-electrolysis and stripping are carried out in a DCTA solution, because of the high stability of the cadmium–DCTA chelate, which prevents the reduction of cadmium(II) in the given potential range. If, however, the pre-electrolysis is carried out in an acetate buffer, cadmium ions are reduced, and, after transfer into a DCTA solution, the cadmium anodic peak is recorded ($E_{p/2}$ −0·67 V).

CONCLUSIONS

It follows from the results given that a DCTA solution is convenient for determination of very low concentrations of bismuth in lead and of thallium in cadmium. The sensitivity for bismuth (and the separation factor) could be further increased by prolonging the pre-electrolysis time. Of the common metals, copper in higher concentrations could interfere in the determinations; other metallic elements undergo the electrode reaction at much more negative potentials as follows from the polarographic data.

Anodic stripping voltammetry can be used for a very fast and sensitive determination of certain impurities in chelating agents as has been demonstrated by the determination of copper in DCTA.

When exchange of solution after pre-electrolysis is desirable, the use of the flow-through cell is recommended. It is, however, necessary to evaluate carefully the influence of the exchange on the peak separation. The $E_{p/2}$ values are very useful for the prediction of the separation factor.

Zusammenfassung—Die $E_{p/2}$-Werte der Ionen Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, und Tl^{+} wurden in Lösungen von Acetat- und Britton-Robinson-Puffern sowie in EDTA und DCTA enthaltenden Lösungen durch cyclische Voltammetrie ermittelt. DCTA wurde dann eingesetzt (a) bei der invers-voltammetrischen Bestimmung von kleinen Wismutmengen, bis herunter zu $10^{-7}M$, in Gegenwart von 10^{4}-mal so viel Blei und (b) bei der Bestimmung von Thalliumspuren bis herunter zu $5 \cdot 10^{-9}M$ in Gegenwart von $2 \cdot 10^{5}$-mal so viel Cadmium. Die Genauigkeit war gut. Ferner wurde die Kupferkonzentration in analysenreiner DCTA bestimmt. Außerdem wird ein neues Durchfluß-Gefäß für die Auflösung mit Lösungsaustausch beschrieben; die Reproduzierbarkeit der Ergebnisse ohne Lösungsaustausch, mit Lösungsaustausch von Hand und mit dem Durchflußgefäß wird für eine Modellbestimmung von Thallium in DCTA-Lösung ermittelt.

Résumé—On a déterminé les valeurs $E_{p/2}$ des ions Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, Tl^{+} au moyen de la voltammétrie cyclique dans des solutions de tampons acétate et Britton-Robinson et dans des solutions contenant de l'EDTA et du DCTA. On a alors utilisé le DCTA dans la détermination de petites quantités de bismuth, descendant jusqu'à $10^{-7}M$, en la présence de 10^{4} fois plus de plomb, et de traces de thallium descendant jusqu'à $5 \times 10^{-9}M$ en la présence de 2×10^{5} fois plus de cadmium par voltammétrie de dissolution anodique. La précision est bonne. De plus, on a déterminé la concentration de la trace de cuivre présente dans le DCTA de qualité analytique. On décrit aussi un nouveau récipient à écoulement continu pour l'analyse par dissolution avec échange de solution et l'on évalue la reproductibilité des résultats sans échange de solution, avec échange manuel de solution, et avec le récipient à écoulement continu pour une détermination type de thallium dans une solution de DCTA.

REFERENCES

1. V. A. Igolinskii and A. G. Stromberg, *Metody Analiza Khimicheskikh Reaktivov i Preparatov*, p. 29. IREA Moscow, 1963.
2. W. Kemula, Z. Kublik and S. Glodowski, *J. Electroanal. Chem.*, 1959, **1**, 91.
3. A. G. Stromberg, M. S. Zakharov, V. S. Smorodinov and V. M. Pichugina, Ref. 1., p. 72.
4. S. I. Sinyakova, A. G. Dudareva, I. V. Markova and I. N. Talalayeva, Ref. 1., p. 58.
5. R. Neeb and I. Kiehnast, *Naturwissenschaften*, 1970, **57**, 37.
6. R. Neeb, *Z. Anal. Chem.*, 1959, **171**, 321.
7. *Idem, ibid.*, 1961, **180**, 161.
8. M. Ariel, U. Eisner and S. Gottesfeld, *J. Electroanal. Chem.*, 1964, **7**, 307.
9. L. F. Zaichko and M. S. Zakharov, Ref. 1., p. 79.
10. M. S. Zakharov, A. G. Stromberg, O. S. Stepanova and S. F. Gurskaya, Ref. 1., p. 95.
11. N. A. Mesiac, B. F. Nazarov, M. S. Zakharov and A. G. Stromberg, *Zh. Analit. Khim.*, 1964, **19**, 959.
12. R. Neeb and I. Kiehnast, *Z. Anal. Chem.*, 1968, **241**, 142.
13. M. Ariel and U. Eisner, *J. Electroanal. Chem.*, 1963, **5**, 362.
14. S. L. Philips and I. Shain, *Anal. Chem.*, 1962, **34**, 262.
15. V. Sýkora and V. Zátka, *Tables for Chemists*, pp. 66, 72. SNTL, Prague, 1967.
16. R. Přibil, Z. Roubal and E. Svátek, *Chem. Listy*, 1952, **46**, 396.
17. T. Iga, S. Yamashita and H. Uehara, *Bunseki Kagaku*, 1961, **10**, 227.
18. M. S. Zakharov and N. A. Mesiac, Ref. 1., p. 88.
19. J. G. Nikelly and W. D. Cooke, *Anal. Chem.*, 1957, **29**, 933.
20. M. Spálenka, *Handbook of Inorganic Polarographic Analysis*, p. 209. SNTL, Prague, 1961.
21. A. A. Kaplin, M. S. Zakharov and A. G. Stromberg, Ref. 1., p. 92.

Talanta, 1971, Vol. 18, pp. 615 to 629. Pergamon Press. Printed in Northern Ireland

VERWENDUNG VON MÄSSIG DISSOZIIERTEN KOMPLEXEN BEI SPEKTRALPHOTOMETRISCHEN BESTIMMUNGEN—III

AUSWERTUNG LINEARER PHOTOMETRISCHER TITRATIONSKURVEN OHNE INDIKATOR

J. Fischer, Z. Slovák und J. Borák
Forschungsinstitut für reine Chemikalien,
LACHEMA Brno, Tschechoslowakei

(*Eingegangen am* 20 *Mai* 1969. *Revisdiert am* 29 *Juli* 1970. *Angenommen am* 13 *Oktober* 1970)

Zusammenfassung—Ausgehend von der Hyperbelform der linearen Titrationskurven ohne Indikator wurden besonders die photometrischen Titrationskurven eingehend untersucht. Die Titrationskurven bei der Bildung von Komplexen des Typus ML können auch bei weitgehender Dissoziation quantitativ ausgewertet werden. Der Wert des Produktes der Beständigkeitskonstante und der Konzentration des zu bestimmenden Stoffes kann bis auf eins sinken. Die Grenzbedingungen für eine erfolgreiche Auswerteng von Titrationskurven bei der Bildung von schwachen ML-Komplexen bei realen Titrationen wurden diskutiert. Die Anwendbarkeit der angeführten mathematischen und graphischen Auswertungsmethoden wurde an konkreten Systemen überprüft.

Die Bildung von schwachen Komplexen bedeutet keinesfalls ein Hindernis für die analytische Anwendung solcher Reaktionen. Die abgeleiteten Beziehungen wurden an realen Systemen bestätigt,[1–3] sie gaben uns die Möglichkeit, allgemeine Schlußfolgerungen zu formulieren, die sich aus umfassender Auswertung von photometrischen Titrationskurven für die Bedingungen und Ausführungen von spektralphotometrischen Bestimmungen, für die quantitative Auswertung von photometrischen Titrationskurven und schließlich für das Studium der Komplexbildung ergeben. Diese Gesichtspunkte können voneinander nicht völlig getrennt werden. Deshalb wurde auch bereits in der Arbeit, die den allgemeinen Fragen der spektralphotometrischen Bestimmungen bei der Bildung von schwachen Komplexen gewidmet wurde,[2] auf die Probleme der Auswertung von photometrischen Titrationen hingewiesen, und gezeigt, daß bei einer üblichen extrapolativen Auswertung einer Titrationskurve bei der Bildung eines ML_b-Komplexes ein Fehler von $1/(K.\ c_L{}^b)\ 100\%$ entsteht.

Die Fortsetzung dieser Arbeit hat zum Ziel, die geeignetste mathematische Beschreibung von photometrischen Titrationskurven zu finden und die daraus folgenden Gesetzmäßigkeiten in der analytischen Praxis auszunutzen. Die abgeleiteten Beziehungen haben jedoch eine allgemeinere Geltung und können auch zur Auswertung von anderen linearen Titrationskurven, die auf einer Reaktion mit dem stöchiometrischen Verhältnis 1:1 beruhen, herangezogen werden. In der vorliegenden Mitteilung werden die erzielten Ergebnisse am Beispiel der photometrischen Titrationen beschrieben.

Charlot[4] unterteilt die Titrationskurven in zwei Gruppen: lineare, bei welchen das angezeigte Signal eine lineare Funktion der Konzentration des gebildeten Reaktionsproduktes ist, und logarithmische. Eine ähnliche Unterteilung schlägt auch Flaschka[5] vor. Er weist dabei auf Vorteile der linear-extrapolierbaren Titrationskurven hin. Zu den üblichsten linearen Titrationskurven gehören jene, die bei amperometrischen und photometrischen Titrationen resultieren. Im Mittelpunkt des Interesses dieser Abhandlung stehen die photometrischen Titrationskurven.

Bei den linearen Titrationskurven, die mehr oder weniger ausgeprägte lineare Äste aufweisen, wurde manchmal das Problem der Äquivalenzpunktbestimmung nur auf die Bestimmung des Schnittpunktes von zwei Geraden reduziert.[6–8] Diese Methode wurde am weitesten von Lydersen[8] auf Grund seiner Untersuchung von konduktometrischen Titrationskurven ausgearbeitet. Es wurden dabei auch die durch unvollständige Dissoziation entstehenden systematischen Fehler berücksichtigt. Bei einer formalen geometrischen Lösung muß man jedoch beachten, ob das indizierte Signal nur eine Funktion der Konzentration des titrierten Stoffes und des Titranten (z.B. Photometrie) ist, oder ob es sich um eine Abhängigkeit von mehreren Komponenten des Systems handelt (z.B. Konduktometrie). Auf diese Tatsache wies bereits Underwood[9] hin.

Eine Reihe von Veröffentlichungen über die linearen Titrationskurven ging von physikalisch-chemischen Standpunkten aus, die sich mit den Fragen der theoretischen Empfindlichkeit und der Ausführung der Titrationen bei extremen Bedingungen beschäftigen. Besonders ausführlich wurden die amperometrischen Titrationen behandelt.[10–13] Meites und Goldman[14] befaßten sich in einer umfassenderen Arbeit auch mit den photometrischen Titrationen.

Mit einer Analyse der photometrischen Titrationskurven beschäftigten sich vor allem Goddu und Hume.[15] Sie fanden bei der Untersuchung photometrischer Titrationen von schwachen Säuren ohne Indikator, daß eine Titration nur ausgeführt werden kann, wenn das Produkt der Ionisationskonstante und der Konzentration größer als 10^{-12} ist. Flaschka[5] untersuchte die chelatometrischen und photometrischen Titrationen in selbstindizierenden Systemen und fand, daß zwei Kationen nebeneinander bestimmt werden können, falls die entsprechenden Stabilitätskonstanten der gebildeten Komplexe sich um einen Faktor von 10^2 bis $2 \cdot 10^2$ unterscheiden. Ringbom[16] beschäftigte sich mit photometrischen Titrationskurven ohne Indikator vor allem mit Rücksicht auf die Genauigkeit der Bestimmungen. Er betrachtete dabei nicht nur die Fehler der Auswertung, sondern auch die Folgen einer fehlerhaft bestimmten Extinktion.

Eine eingehendere geometrische Betrachtung, die für die graphische Auswertung notwendig ist, findet man in der Literatur seltener. Langer und Stevenson[17] gingen von der Arbeit von Majer[18] aus, sie analysierten die amperometrischen Titrationskurven sowohl bei der Bildung eines Niederschlages, als auch bei dissoziierten Reaktionsprodukten. Im letzteren Fall lag der Äquivalenzpunkt in der Mitte zwischen dem Mittelpunkt der Hyperbel und dem Schnittpunkt ihrer Asymptote mit der Tangente dieser Hyperbel im Anfang der Titration. In der gleichen Abhandlung wurden auch einfache geometrische Auswertungsmethoden beschrieben, die von der Hyperbelform der Titrationskurven ausgehen. Adámek, Doležal und Zýka[19] beschäftigten sich mit der Form der amperometrischen Titrationskurven bei Redox-Titrationen sowie mit dem Einfluß der Verdünnug der Lösung während einer Titration. Sie fanden, daß für Redox-Titrationen bei denen ein Niederschlag entsteht, keine übliche Volumenkorrektur eingeführt werden kann. Khadeev[20] beschrieb in seiner Arbeit über die Endpunktsbestimmung bei amperometrischen Fällungstitrationen eine graphische Methode, die auf dem Richtungskoeffizienten einer Tangente im Endpunkt der Titration gegründet ist.

Grunwald[21] bestimmte den Äquivalenzpunkt als Schnittpunkt zweier Geraden, die durch zwei Paare konjugierter Punkte führen. Drei Punkte werden an den linearen Ästen der Titrationskurve, doch möglichst in der Nähe des Äquivalenzpunktes, gewählt, der vierte Punkt wird aus der kanonischen Gleichung der betreffenden Titration berechnet. Dieser Schritt muß mehrmals wiederholt werden. Nach Underwood[9] hat die Grunwaldsche Methode kaum eine praktische Bedeutung erlangt.

Verwendete Symbole und Bezeichnungen

A	indiziertes Signal
A_0	indiziertes Signal bei $u \to \infty$
A_t	indiziertes Signal bei u_t
F	Konzentration der Maßlösung [Mol. Liter^{-1}]
K	Beständigkeitskonstante (scheinbare Konstante)
$[\mathrm{L}]$, $[\mathrm{M}]$	Ligand- (Metall-) Gleichgewichtskonzentration
$[\mathrm{M}_a\mathrm{L}_b]$	Gleichgewichtskonzentration des Reaktionsproduktes
V	Volumen des zugesetzten Titrants [Liter]
V_0	Anfangsvolumen vor der Titration [Liter]
a	reelle Hyperbelachse
a_1, a_2	Hyperbelasymptoten
c_L, c_M	totale Ligand- (Metall-) Konzentration [Mol. Liter^{-1}]
p	Proportionalgröße; $p = u/v$
p_i	Pascalsche Gerade
p_t	p für den Schnittpunkt der Titrationskurve mit ihrer Polare (Äquivalnzpunkt als Pol)
q	Proportionalgröße; $q = F/v$
r	Proportionalgröße; $r = (A_0 - A_t)/A_0$
Δs	relativer Fehler (s. Gl.24)
t_0	Tangente der Titrationskurve im Koordinatenursprung
u	Konzentration des Titrants (c_M falls $v = c_\mathrm{L}$; c_L falls $v = c_\mathrm{M}$) [Mol. Liter^{-1}]
u_t	u bei dem Schnittpunkt von t_0 mit a_1
Δu	relativer Fehler (s. Gl.13)
v	gesuchte Konzentration [Mol. Liter^{-1}]
x	gemessene Konzentration [ML] bzw. [L] oder [M] [Mol. Liter^{-1}]
α	veränderliche Hilfsgröße; $\alpha = A(V_0 + V)$
β	veränderliche Hilfsgröße; $\beta = A(V_0 + V)/V_0$
ε'	Proportionalitätsfaktor; $\varepsilon' = A/x$, falls A nur eine Funktion von x ist
ε_u'; ε_v'; ε_x'	Proportionalitätsfaktoren zwischen dem indizierten Signal und u, v, x
ε_d'	Proportionalitätsfaktor; $\varepsilon_d' = \varepsilon_x' - \varepsilon_u' - \varepsilon_v'$
ψ	Steigung von t_0

$$\psi = \frac{Kv}{Kv + 1}$$

Allgemeine Charakteristik der linearen Titrationskurven

Falls in dem untersuchten System bei konstanten weiteren Bedingungen zwei Stoffe M und L miteinander nach Gl. (1)

$$M + bL \rightleftharpoons ML_b \tag{1}$$

reagieren, und falls in diesem System nur dieses Gleichgewicht angenommen wird, kann die entsprechende Beständigkeitskonstante K folgendermaßen geschrieben werden:

$$K = \frac{[ML_b]}{(c_M - [ML_b])(c_L - b[ML_b])^b} \tag{2}$$

Nach der Substitution $t^{b+1} = K^{-1}$; $c_L - b[ML_b] = z$; $(c_M/ML_b) - 1 = w$, bekommt man Gl. (3)

$$t^{b+1} = w \,.\, z^b, \tag{3}$$

welche einer höheren Hyperbel entspricht.[22] Für den Fall der Bildung eines ML_2-Komplexes entspricht Gl. (3) der sog. "iperbola mesolabica" von Viviani (1647).[22] Weiter beschränken wir uns auf den einfachsten, aber geläufigsten Fall der photometrischen Titration: Entstehung eines ML-Komplexes.

Geometrische Charakteristik der Titrationskurve bei der Bildung eines ML-Komplexes

Aus Gl. (2) folgt

$$[ML]^2 - [ML](c_M + c_L + K^{-1}) + c_M c_L = 0. \tag{4}$$

Das indizierte Signal sei eine lineare Funktion der Konzentration eines einzigen Bestandteiles des untersuchten Systems, und der Proportionalitätsfaktor gleiche zuerst eins. Aus Gl. (4) erhält man dann Gl. (5a) und (5b):

$$-ux + x^2 + uv - (v + K^{-1}) \,.\, x = 0 \tag{5a}$$

$$-ux + x^2 - uK^{-1} + (v + K^{-1}) \,.\, x = 0 \tag{5b}$$

wobei $u = c_M$, (c_L); $v = c_L$, (c_M); in Gl. (5a) $x = [ML]$, in (5*b*) $x = [M]$ oder [L]. Aus dieser Schreibweise ist leicht zu erkennen, daß es sich um eine Kegelschnittlinie handelt, deren absolutes Glied und Koeffizient bei u^2 gleich Null sind. Die Invarianten der Kegelschnittlinie (5*a*) lauten:

$$\delta = -\frac{1}{4} \tag{6}$$

$$\Delta = \frac{1}{4}\frac{v}{K} \tag{7}$$

Das gleiche Ergebnis gilt auch für Gl. (5*b*). Es handelt sich um eine Hyperbel, da $\delta < 0$ und $\Delta \neq 0$, wie es schon früher festgestellt wurde.[18,23] Für $K \rightarrow \infty$, d.h. bei Bildung eines in erster Näherung unendlich stabilen Komplexes, ist $\Delta = 0$, wobei die Hyperbel in eine degenerierte Hyperbel, nämlich in zwei sich schneidende Geraden, übergeht.

In Abb. 1 ist eine typische Titrationskurve mit eingezeichneten Hyperbelcharakteristiken dargestellt. Um diese Titrationshyperbel noch näher zu beschreiben, sei

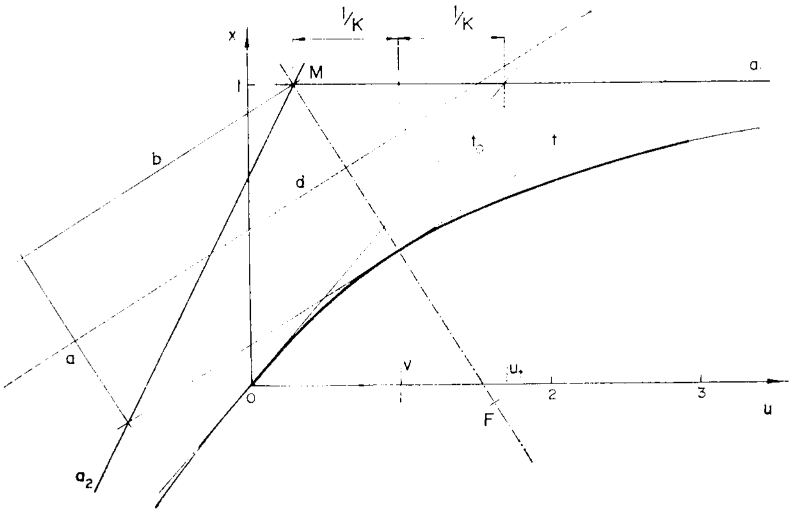


Abb. 1.—Titrationshyperbel bei der Bildung eines ML-Komplexes mit eingezeichneten Charakteristiken.

hier nur noch der Wert ihrer realen Halbachse a angeführt:

$$a = \frac{2}{Kv \,.\, (\sqrt{2} + 1)} \tag{8}$$

Zusammenhänge zwischen der Geometrie der Titrationskurve und dem Äquivalenzpunkt

Die klassische Auswertung einer Titrationskurve beruht in linearer Extrapolation der Teile der Kurve, die maximal von dem Äquivalenzpunkt entfernt sind, d.h. des Anfangs der Titration und des Astes bei einem großen Titrantüberschuß. Dabei nimmt man gewöhnlich an, daß bei diesen Bedingungen die Gleichgewichtskonzentration des Titrants bzw. des titrierten Stoffes vernachlässigt werden können, also daß es sich um einen in erster Näherung unendlich festen Komplex handelt.

Es wurde oben gezeigt, daß in diesem Fall die Titrationskurve als eine degenerierte Hyperbel angesehen werden muß. Die Gleichungen der Asymptoten der Titrationshyperbel (ML-Komplex) lauten

$$x = u + K^{-1} \qquad (\equiv a_2) \tag{9}$$

und

$$x = v \qquad (\equiv a_1) \tag{10}$$

Für den Mittelpunkt der Titrationshyperbel ($\equiv$ Schnittpunkt der Asymptoten) gelten die Koordinaten ($v - K^{-1}$; v). Der Schnittpunkt der Asymptoten der Titrationshyperbel liegt also bei der Bildung eines ML-Komplexes um den Wert von K^{-1} vor dem Äquivalenzpunkt.

Der ansteigende Ast der Titrationskurve gibt keinesfalls (erst recht nicht bei dissoziierten Komplexen) die Richtung der Hyperbel-Asymptote a_2 an. Es handelt sich dabei nur um die Tangente der Titrationshyperbel im Koordinatenursprung (t_0), die nach unserer früheren Ableitung[1] durch Gl. (11) gegeben ist:

$$x = \frac{Kv}{Kv + 1} \,.\, u \tag{11}$$

Man sieht, daß nur bei einer degenerierten Titrationshyperbel diese Tangente mit a_2 zusammenfällt, für $K \to \infty$ resultiert $x = u$ sowohl aus (9) als auch aus (11).

Der zweite extrapolierte Ast der Titrationskurve kann degegen mit a_1 identisch sein (vgl. z.B. die Ergebnisse bei großen Titrantüberschüssen in Zitaten 1 und 3). Der Endpunkt einer auf diese Weise (Schnittpunkt $t_0 - a_1$) ausgewerteten Titration wird, wie aus (10) und (11) folgt, durch Gl. (12) bestimmt:

$$u_t = v + K^{-1} \tag{12}$$

Er liegt bei einem um K^{-1} größeren Wert als der gesuchte Äquivalenzpunkt. Der relative Fehler Δu beträgt dann

$$\Delta u = \frac{1}{Kv} \tag{13}$$

und kann bei praktischen Bestimmungen zehn und mehr % betragen, wie es schon gezeigt werden konnte.[2]

Der Äquivalenzpunkt der Titration liegt in der Mitte zwischen dem Mittelpunkt der Titrationshyperbel und dem Schnittpunkt von a_1 mit t_0. Diese Feststellung steht im Einklang mit den Ergebnissen von Langer und Stevenson,[17] und weist auf die Ungenauigkeit von häufig verwendeten Auswertungsmethoden sowohl in ihren Voraussetzungen als auch in der Ausführung hin. Sie gestattet aber auch die Ausarbeitung theoretisch begründeter Auswertungsmethoden.

Bei praktischen Analysen wird oft der Endpunkt einer Titration als der Schnittpunkt von zwei Tangenten der Titrationskurve angesehen, die in dem Koordinatenursprung ($u = 0$) und in einem hinter der Äquivalenz gewählten Punkt ($u = pv$) konstruiert werden. Der Wert von p kann, wenn der bestimmte Endpunkt mit dem Äquivalenzpunkt zusammenfällt (p_t), als die Polarebestimmung berechnet werden. Die Gleichung der Polaren des Punktes $\left(v; \dfrac{Kv^2}{Kv+1}\right)$ lautet, vgl. z.B. Zitat 24,

$$x = \frac{Kv}{3kv + 1}\, u. \tag{14}$$

Die Koordinaten des gesuchten Schnittpunktes werden durch Einsetzen aus (14) in Gl. (5*a*) ethalten:

$$u = \frac{2v(3Kv + 1)}{2Kv + 1} \tag{15a}$$

$$p_t = \frac{2(3Kv + 1)}{2Kv + 1} \tag{15b}$$

Für die beiden extremen Zustände, d.h. eines unendlich stabilen ($K \to \infty$) und eines unendlich dissoziierten ($K \to 0$) Komplexes folgt aus (15*b*):

$$\lim_{K \to \infty} p_t = 3 \tag{16a}$$

$$\lim_{K \to 0} p_t = 2 \tag{16b}$$

Das interessante Ergebnis erklärt einige offene Fragen bei der Bestimmung des extremen Wertes des Produktes Kv, bei dem die extrapolative Auswertung einer Titration noch ausführbar ist.

Grenzen der linearen extrapolativen Auswertung einer Titrationskurve (ML-Komplex)

Das Produkt Kv, das als Grundparameter der Gl. (11), (13) und (15) vorkommt, spielt bei der Äquivalenzbestimmung eine wesentliche Rolle. Diese Feststellung machten bereits Goddu und Hume.[15] Der von ihnen gefundene niedrigste zulässige Wert von $Kv = 100$ steht mit der Arbeit von Reilley *et al.*[25] im Einklang, wie Underwood[9] bei einem Vergleich beider Arbeiten nachwies. Auch von Ringbom[16] wird ein Kv-Wert von 100 als die untere Grenze der Auswertbarkeit angesehen. Bei Flaschka[5] liegt diese Grenze bei $Kv = 50$.

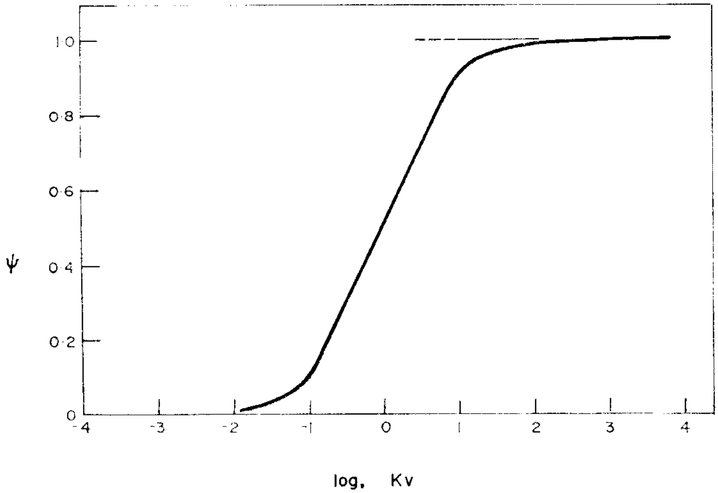


ABB. 2.—Steigung von t_0 als Funktion von Kv.

Die Bedeutung von Kv geht aus Gl. (13) hervor. Es ist ersichtlich, daß der Kehrwert von Kv die Genauigkeit der Endpunktbestimmung charakterisiert. In anderen Worten ausgedrückt, der Wert von Kv bestätigt oder widerlegt die Voraussetzung, daß die Titrationskurve als eine degenerierte Hyperbel angesehen werden kann. Während die Steigung der Asymptote a_2 von Kv unabhängig ist [Gl. (9)], ist die Steigung der Tangente t_0 von dem Produkt Kv stark abhängig [Gl. (11)]. Mit einem wachsenden Wert von Kv geht t_0 in a_2 über (degenerierte Hyperbel). Die Abhängigkeit der Steigung ψ der Tangente t_0 von dem Produkt Kv ist in Abb. 2 dargestellt. Läßt man eine Differenz zwischen dem gefundenen Endpunkt und dem Äquivalenzpunkt (Titrationsfehler) von 1% zu, so wird $\log Kv = 2$, im Einklang mit den oben erwähnten Arbeiten.[9,15,16]

Abbildung 3 zeigt die Abhängigkeit der p_t-Werte von dem Produkt Kv. Es wird verständlich, daß annehmbare Ergebnisse auch bei $50 < Kv < 100$ erzielt wurden.[5]

Bei einer realen Titration muß man annehmen, daß der Proportionalitätsfaktor ε' zwischen dem angezeigten Signal und der bestimmten Konzentration nicht gleich eins ist. Aus Gl. (5*a*) erhält man dann

$$-uA + \frac{1}{\varepsilon'} A^2 + \varepsilon' uv - (v + K^{-1}) A = 0. \tag{17}$$

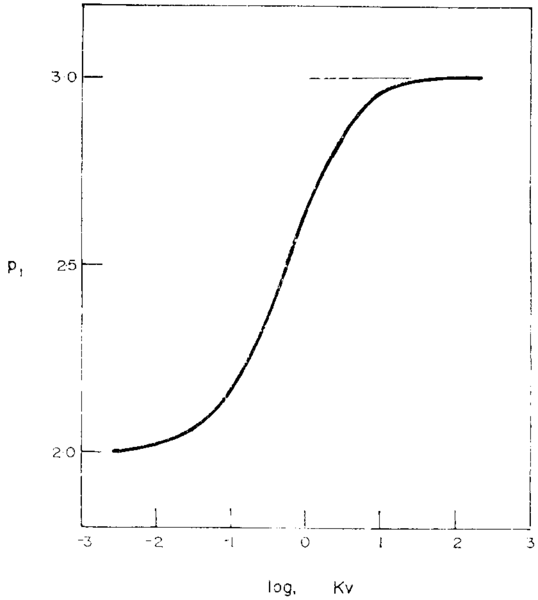


ABB. 3.—p_t als Funktion von Kv.

Gl. (9) und (11) gehen dann in (18) und (19) über:

$$A = \varepsilon'(u + K^{-1}) \qquad (\equiv a_2) \tag{18}$$

$$A = \frac{\varepsilon' Kv}{Kv + 1} \cdot u \qquad (\equiv t_0) \tag{19}$$

Der Endpunkt wird genauso bestimmt, wie in dem Fall von $\varepsilon' = 1$. Gl. (15) und somit auch Abb. 3 gelten ohne Einschränkung.

Reale Titrationskurven

Die oben diskutierten Abhängigkeiten gelten für den idealen Fall, daß während der Titration das Gesamtvolumen der Lösung konstant bleibt. Wenn man das Volumen des zugesetzten Titranten berücksichtigt, ohne daß eine Verschiebung des Gleichgewichtes angenommen wird, kann Gl. (2) für $b = 1$ wie folgt geschrieben werden:

$$K = \frac{\varepsilon' A}{\left(\dfrac{\varepsilon' F V}{V_0 + V} - A\right)\left(\dfrac{\varepsilon' v V_0}{V_0 + V} - A\right)} \tag{20}$$

Hierbei bedeuten F die Molarität der Maßlösung, V_0 und V das ursprüngliche Volumen der titrierten Lösung und das Volumen der zugesetzten Lösung. Aus Gl. (20) folgt dann für die reale Titrationskurve die Beziehung

$$-A(V_0 + V)V(\varepsilon' F + \varepsilon' K^{-1}) + A^2(V_0 + V)^2 + \varepsilon'^2 F V_0 v V$$
$$-A(V_0 + V)(\varepsilon' V_0 v + \varepsilon' V_0 K^{-1}) = 0. \tag{21}$$

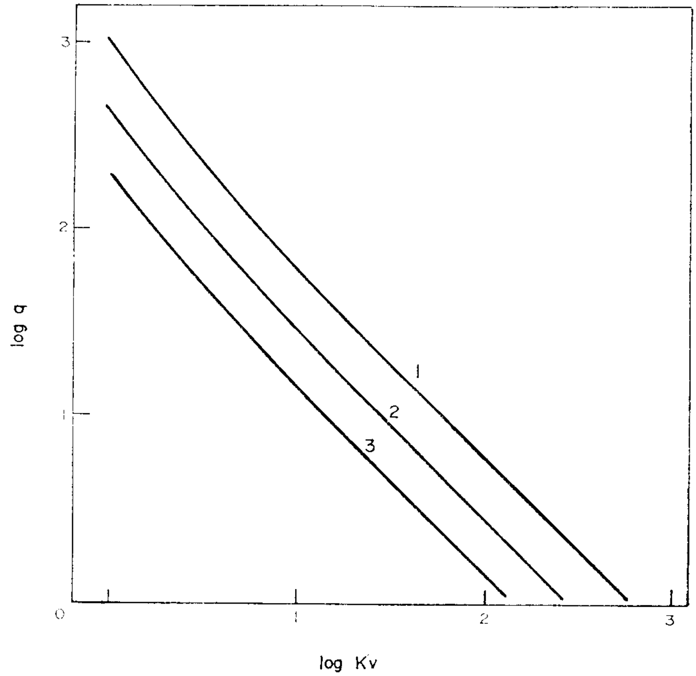


Abb. 4.—Titrationsfehler bei realer Titration. *1*, *2*, *3*—berechnet für rel. Fehler 0,5%, 1% und 2%.

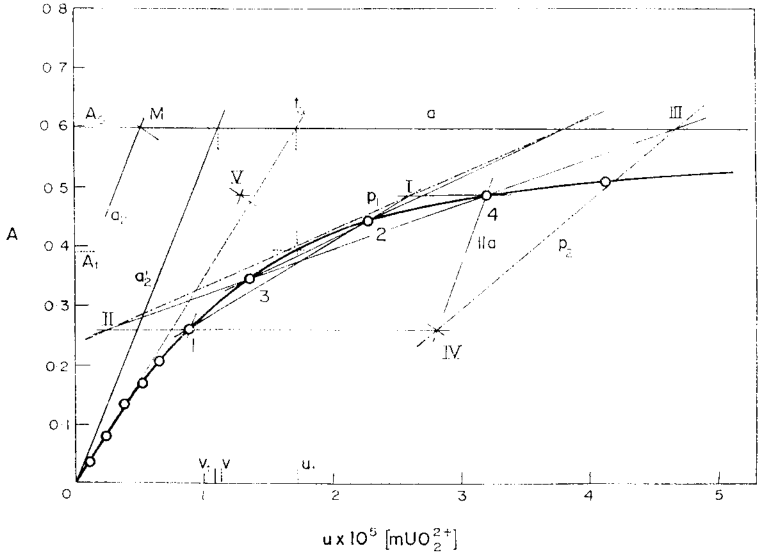


Abb. 5.—Graphische Auswertung einer photometrischen Titration von Arsenazo III durch UO_2^{2+}.

$c_L = v = 1{,}112 \cdot 10^{-5}M$; $F = 5{,}1 \cdot 10^{-3}M$; $Kv = 1{,}8$.

Nach der Vereinfachung durch die Substitution $\alpha = A(V_0 + V)$ oder $\beta = A\,\dfrac{V_0 + V}{V_0}$ geht (21) in eine der Gl. (17) analoge Gleichung über. Bei der üblicheren β-Substitution ist die Tangente t_0 durch Gl. (22) gegeben:

$$\beta = \frac{\varepsilon' K v}{V_0(Kv + 1)}\, FV \tag{22}$$

Für den Mittelpunkt dieser Hyperbel gilt:

$$\beta = \varepsilon' v\,\frac{F}{F + K^{-1}} \tag{23a}$$

und

$$V = \frac{2vF}{(F + K^{-1})^2} - \frac{v + K^{-1}}{F + K^{-1}} \tag{23b}$$

Eine einfache Auswertung ist möglich, wenn $K^{-1} \ll F$. Um diese Ungleichheit näher zu spezifizieren, wurde der relative Fehler der V-Mittelpunktkoordinate Δs als eine Funktion von Kv und $q(q = F/v)$ berechnet,

$$\Delta s = 1 - \frac{(qKv + 1)(vK - 1)}{qKv\left[\left(\dfrac{2qKv}{qKv + 1} - 1\right)Kv - 1\right]} \tag{24}$$

und für $\Delta s = 0{,}005$; $0{,}01$ und $0{,}02$ in Abb. 4 graphisch dargestellt. Es ist ersichtlich, daß die Bedingungen für die Gültigkeit von Gl. (25*a*) und (25*b*), die man durch direktes Einsetzen in Gl. (9) und (10) erhält, bei $Kv \gg 10^2$ immer, bei $Kv < 10^2$ mit $q \gg 10^2$ erfüllt sind. Es ist:

$$\beta = \varepsilon' v \tag{25a}$$

$$FV = (v - K^{-1})V_0 \tag{25b}$$

Für den Schnittpunkt von t_0 mit a_1 erhält man analog zu (12)

$$FV = (v + K^{-1})V_0. \tag{26}$$

Die Titration kann dann wie in dem oben beschriebenen idealen Fall ausgewertet werden. Die Forderung $q \gg 10^2$ bereitet in der Praxis keine Schwierigkeiten, da man handelsübliche Mikrodosierungseinrichtungen verwenden kann. Die praktische Erfahrung hat gezeigt, daß eine photometrische Titration unmittelbar in der Meßküvette mit konzentrierten Maßlösungen schnell und verläßlich durchführbar ist,[3] vgl. auch Abb. 5.

Bei einer realen Titration ist es notwendig, auch die möglichen Nebenreaktionen in Betracht zu ziehen. Dabei kann es sich z.B. um eine Reaktion weiterer Kationen mit dem Reagens handeln. Sollen die gemessenen Punkte (reale Titrationshyperbel) in einem Gebiet von 0 bis 2,5 v von dem theoretischen Verlauf der Titrationskurve maximal um 1% abweichen, folgt für das zweite (störende) Gleichgewicht die Bedingung $300\,K'v < Kv$, wobei K' die scheinbare Konstante des störenden Gleichgewichtes bedeutet.

Falls das indizierte Signal gleichzeitig eine Funktion von u und v ist, dann gilt

$$A = \varepsilon_u'(u - x) + \varepsilon_v'(v - x) + \varepsilon_x'x \tag{27a}$$

und nach Umformung

$$A = \varepsilon_d'x + \varepsilon_u'u + \varepsilon_v'v, \tag{27b}$$

wobei $\varepsilon_d' = \varepsilon_x' - \varepsilon_u' - \varepsilon_v'$. Wenn $\varepsilon_u' = 0$, wird die Titration gegen eine Vergleichslösung mit der Konzentration v ausgeführt. Ist $\varepsilon_u' \neq 0$, müssen die gemessenen Werte um den Betrag $\varepsilon_u'u$ graphisch oder nummerisch vermindert werden (bzw. für ε_v', $\varepsilon_u' \neq 0$ muß die Titration gegen eine Vergleichslösung durchgeführt und die gemessenen Werte noch um den Betrag $\varepsilon_u'u$ vermindert werden). Dann in allen angeführten Fällen ist $A = \varepsilon_d'x$.

Auswertung von Titrationskurven bei Bildung von dissoziierten Komplexen (ML-Komplex, $Kv < 100$)

Nummerische Berechnung. Mit Hilfe der Ausgleichsrechnung kann man die Konstanten der Gl. (17), d.h. ε'^{-1}, $\varepsilon'v$ und $(v + K^{-1})$, bestimmen. Das Verfahren ist jedoch umständlich und bei Verwendung eines Computers auch zu aufwendig. Außerdem kann man keine große Genauigkeit der Bestimmungen erwarten, da v als ein Produkt von zwei Proportionalitätskonstanten (ε'^{-1} und $\varepsilon'v$) bestimmt wird.

Ergebnisse, die mit Hilfe dieses Verfahrens bei Titrationen von einigen Bisazoderivaten der Chromotropsäure mit Ba^{2+}-bzw. UO_2^{2+}-Ionen erzielt wurden, sind in Tab. I zusammengestellt. Die Berechnung erfolgte auf der Rechenmaschine MSP 2.*

Kombinierte nummerisch-graphische Auswertung. Den Verlauf einer Titrationskurve kann man statt der impliziten Gl. (5*a*) auch explizit ausdrücken:

$$x = \tfrac{1}{2}(u + v + K^{-1}) - [\tfrac{1}{4}\,(u + v + K^{-1})^2 - uv]^{1/2} \tag{28}$$

Die Ordinate für den Schnittpunkt von t_0 mit a_1 lautet unter Berücksichtigung von Gl. (12):

$$x = u_t - (u_t^2 - u_t v)^{1/2} \tag{29}$$

Nach Quadrierung und Umformung resultiert für v:

$$v = 2x - \frac{x^2}{u_t} \tag{30a}$$

Aus Gl. (17) erhält man analog

$$v = u_t\left(2\frac{A_0}{A_t} - \frac{A_0^2}{A_t^2}\right). \tag{30b}$$

Diese Auswertungsmethode ist besonders günstig, wenn Messungen bei sehr großen Titrant-Überschüssen (A_0) möglich sind (z.B. durch Zugabe eines Kriställchens in die Meßküvette, vgl. Ref. 3). Die Tangente t_0 wird unmittelbar durch die gemessenen Punkte am Anfang der Titration gelegt.[2] Die Tangente t_0 kann auch gemäß den Gesetzmäßigkeiten der Titrationskurve als einer Hyperbel konstruiert werden.

Graphische Auswertungsmethoden. Die graphischen Auswertungsmethoden folgen aus der Definition der Titrationskurve als einer Hyperbel, die wie jede Kegelschnittlinie durch fünf Elemente eindeutig definiert ist. Für die graphische Lösung der Gl. (17)

---

* Herrn Dr. J. Lang aus UJEP Brno danken wir für die Programmierung und Berechnung.

müssen nur drei auf der Titrationskurve liegende Punkte experimentell bestimmt werden. Zwei weitere Angaben sind von Anfang an bekannt: die Titrationskurve geht durch den Koordinatenursprung und eine der Asymptoten (a_1) liegt parallel zur Abszissenachse. Diese interessante Auswertungsmöglichkeit hat jedoch nur geringe praktische Bedeutung. Nur selten liegen diese drei Punkte in einer günstigen Lage auf der Kurve und außerdem werden hohe Forderungen an die Meßgenauigkeit gestellt.

Aus der Diskussion der Zusammenhänge zwischen der Geometrie der Titrationshyperbel und dem Äquivalenzpunkt geht hervor, daß es für eine geometrische Bestimmung des Äquivalenzpunktes genügt, die Asymptote a_1 und die Richtung der Asymptote a_2 zu konstruieren. Der Schnittpunkt der durch den Koordinatenursprung führenden Parallele zu a_2 mit a_1 ist der gesuchte Äquivalenzpunkt. Man kann auch den Äquivalenzpunkt bestimmen, indem die Entfernung zwischen dem Mittelpunkt der Titrationshyperbel und dem Schnittpunkt von a_1 mit t_0 halbiert wird.

Die Asymptoten der Titrationshyperbel werden zweckmässig mit Hilfe des Pascalschen Satzes konstruiert (Abb. 5): Auf der Titrationskurve werden 4 Punkte markiert (drei dieser Punkte dürfen zusammen nicht auf einer Geraden liegen). Man beziffert sie zweckmässig in der Reihenfolge *1*, *3*, *2*, *4*. Die Punkte *1* und *2* werden zu einer Geraden verbunden und durch Punkt *4* wird eine Parallele zu a_1 (d.h. der Abszissenachse) geführt. Der Schnittpunkt dieser Geraden wird als I bezeichnet. Auf ahnliche Weise wird der Schnittpunkt II der Geraden $\overline{34}$ mit einer Asymptotenparallele im Punkt 1 bestimmt. Die Verbindung I–II stellt die Pascalsche Gerade p_1 dar. Durch den Schnittpunkt der Geraden $\overline{23}$ und p_1 führt die Asymptote a_1.

Zur Konstruktion der schrägen Asymptote a_2 und des Mittelpunktes der Titrationshyperbel wird durch den Schnittpunkt III der Geraden $\overline{34}$ mit der Asymptote a_1 die Pascalsche Gerade p_2 (Parallele mit $\overline{13}$) geführt. Die Gerade, die den Schnittpunkt IV der Geraden p_2 mit einer durch *1* geführten Parallele zu a_1 mit *4* verbindet, gibt die Richtung der Asymptote a_2 an. Durch den Koordinatenursprung wird nun eine Parallele zu a_2 geführt und ihr Schnittpunkt mit a_1 bestimmt.

Die durch *1* geführte Parallele zu a_2 und die durch 4 gelegte Parallele zu a_1 schneiden sich im Punkt V. Die Gerade IV–V schneidet a_1 in dem Mittelpunkt der Hyperbel.

Außer den angeführten Konstruktionen, deren Beschreibung als eine Arbeitsanweisung zu betrachten ist und deshalb einige formelle Gepflogenheiten der Geometrie nicht respektiert, können auch weitere geometrische Konstruktionen[17] verwendet werden. Sie sind in den Lehrbüchern der Geometrie zu finden (siehe z.B. Ref. 26).

Die beschriebenen Konstruktionen wurden an Modell-Titrationskurven überprüft, die mit Hilfe* des Computers MINSK 22 für einen Komplex M_aL_b berechnet wurden nach:

$$\frac{X}{(1-aX)^a} = k(B-bX)^b \tag{31}$$

wobei $X = x/v$; $B = u/v$; $k = K.v^{a+b-1}$. Für diese Versuche wurden Kurven mit $a = b = 1$ bei $1 < Kv < 50$ verwendet. Es wurde empirisch festgestellt (Änderung von x), daß reproduzierbare Ergebnisse nur bei einer Genauigkeit der experimentellen Messungen besser als 1% erzielt werden können. In Abb. 5 wird als Beispiel die photometrische Titration von Arsenazo III mit UO_2^{2+} bei pH 1,03 ausgewertet. Der Endpunkt v_t wird einem theoretischen Äquivalenzpunkt gleichgesetzt; er wurde mit Hilfe der coulometrischen Titration[27] bestimmt. Der festgestellte Fehler $(v - v_t) = +3{,}9\%$ kann den Bedingungen als angemessen betrachtet werden. Für die Titration gilt $Kv = 1{,}8$ und sie kann "klassisch" keinesfalls ausgewertet werden (Fehler +56%).

---

* Für Programm und Berechnung sind wir den Herren Dr. Štych und ing. A. Prokop aus VAAZ Brno zu Dank verpflichtet.

TABELLE I.—ERGEBNISSE DER NUMMERISCHEN TITRATIONSAUSWERTUNG

Verbindung	Kv	v_{gegeben},* M	v_{gefunden}, M	s,† M
Sulfonazo III	4,3	$1{,}00 \cdot 10^{-4}$	$1{,}07 \cdot 10^{-4}$	$0{,}04 \cdot 10^{-4}$
Arsenazo III	1,8	$0{,}112 \cdot 10^{-4}$	$0{,}116 \cdot 10^{-4}$	$0{,}002 \cdot 10^{-4}$
Methylsulfonazo III	1,6	$0{,}20 \cdot 10^{-4}$	$0{,}17 \cdot 10^{-4}$	$0{,}01 \cdot 10^{-4}$

* Coulometrisch nach Ref. 27 bestimmt.

† Standardabweichung aus der Streuung der Meßpunkte um die Titrationshyperbel berechnet.

Um den hohen Forderungen auf die Genauigkeit der experimentellen Bestimmung der Ausgangspunkte für weitere geometrische Konstruktionen zu genügen, ist es zweckmässig, zuerst die Titrationskurve in einem Gebeit bis etwa 2–3 v aus einer großen Anzahl von Meßpunkten zu konstruieren, und erst dann passende, auf der Kurve liegende Punkte auszuwählen.

Auswahl und Begrenzung der graphischen Auswertungsmethoden. Die graphische Auswertung einer Titrationshyperbel erfordert, daß die Kurve eine angemessene Krümmung aufweist. An den Modell-Kurven wurde gezeigt, daß die Bedingung etwa bei $1 < Kv < 30$ erfüllt ist. Bei $Kv < 1$ verlaufen die Kurven zu flach. Bei $Kv > 30$ ist es möglich, die kombinierte Auswertung nach Gl. (30) anzuwenden. Die erforderliche Asymptote a_1 wird entweder aus A_0 (experimentell) oder auch mit Hilfe des Pascalschen Satzes konstruiert.

Es ist sinnvoll, einen Quotienten r für die Beurteilung des Wertes von Kv (der bei praktischen Titrationen unbekannt ist) und somit auch für die Wahl der Auswertungsmethode zu definieren:

$$r = \frac{A_0 - A_t}{A_0} \tag{32}$$

Aus Gl. (12) und (30) folgt weiter

$$r = \frac{1}{Kv}\left(\sqrt{Kv + 1} - 1\right). \tag{33}$$

In Abb. 6 ist die Funktion $r = f(Kv)$ dargestellt. Daraus folgt, da eine übliche lineare Extrapolation bei $r < 0{,}1$ möglich ist. Für $0{,}1 < r < 0{,}2$ ist die graphisch-nummerische, für $0{,}2 < r < 0{,}4$ die graphische Auswertung vorzuziehen. Bei $r > 0{,}4$ ist die Auswertung einer Titrationskurve nicht empfehlenswert.

Schlußfolgerungen

Die Kenntnis der geometrischen Form der Titrationskurven bei Titrationen ohne Indikator ermöglicht auch eine Auswertung von Titrationskurven, wenn relativ dissoziierte Reaktionsprodukte entstehen. Aus den abgeleiteten Beziehungen für die Bildung von Komplexen ML (1:1) folgt eine allgemeine Empfehlung für die Auswertung der Titration: (*a*) Die Maßlösung muß mindestens 10^2mal konzentrierter sein als die Konzentration des zu bestimmenden Stoffes. (*b*) Die Titration wird so lange fortgesetzt, bis ein etwa dreifacher Überschuß des Titrants vorhanden ist. (*c*) Durch die Bestimmung von r wird der Wert von Kv abgeschätzt. Die experimentellen Bedingungen bei einer Titration, bei der dissoziierte Reaktionsprodukte entstehen, müssen äußerst streng konstant gehalten werden, da eine Verschiebung

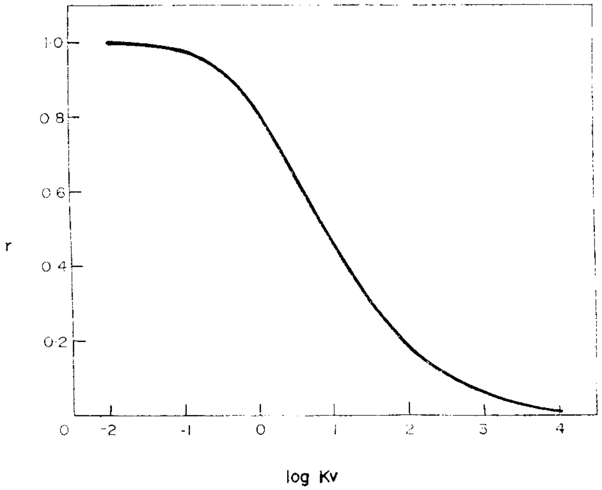


Abb. 6.—Schätzung des Wertes von *Kv* aus der Form der Titrationskurve.

des *K*-Wertes zu bedeutenden Deformationen der Titrationskurven führt. Der Analytiker sollte daher zuerst bestrebt sein, durch geeignete Maßnahmen die Bedingungen der Titration so zu ändern, daß die Dissoziation möglichst unterdrückt wird.

Herrn Prof. Dr. Lumír Sommer, DrSc., aus UJEP Brno, sind wir für sein Interesse und Unterstützung zu besonderem Dank verpflichtet.
Herrn Prof. Dr. Karel Svoboda, DrSc., aus UJEP Brno, danken wir für fachliche Beratung in geometrischen Fragen.

Summary—Photometric titration curves have been analysed in terms of the hyperbola form derived from a plot of a linearly related variable, in the absence of an indicator. Titration curves can be evaluated for the formation of ML-type complexes even when these are considerably dissociated, *i.e.*, when the product of the formation constant and the concentration of the species being determined falls as low as unity. Limiting conditions for the successful evaluation of curves are discussed. The applicability of the method has been checked on practical systems.

Résumé—On a analysé des courbes de titrage photométrique en fonction de la forme hyperbole déduite d'un graphique d'une variable reliée linéairement, en l'absence d'un indicateur. On peut évaluer les courbes de titrage pour la formation de complexes du type NL même lorsque ceux-ci sont considérablement dissociés, c'est-à-dire lorsque le produit de la constante de formation par la concentration de l'espèce à déterminer s'abaisse jusqu'à l'unité. On discute des conditions qui limitent l'évaluation satisfaisante des courbes. Les possibilités d'application de la méthode ont été vérifiées dur des systèmes pratiques.

LITERATUR

1. Z. Slovák, J. Fischer und J. Borák, *Talanta*, 1968, **15**, 831.
2. *Idem*, *ibid.*, 1969, **16**, 215.
3. J. Borák, Z. Slovák und J. Fischer, *ibid.*, 1970, **17**, 215.
4. G. Charlot, *Les méthodes de la chimie analytique. Analyse quantitative minerale.* Russ. Übersetzung, Khimiya, Moskau, 1965.
5. H. Flaschka, *Talanta*, 1961, **8**, 381.
6. J. H. Boulad, *Bull. Soc. Chim. France*, 1936, 408.
7. J. Mika, *Z. Anal. Chem.*, 1934, **98**, 3.

8. D. L. Lydersen, *ibid.*, 1966, **218**, 161.
9. A. L. Underwood, *Advan. Anal. Chem. Instrumentation*, 1964, **3**, 31.
10. B. M. Marianow, *Zh. Analit. Khim.*, 1966, **21**, 905.
11. *Idem*, *ibid.*, 1967, **22**, 5.
12. C. Liteanu und D. Cörmös, *Talanta*, 1960, **7**, 18.
13. I. M. Kolthoff und J. J. Lingane, *Polarography*, Interscience, New York 1946.
14. L. Meites und J. A. Goldman, *Anal. Chim. Acta*, 1964, **30**, 280.
15. R. F. Godu und D. N. Hume, *Anal. Chem.*, 1954, **26**, 1679.
16. A. Ringbom, *Complexation in Analytical Chemistry*, Interscience, New York, 1st Revised Printing, 1968.
17. A. Langer und D. P. Stevenson, *Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 770.
18. V. Majer, *Z. Elektrochemie*, 1936, **42**, 123.
19. P. Adámek, J. Doležal und J. Zýka, *Collection Czech. Chem. Commun.*, 1963, **28**, 2131.
20. V. A. Khadeev, *Uzb. Khim. Zh.*, 1959, No. 2, 27.
21. E. Grunwald, *Anal. Chem.*, 1956, **28**, 1112.
22. G. Loria, *Spezielle algebraische und transzendente ebene Kurven*, Band I und II, G. B. Teubner, Leipzig, 1910.
23. G. den Boef, *Chem. Weekblad*, 1967, **63**, 201.
24. O. Th. Bürklen, *Mathematische Formelsammlung*, 3. Ed., Göschen, Leipzig, 1904.
25. C. N. Reilley, R. W. Schmied und F. S. Sadek, *J. Chem. Educ.*, 1959, **36**, 555.
26. R. Haussner, *Darstellende Geometrie*, Band I und II, 2. Ed., Göschen, Berlin, 1912.
27. Z. Slovák und J. Borák, *Chem. Průmysl*, 1968, **18**, 82.

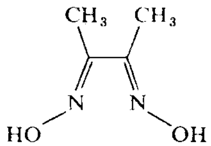
Talanta, 1971, Vol. 18, pp. 631 to 634. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

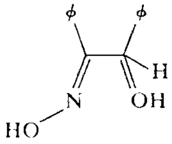
Chelating properties of α-oximinocarboxamides—I α-Oximinophenylacetamide isomers

(*Received* 8 *August* 1969. *Accepted* 9 *January* 1971)

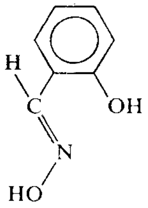
SINCE the introduction of α-nitroso-β-naphthol by Ilinski and Von Knorre for gravimetric determination of Co(II), extensive studies have been devoted to the development of organic reagents suitable for metal ion analysis.[1,2] Such organic reagents have a combination of atoms—the so-called functional analytical group—through which the metal ion is captured with the formation of one or more chelate rings. The high stability shown by complexes of this type is apparently due to ring formation.[3] An oxime group proximal to another electron-donor in an organic molecule constitutes a potential chelating agent. Many oxime-containing chelating agents are very useful in metal ion analysis. *anti*-Dimethylglyoxime (I) is a notable example. Others include benzoin-*anti*-oxime (II), salicylaldoxime (III), benzil monoxime (IV) and phenyl 2-pyridyl ketone oxime (V).



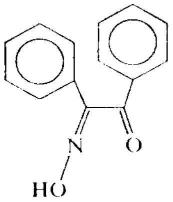
(I)



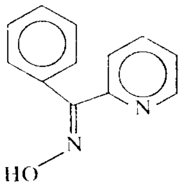
(II)



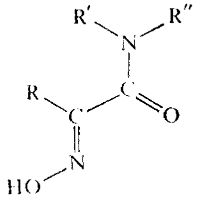
(III)



(IV)



(V)



(VI)

In the present work, α-oximinocarboxamides (VI) are proposed as chelating agents of potential analytical value. In these compounds the functional analytical group is an oxime in which the ketone or amine moieties of the adjacent amide group can function as donors.

The prototype chosen was α-oximinophenylacetamide (AOPA). The two geometric isomers were prepared and the structure assignment was made by spectrometric methods.

EXPERIMENTAL

Reagents

Hydroxylamine hydrochloride and ethyl phenylglyoxylate were used without further purification. Ethyl phenylmalonate was distilled prior to use.

Preparation of syn-*α-oximinophenylacetamide*

Ethyl α-oximinophenylacetate was prepared[4] (m.p. 110–1°; literature[4] 112°) and 8 g (0·04 mole) were dissolved in 40 ml of aqueous ammonia (28%). The solution was allowed to stand for one week. Excess of ammonia was removed on the flash evaporator, and the corresponding α-oximinocarboxamide crystallized out. The product was recrystallized from 50% alcohol, m.p. 166–7° (all melting points are uncorrected).

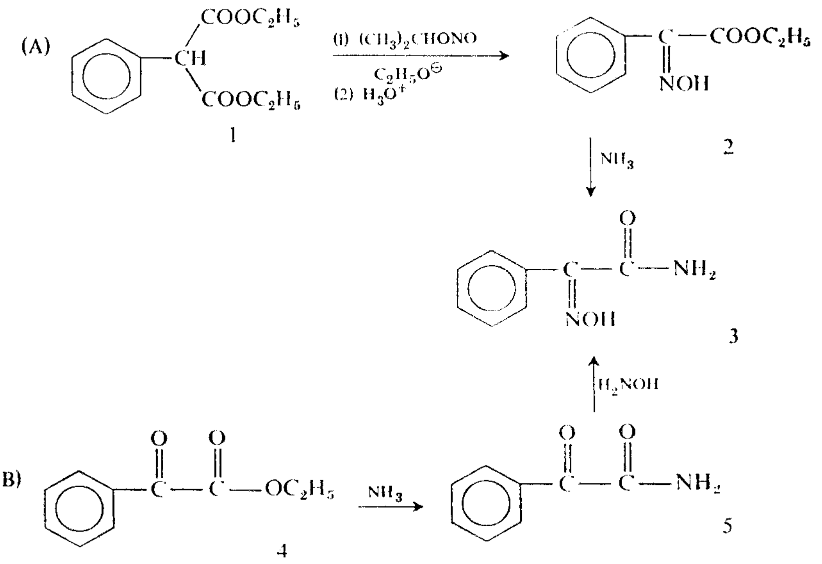
Found: C 58·6%; H 4·8%; N 17·1%; Calcd. for $C_8H_8N_2O_2$: C 58·53%; H 4·91%; N 17.06%.

Preparation of anti-*α-oximinophenylacetamide*

The compound was prepared according to the procedure of Moses *et al.*,[5] and melted at 195–7° (literature[6] 200°).

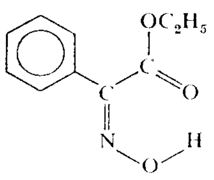
RESULTS AND DISCUSSION

α-Oximinophenylacetamide was prepared according to the schemes indicated:

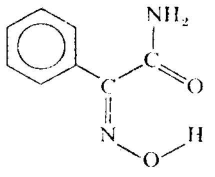


The product obtained according to route (A) melts at 166–7° while route (B) gives a product melting at 195–7°. It seemed obvious that two isomers of AOPA could be obtained, depending on the method of preparation. Structure assignments were based on spectrometric data described below. The infrared spectra of ethyl α-oximinophenylacetate in chloroform and carbon tetrachloride were found to be concentration independent. This suggests the presence of intramolecular hydrogen-bonding. In order to participate in intramolecular hydrogen-bonding, the —OH group of the oxime function should be *cis* to the carbonyl group. This isomer was designated the *syn*-isomer as indicated in structure VII.

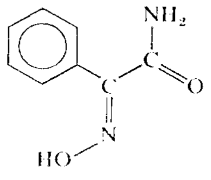
The infrared dilution technique was then extended to study the two isomers of AOPA. With acetonitrile and tetrahydrofuran as solvents, absorption in the high-frequency region (3200–3600 cm^{-1}) of the low-melting isomer was found to be concentration independent. However, in the case of the high-melting isomer, high-frequency bands (3200–3600 cm^{-1}) changed with concentration. Accordingly, it was concluded that the low-melting isomer exhibits intramolecular hydrogen-bonding as in the case for the ester precursor, and is the *syn*-isomer (VIII). The high-melting compound shows intermolecular hydrogen-bonding and is the *anti*-isomer (IX).



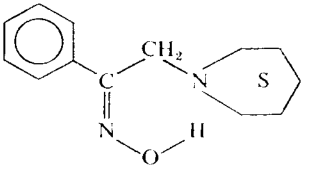
(VII)



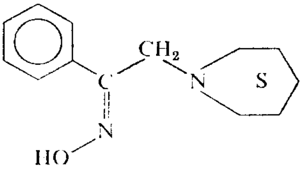
(VIII)



(IX)



(X)



(XI)

Chow and Colon made the isomer assignment of β-piperidinoacetophenone oximes by NMR spectrometry.[7] They found that the —OH proton signal of the *syn*-isomer (X) is further downfield than that of the *anti*-isomer (XI) owing to intramolecular hydrogen-bonding in the former. NMR spectra obtained from deuterated DMSO solutions of the isomers of AOPA showed the —OH proton signal of that assigned as *syn* to appear at 11.4 ppm whereas it appeared at 11.0 ppm for the one assigned as *anti* (TMS external). The NMR data are in agreement with the case cited, thus confirming the structure assignments based on the infrared dilution studies.

It was found that the *syn*-isomer has chelating properties toward Cu(II), Ni(II) and Co(II) but the *anti*-isomer lacks this property. Quantitative studies concerning the chelating properties of *syn*-AOPA will be published elsewhere.

Acknowledgement—The authors gratefully acknowledge the gift of a sample of α-oximinophenylacetamide (high melting) from Dr. Pinchas Moses of Kungl. Farmaceutiska Institutet.

Department of Chemistry, College of Pharmacy
University of Illinois at the Medical Center
Chicago, Illinois 60612

Dominick A. Coviello®
Hamed M. El-Fatatry*

Summary—Various polyfunctional oximes chelate with metals provided that the other functional group is proximal to the oxime and contains a good donor atom or is a good donor itself. Thus α-oximinocarboxamides are potential chelating agents of analytical value since the amide function attached to the carbon atom bearing the oxime has two groups capable of functioning as donors (ketone and amine). Two isomers of α-oximinophenylacetamide (AOPA) were obtained by two different synthetic routes, and structures were assigned by spectrometric methods. *syn*-AOPA was found to have chelating properties, but the *anti*-isomer did not. The synthesis and details of structure assignments are reported here.

Zusammenfassung—Verschiedene mehrfunktionelle Oxime bilden Chelate mit Metallen, wenn die andere funktionelle Gruppe zur Oximgruppe benachbart ist und ein gutes Donoratom enthält bzw. selbst ein guter Donor ist. So stellen α-Oximinocarboxamide potentielle Chelatbildner von analytischem Wert dar, da die Amidfunktion an dem die Oximgruppe tragenden Kohlenstoffatom zwei Gruppen mit Donoreigenschaften enthält (Keton und Amin). Zwei Isomere von α-Oximinophenylacetamid (AOPA) wurden auf zwei verschiedenen Synthesewegen erhalten und mit spektrophotometrischen Methoden die Strukturen festgestellt. Syn-AOPA hat chelatbildende Eigenschaften, anti-AOPA nicht. Die Synthese und Einzelheiten der Strukturzuordnung werden hier mitgeteilt.

Résumé—Diverses oximes polyfonctionnelles forment des chélates avec les métaux lorsque l'autre groupe fonctionnel est le plus rapproché de l'oxime et contient un atome bon donneur ou est un bon donneur lui-même. Ainsi, les α-oximinocarboxamides sont des agents chélatants potentiels de valeur analytique car la fonction amide attachée à l'atome de carbone portant l'oxime a deux groupes capables de fonctionner comme donneurs (cétone et amine). On a obtenu deux

---

* Present address: Department of Chemistry, College of Pharmacy, Cairo University, Cairo, U.A.R.

isomères de l'α-oximinophénylacétamide (AOPA) par deux voies synthétiques différentes, et les structures ont été assignées par des méthodes spectrophotométriques. On a trouvé que le *syn*-AOPA a des propriétés chélatantes, mais l'*anti*-isomère n'en a pas. On rapporte ici les synthèses et les détails sur l'attribution de structure.

REFERENCES

1. A. I. Busev and N. G. Polianski, *The Use of Organic Reagents in Inorganic Analysis*, translated J. T. Graves, Pergamon, New York, 1960.
2. M. Ilinski and G. Von Knorre, *Ber.*, 1885, **18**, 699.
3. G. Schwarzenbach, *Helv. Chim. Acta*, 1952, **35**, 2344.
4. W. Wislicenus and R. Grutzner, *Ber.*, 1909, **42**, 1930.
5. P. Moses, R. Dalilbom and B. Sjöberg, *Arkiv Kemi*, 1964, **22**, 451.
6. A. J. van Peski, *Rec. Trav. Chim.* 1922, **41**, 687.
7. Y. L. Chow and C. J. Colon, *J. Org. Chem.*, 1968, **33**, 2598.

Talanta, 1971, Vol. 18, pp. 634 to 638. Pergamon Press. Printed in Northern Ireland

Rapid polarographic method for the microdetermination of organically-bound phosphorus

(*Received* 22 *July* 1970. *Accepted* 12 *October* 1970)

SEVERAL procedures have been reported in the literature for the microdetermination of phosphorus in organic compounds. The most widely applied methods depend principally on the precipitation of phosphorus, after oxidation to phosphate, either as ammonium phosphomolybdate[1,2] or as quinoline phosphomolybdate.[3,4] The phosphorus content is then determined gravimetrically[1,2] or titrimetrically[1-4] after dissolution of the precipitate in a measured excess of alkali and back-titration with standard acid. However, the ammonium phosphomolybdate method has its shortcomings[3,4] compared with the quinoline phosphomolybdate method, which has proved suitable not only for micro work but also for the submicro scale.[5]

For compounds of low phosphorus content or generally for small amounts of phosphorus (0·01–0·4 mg), the determination is usually carried out spectrophotometrically. Kirsten,[6] and Kirsten and Carlsson,[7] measured the absorbance of phosphomolybdic acid; most other investigators[2,8] measured the molybdenum blue obtained on reduction.

Surprisingly, the potentialities of a polarographic finish seem to have been ignored. The only work reported is that of Stern[9] who applied a polarographic finish for the estimation of phosphorus in biological material after precipitation as ammonium phosphomolybdate. Indirect polarography, in particular, has already proved to be a rapid and sufficiently accurate means for the estimation of sulphur[10] and functional groups.[11] In the present method, a measured excessive volume of molybdate solution is added to the phosphate solution to precipitate the quinoline phosphomolybdate complex. The polarogram is recorded without separation of the precipitate, and the wave-height corresponding to the amount of unconsumed molybdate is measured. This is then subtracted from the wave-height obtained for a blank solution containing the same total amount of molybdate but no organic sample.

EXPERIMENTAL

Apparatus

Combustion was carried out in a 300-ml conical flask filled with oxygen. An Orion OH-101 polarograph was used. The electrolytic vessel was the universal U-shaped Kalousek cell. The dropping mercury electrode had a drop-time of 4 sec under an open head of 0·60 m of mercury. The molybdenum wave was recorded with the saturated calomel electrode as the anode.

Reagents

All reagents used were analytical or microanalytical-reagent grade.

Sodium hydroxide, 0·5*M*.

Hydrochloric acid, 5*M*.

Sodium molybdate. Prepared by mixing 7·802 g of molybdenum trioxide, 3·750 g of sodium hydroxide and 125 ml of water. The mixture was heated for 15–20 min then filtered. To the filtrate, 115 ml of concentrated hydrochloric acid were added and the volume made up to 250 ml with doubly distilled water (1 ml ≡ 20·8 mg of Mo). The solution was kept in a polythene bottle.

Quinoline hydrochloride. Doubly distilled quinoline (14 ml) was dissolved in 300 ml of 1·5*M* hydrochloric acid.

Gelatine solution, 1·5%. Prepared weekly.

Procedure

Burn an accurately weighed amount (3–8 mg) of the organic sample in the usual way in the oxygen flask, absorbing the products in a mixture of 7 ml of 0·5*M* sodium hydroxide and 3 ml of saturated bromine water. After combustion, shake for 10 min, rinse the stopper and platinum gauze with *ca.* 10 ml of doubly distilled water and boil gently for 2–3 min. Add 1 ml of 5*M* hydrochloric acid and continue boiling till all the bromine is expelled. To the colourless solution add exactly 3 ml of sodium molybdate solution. At this stage, the total volume of solution is 15–25 ml. Precipitate by introducing 3 ml of quinoline hydrochloride to the hot solution slowly with swirling. Boil briefly, then leave to cool.

Transfer the solution and precipitate quantitatively to a 50-ml measuring flask. Add 20 drops of 1·5% gelatine solution, then doubly distilled water up to the mark. Mix well, transfer an aliquot to the cathode compartment of the cell and record the polarogram starting from +0·10 V *vs.* the S.C.E. as anode. Repeat for a blank run.

The phosphorus content is calculated from the equation;

$$\%P = \frac{100AB(T - S)}{12CTW}$$

where A = atomic weight of phosphorus.
B = mg of Mo/3 ml of the sodium molybdate solution.
C = atomic weight of molybdenum.
W = weight of sample, mg.
T = height of blank wave.
S = height of sample wave.

RESULTS AND DISCUSSION

The present work makes use of the already established procedure of Wilson[3] for precipitation of quinoline phosphomolybdate, but uses polarography to determine the surplus molybdate, thus avoiding the filtration.

A well-defined molybdate wave had therefore to be obtained, with a linear relationship between wave-height and molybdenum concentration.

The molybdenum wave

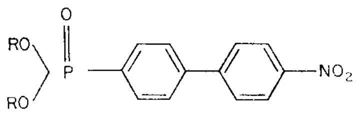
In the quinoline phosphomolybdate method,[3–5] precipitation is from hydrochloric acid medium. The cathodic reduction wave of Mo(VI) in this medium has been studied by Holtje and Geyer,[12] who reported that the acidity affected the reduction process, whether to Mo(V), the red Mo(III), the green Mo(III) or to $Mo(OH)_3$. Later, Carritt[13] found that in 0·3*M* hydrochloric acid, two waves were obtained corresponding to the reductions to Mo(V) and Mo(III) with half-wave potentials of −0·26 and −0·63 V *vs.* S.C.E. In 0·8*M* acid, three waves were obtained, the first two not completely resolved.

In our preliminary experiments, 0·013*M* molybdenum in 0·75*M* hydrochloric acid with 0·02% gelatine gave a single well-defined wave with $E_{1/2}$ at +0·10 V *vs.* S.C.E. It seemed that under these conditions and at such relatively high concentrations, the anodic oxidation wave of Cl^- and the cathodic reduction wave of Mo(VI) were fused into a single wave. Consequently, the wave-height corresponded to the concentrations of both ions.

Another solution containing the same concentration of molybdenum, and gelatine, but in 0·43*M* hydrochloric acid gave a well-developed wave at −0·25 V *vs.* S.C.E. and the wave-height corresponded only to the concentration of Mo(VI), and varied linearly with concentration over the range $1·3 \times 10^{-2}$ to $4·3 \times 10^{-3}M$.[14]

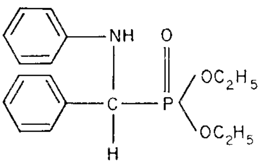
TABLE I.—MICRODETERMINATION OF PHOSPHORUS IN ORGANIC COMPOUNDS

Compound	Weight, *mg*	P, %		Error, %
		Calc	Found	
Triphenylphosphine	5·574	11·82	11·8$_0$	−0·0$_2$
	5·209		11·8$_3$	+0·0$_1$
	5·456		12·3$_1$	+0·4$_9$
	4·646		12·1$_5$	+0·3$_3$
	6·645		11·6$_5$	−0·1$_7$
Triphenylphosphine sulphide	5·940	10·53	10·5$_6$	+0·0$_3$
	6·900		10·1$_0$	−0·4$_3$
p-Phenylenebisdiphenylphosphonamide	6·895	12·18	12·3$_4$	+0·1$_6$
	5·462		12·3$_6$	+0·1$_8$
Diphenylphosphinodithioic acid	7·975	12·37	12·0$_1$	−0·3$_6$
	6·213		12·1$_2$	−0·2$_5$
Research compound, I	7·464	10·21	10·2$_6$	+0·0$_5$
	5·557		10·8$_1$	+0·6$_0$
	7·738		9·6$_5$	−0·5$_6$
Research compound, II	5·545	9·35	8·9$_3$	−0·4$_2$
	6·976		9·7$_1$	+0·3$_6$
	6·527		9·2$_8$	−0·0$_7$
Research compound, III	3·007	8·62	8·1$_0$	−0·5$_2$
	6·573		8·5$_2$	−0·1$_0$
Research compound, IV	6·181	9·69	9·9$_3$	+0·2$_4$
	6·229		9·1$_6$	−0·5$_3$
	6·226		10·0$_4$	+0·3$_5$
Research compound, V	5·764	6·67	6·1$_6$	−0·5$_1$
	6·567		6·9$_1$	+0·2$_4$

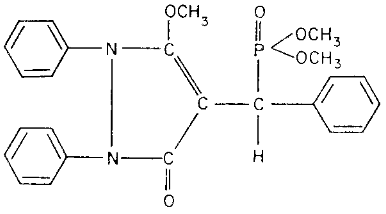


$R = CH_3,\ C_2H_5$ and $i-C_3H_7$

For research compounds I, II and III respectively



IV



V

FIG. 1.

The polarograms were recorded from +0·1 to −0·8 V *vs.* S.C.E. Oxygen was found not to interfere, especially at the low sensitivity used, so bubbling with nitrogen was not necessary.

Conditions of precipitation

The relatively low final acidity of 0·43*M* hydrochloric acid did not affect the quantitative precipitation of the quinoline phosphomolybdate. This is evident from the results given in Table I.

In order to attain complete precipitation, all procedures applying the quinoline phosphomolybdate method employ a large excess of molybdenum, but in any indirect method maximal precision is attained when the amount of precipitant added in excess is kept small compared to that precipitated. The phosphorus content of the available organophosphorus compounds ranged from 5 to 15%. Therefore, a volume of 3 ml of sodium molybdate (62·4 mg of Mo) was slightly more than sufficient to react with up to 8 mg of the compound with the highest phosphorus content leaving a slight excess of Mo(VI) to be determined polarographically. In the analysis of 8 mg of diphenylphosphinodithioic acid (*ca.* 1 mg of phosphorus), the excess of Mo(VI) amounted to 65%. This slight excess, however, proved adequate for the complete precipitation of phosphorus as quinoline phosphomolybdate (*cf.* Table I).

Decomposition of organophosphorus compounds

This can be achieved in a number of ways, *e.g.*, fusion with a mixture of sodium carbonate and potassium nitrate, wet oxidation with sulphuric or nitric acid, fusion in a nickel bomb, or the oxygen flask method of combustion. The last named method is undoubtedly the simplest. Different absorbing media were suggested; dilute nitric acid,[15] dilute sulphuric acid,[8] hydrogen peroxide[16] or sodium hypobromite.[4,5] Nitric acid or hydrogen peroxide were found to be ineffective[4] and sulphuric acid may lead to high and erratic results.[2] An alkaline sodium hypobromite solution has proved to be an efficient absorbent for all the available organophosphorus compounds.

Interferences

Silicon, like phosphorus, forms an insoluble quinoline heteropolymolybdate. This interference was kept at a minimum by storing the molybdate reagent in a polythene bottle. During combustion and subsequent boiling, the attack of phosphorus pentoxide on the walls of the flask did not vitiate the results obtained (Table I).

Besides C, H, O and P, the available organic compounds contained S and N; Cl^- was also present in the final solution. None of these elements affected either the precipitation or the polarographic determination. Up to 2 mg of sulphur could be tolerated. Bromide, if present, would give an anodic oxidation wave[17] which does not interfere with that of Mo(VI). In the oxygen flask method, the presence of iodine in the organic sample would result in the formation of some iodate.[18] In acidic medium, iodate gives a cathodic reduction wave at −0·04 V *vs.* S.C.E.,[17] which would interfere with the molybdenum wave.

The time required for a sample determination is 40 min. About ten determinations can be carried out in a working day. The blank solution is prepared every morning and its polarogram recorded once in between the successive sample runs. In the case of considerable temperature variations, it is advisable to record the blank for every sample determination. Another advantage lies in the possibility of separating the quinoline phosphomolybdate precipitate and determination of the phosphorus content volumetrically.[3,4] Separation can be achieved before or after the polarographic determination of the unconsumed Mo(VI). In this way, two results can easily be obtained for one sample weight.

Besides being rapid and simple the method gives reasonably accurate results, as shown in Table I. The average error for 24 determinations amounts to ±0·28% absolute and the maximum error to 0·60%.

The twelvefold amplification reaction between phosphorus and molybdenum, to form phosphomolybdate, necessitates the use of a relatively large concentration of molybdenum. This, if scaled down to the submicro scale would still give a molybdenum concentration that could be measured polarographically at not too high a sensitivity. Further work will be carried out on this aspect.

Acknowledgment—We wish to thank Dr. M. M. Sidky and co-workers in the laboratory of Chemical Pesticides, for synthesis of almost all compounds used in this work.

National Research Centre
Dokki, Cairo, U.A.R.

S. W. Bishara
M. E. Attia

Summary—An indirect polarographic method for the microdetermination of phosphorus in organophosphorus compounds is described. Alkaline hypobromite is used as oxidizing absorbent. Quinoline phosphomolybdate is precipitated with a measured excess of standard molybdate solution. The unreacted Mo(VI) is determined polarographically. Nitrogen, chlorine, bromine and sulphur do not interfere. One determination takes 40 min. The results obtained fall generally within the acceptable limits of error.

Zusammenfassung—Ein indirektes polarographisches Verfahren zur Mikrobestimmung von Phosphor in phosphororganischen Verbindungen wird beschrieben. Als oxidierendes Absorptionsmittel wird alkalische Hypobromitlosung verwendet. Mit einem bekannten Überschuß an eingestellter Molybdatlösung wird dann Chinolinphosphomolybdat gefällt. Das nicht verbrauchte Mo(VI) wird polarographisch bestimmt. Stickstoff, Chlor, Brom und Schwefel stören nicht. Eine Bestimmung braucht 40 min. Die Ergebnisse liegen im allgemeinen innerhalb der annehmbaren Fehlergrenzen.

Résumé—On décrit une méthode polarographique indirecte pour le microdosage du phosphore dans des composés organo-phosphorés. On utilise l'hypobromite alcalin comme absorbant oxydant. On précipite le phosphomolybdate de quinoléine avec un excès mesuré de solution étalon de molybdate. Le Mo(VI) qui n'a pas réagi est déterminé polarographiquement. Azote, chlore, brome et soufre n'interfèrent pas. Un dosage nécessite 40 mn. Les résultats obtenus se situent généralement dans les limites d'erreur acceptables.

REFERENCES

1. I. M. Kolthoff and E. B. Sandell, *Quantitative Inorganic Analysis*, pp. 377, 682. Macmillan, London 1952.
2. G. Ingram, *Methods of Organic Elemental Microanalysis*, p. 339. Reinhold, New York, 1962.
3. H. N. Wilson, *Analyst*, 1951, **76**, 65; 1954, **79**, 535.
4. R. Belcher and A. M. G. Macdonald, *Talanta*, 1958, **1**, 185.
5. R. Belcher, A. M. G. Macdonald, S. E. Phang and T. S. West, *J. Chem. Soc.*, 1965, 2044.
6. W. J. Kirsten, *Microchem. J.*, 1967, **12**, 307.
7. W. J. Kirsten and M. E. Carlsson, *ibid.*, 1960, **4**, 3.
8. N. E. Gel'man and T. M. Shanina, *Zh. Analit. Khim.*, 1962, **17**, 969.
9. A. Stern, *Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 74.
10. S. W. Bishara, *Microchem. J.*, 1970, **15**, 211.
11. Y. A. Gawargious and S. W. Bishara, *Z. Anal. Chem.*, 1969, **245**, 366.
12. R. Holtje and R. Geyer, *Z. Anorg. Allgem. Chem.*, 1941, **246**, 258.
13. D. E. Carritt, cf. *Polarography* by I. M. Kolthoff and J. J. Lingane, 2nd Ed., Vol. 2, p. 457. Interscience, New York, 1952.
14. D. Ilkovič, *Collection Czech. Chem. Commun.*, 1934, **6**, 498.
15. A. M. Ryadnina, *Zavodsk. Lab.*, 1961, **27**, 405.
16. E. Meier, *Mikrochim. Acta*, 1961, 70.
17. I. M. Kolthoff and J. J. Lingane, *Polarography*, 2nd Ed., Vol. 2, p. 573. Interscience, New York, 1952.
18. A. M. G. Macdonald, *Analyst*, 1961, **86**, 3.

Talanta, 1971, Vol. 18, pp. 638 to 642. Pergamon Press. Printed in Northern Ireland

Amperometrische Bestimmung der Metalle unter Anwendung von Thioacetamid—X

Bestimmung von Kupfer in saurem pH-Gebiet

(*Eingegangen am* 29. *August* 1969. *Angenommen am* 15. *Mai* 1970)

IN FORTSETZUNG unserer Studien über Thioacetamid (TAA),[1–9] haben wir die Möglichkeit der Anwendung von TAA zur amperometrischen Bestimmung von Cu^+-ionen bei niedrigeren pH-Werten und auch bei Anwesenheit von Kationen mancher Begleitmetalle untersucht.

EXPERIMENTELLER TEIL

Apparatur

Wie vorher angegeben.[2]

Lösungen

Spektral-reines Kupfer und analytisch reine Nitrate von Zink, Blei, Eisen(II), Kobalt und Nickel wurden gelöst und komplexometrisch bestimmt. [Die Eisen(II)-Lösung wurde erst oxydiert und nachher komplexometrisch titriert.] Thalliumnitratlösungen wurden aus spektralreinem Thalliumnitrat als Standardlösung vorbereitet. TAA-Lösungen wurden wie vorher angegeben vorbereitet und aufbewahrt.[2]

Prozedur

Amperometrische Titrationen wurden bei konstanter Temperatur (25° ± 0,1°) unter Anwendung der Quecksilbertropfelektrode als Kathode und der gesättigten Kalomelelektrode (GKE) durchgeführt. Vor der Titration wurden die Kupfer(II)-Ionen mittels Hydroxylaminsulfats (HAS) zu Cu^+-Ionen reduziert. Der Grenzstromwert der Reduktion der Cu^+-Ionen wurde im Lauf der Titration bei konstantem Potential zwischen −0,25 und −0,40 V gegen der GKE registriert. Zur Entlüftung der Lösungen eignet sich sauerstoff-freier Stickstoff.

Außer HAS bildeten auch Urotropin und Kaliumnitrat, als Grundelektrolyt, stabile Bestandteile der untersuchten Kupfernitratlösung. Weitere eventuelle Bestandteile der Lösungen bildeten die nicht-oxydierende Säure, Kationen der Begleitionen, sowie entsprechende Komplexbildner, wie z.B. Acetationen. Der pH-Wert der untersuchten Kupfernitratlösungen lag allgemein zwischen 2,0 und 6,0.

Bestimmungen von Kupferionen bei Abwesenheit von Kationen fremder Metalle

Anfangs wurde HAS im Konzentrationsgebiet 0,2–12%, Urotropin 0,6–5,4 und Kaliumnitrat 1,8–3,0% angewendet. Der pH-Wert der Lösung hängt hauptsächlich von dem Konzentrationsverhältnis von HAS zu Urotropin ab.

Die folgende Tatsachen wurden festgestellt:

1. HAS bedingt in saurem Milieu, ähnlich wie in ammoniakalischem, die sofortige Durchführung der Cu^{2+} in Cu^+-Ionen.
2. Die polarographischen Wellen der Reduktion der Cu^+-Ionen sind deutlich ausgebildet, einstufig, mit Halbstufenpotential im Interval +0,05 bis −0,05 V.
3. Die Werte des konstanten Potential zwischen −0,25 und −0,40 V waren für die amperometrische Bestimmung der Cu^+-Ionen in saurem pH-Gebiet entsprechend.
4. Die Reaktionsgeschwindigkeit der Cu^+-Ionen mit TAA ist bei 25° ziemlich groß, und nicht geringer als in ammoniakalischen Lösungen.[1]
5. Sauerstoff, sogar in Spuren, bedingt längere Bestimmungszeiten und bei größerer Konzentration auch fehlerhafte Bestimmungen; unter anderen, infolge der Anwesenheit mancher leicht oxydierbarer Substanzen. Sorgfältige Entlüftung mittels sauerstoff-freien Stickstoffs eliminiert diese schädliche Folgen mit besserem Erfolg als im Fall der Anwendung des elektrolytisch entwickelten Wasserstoffs.

Bestimmung von Kupferionen bei Anwesenheit von Kationen fremder Metalle

Im Zusammenhang mit der Anwesenheit der Kationen fremder Metalle wurden im Laufe der Untersuchungen folgende Probleme berücksichtigt:

1. Die chemische Passivität der Begleitionen gegenüber TAA,
2. Der Einfluß der Begleitionen auf Verlauf und Ergebnisse der Cu^+-Ionenbestimmungen,
3. Die eventuelle Änderung des Bestimmungsvorgangs, infolge der spezifischen chemischen Eigenschaften der Begleitionen.

In diesen Untersuchungen wurden folgende Kationen berücksichtigt: Zn^{2+}, Tl^+, Pb^{2+}, Fe^{2+}, Co^{2+} und Ni^{2+}. Um Vergleiche zu erleichtern wurden die Untersuchungen im Fall jeder Art der Begleitionen in demselben Konzentrationsgebiet der Cu^+-Ionen durchgeführt, wobei dieselben Konzentrationsverhältnisse der Cu^+-Ionen zu Begleitionen, nähmlich $[Cu^+]:[M^{n+}] = 1:1$, 1:10, 1:100, 1:1000, 10:1 und 100:1 angewandt wurden.

Es wurde folgendes festgestellt:

1. Die Aktivität des TAA gegenüber Begleitionen war direkt auf experimentellem Wege nicht wahrnehmbar.
2. Im Fall der Begleitionen war keine nach komplexometrischen Bestimmungsmethoden feststellbare Änderung der Konzentration im Laufe der Kupferbestimmung zu beobachten.
3. Die Geschwindigkeit der TAA-Cu^+-Ionen Reaktion ist von der Konzentration der Begleitionen unabhängig.
4. Spuren von Sauerstoff in den untersuchten Lösungen der Cu^+-Ionen bedingen in Anwesenheit fremder Kationen dieselben unerwünschten Folgen wie in ihrer Abwesenheit, die jedoch durch genaue Entlüftung unter Anwendung des sauerstoff-freien Stickstoff weggelassen werden können.
5. Der Einfluß der pH-Werte der Lösungen auf Bestimmungsergebnisse war bei allen Begleitionen mit Ausnahme der Zinkionen ersichtlich.

Einfluß der Begleitionen auf die Cu^+-Ionen Bestimmung

Bei Anwesenheit von Zinkionen war keine Änderung des Bestimmungsverlaufes zu beobachten. Es wurde bei Anwesenheit übriger Begleitelemente eine mögliche Abweichung der Bestimmung der Cu^+-Ionen von dem Normalverlauf festgestellt, die aber unter Beachtung gewisser Vorsichtsmaßregeln vermieden werden kann.

Tl^+-Ionen. Zu große Kupfer(I) Konzentration ist infolge der engen Nachbarschaft der polarographischen Wellen von Kupfer und Thallium nicht zu bestimmen, besonders im Fall des größten Konzentrationsüberschusses $[Cu^+]:[Tl^+]$ 1:1000. Als maximal wurde die Cu^+-Ionen Konzentration von $4 \times 10^{-4}M$ angewandt. Aus demselben Grunde wurde auch das Bereich der zulässigen Potentialswerte zu dem Wert zwischen −0,15 und −0,25 V verschoben.

HAS, als Katalysator der TAA-Tl^+-Reaktion,[4] kann, besonders im Fall des größten Konzentrationsüberschusses der Tl^+-Ionen die Aktivität dieser Ionen gegenüber TAA verursachen und dadurch eine Abweichung der Cu^+-Ionen Bestimmung vom Normalverlauf bedingen. Als optimal wurden Konzentrationsbereiche 0,25-1,2% für HAS und 0,9-1,2% für Urotropin erachtet.

Pb^{2+}-Ionen. In Anwesenheit der Bleiionen war die Anwendung eines Komplexbildners, besonders im Bereich der höheren pH-Werte, erforderlich. Acetat in Konzentration von 6–12% wurde erfolgreich verwendet. Seine Anwesenheit bedingt keine negativen Nebenwirkungen. In Rücksicht auf die Möglichkeit der Bildung des unlöslichen Bleisulfats darf HAS nur in geringen Konzentrationen angewendet werden. Entsprechend sind HAS-Konzentrationen die den Wert 1,2% nicht übersteigen und zugleich Urotropinkonzentrationswerte von 0,9–1,8%.

Der Abstand −0,25 bis −0,35 V erwies sich als geeignet für die amperometrische Bestimmung des Kupfers in der Anwesenheit von Blei. Die Anwendung größerer Konzentration von Kupferionen, besonders bei tausendfachem Überschuß der Bleiionen ist infolge der Nachbarschaft der polarographischen Wellen von Kupfer und Blei (ähnlich wie im Fall der Thalliumionen) unzulässig. Die in solchem Fall verwendeten Konzentrationen der Kupferionen waren im allgemein nicht größer als $4 \cdot 10^{-4}M$.

Fe^{2+}-Ionen. In Hinsicht auf die Gefahr der Oxydation des TAA durch die Fe^{3+}-Ionen, welche oft zusammen mit den Fe^{2+}-Ionen vorkommen erwies sich die genaue Reduktion der Fe^{3+}-Ionen vor der eigentlichen Bestimmung der Kupferionen als wichtig. HAS, der als Reduktor der Kupferionen angewandt wird, übt zugleich die Funktion des Reduktors der *Fe^{3+}*-Ionen. Bei denselben Bedingungen verläuft aber die Reduktion der Fe^{3+}-langsamer als die der Cu^{2+}-Ionen, welche mittels HAS fast sofort reduziert werden. Das in diesem Falle zulässige pH-Intervall ist auch durch die Möglichkeit der Hydrolyse der Begleitsalze begrenzt. Konzentrationswerte zwischen 1,8 und 3,6% für HAS und 1,2 und 2,4% für Urotropin sind entsprechend.

Ni^{2+}-und Co^{2+}-Ionen. Kobalt verhält sich analog Nickel als Begleition von Kupfer. In Anwesenheit von Kobalt—wie auch Nickel—sind dieselben Konzentrationen von HAS und Urotropin wie bei Fe^{2+}-Ionen anwendbar.

Tabelle I.—Amperometrische Bestimmung der Cu^+-Ionen unter Anwendung von Thioacetamid in saurem pH-Intervall

				Auf 100 Bestimmungen	
$Cu(NO_3)_2$	$(NH_2OH)_2 . H_2SO_4$ %	Urotropin %	Art der Begleitionen	Fehler $\leqslant 1{,}0$ %	$1{,}0\% <$ Fehler $\leqslant 2{,}0$
$\geqslant 1{,}0 . 10^{-4}M$	0,3–2,4	0,9–1,8	—	77	18
			Zn^{2+}	82	14
	0,3–1,2		Pb^{2+}	74	22
			Tl^+	67	31
$<1{,}0 . 10^{-4}M$	0,3–2,4		—	54	39
			Zn^{2+}	58	34
	0,3–1,2		Pb^{2+}	66	33
			Tl^+	59	38
	1,8–3,6	1,2–2,4	Fe^{2+}	58	38
			Co^{2+}	64	30
			Ni^{2+}	64	32
	0,3–1,2	0,9–1,8	Pb^{2+}, Zn^{2+}	72	22
			Tl^+, Zn^{2+}	69	26
	1,8–3,6	1,2–2,4	Fe^{2+}, Zn^{2+}	58	30
			Co^{2+}, Zn^{2+}	42	55
			Ni^{2+}, Zn^{2+}	52	44

Aus den durchgeführten Untersuchungen folgt, daß die amperometrischen Bestimmungen der Cu^+-Ionen in saurem pH-Gebeit in Anwesenheit der Zinkionen bei denselben Bedingungen wie in Abwesenheit der Kationen fremder Metalle durchführbar sind. Die Tabelle I zeigt Bestimmungsergebnisse in Abwesenheit fremder Kationen.

DISKUSSION

TAA wurde für die amperometrische Bestimmung des Kupfers bei nicht erhöhten Temperatur zum ersten Mal in saurem pH-Gebiet angewandt. Die Methode kann folgenderweise kurz charakterisiert werden:

1. Die außerordentlich kleine Löslichkeit von Cu_2S ($2.10^{-17}M$)[11] und konsequent große Reaktionsgeschwindigkeit[12] sowohl die Genauigkeit der Bestimmungsergebnisse,
2. Die Möglichkeit der Bestimmung von Kupferionen in Anwesenheit mehrerer Metalle, ohne Trennung sowie Maskierung,
3. Die Möglichkeit der Abtrennung des Kupfers als Sulfid im Laufe der Bestimmung,
4. Ziemlich kurze Bestimmungszeit (16–20 Min),
5. Die Einfachheit sowohl der Vorbereitung der Lösungen als auch der Ausführung der Bestimmungen, und
6. Ziemlich gute Reproduzierbarkeit der Ergebnisse.

Die fast sofortige Einstellung des Gleichgewichtes, in der Reaktion der Cu_2S-Bildung bei niedrigeren pH-Werten spricht nicht nur dafür daß es hauptsächlich eine direkte Reaktion der Cu^+-Ionen mit TAA ist, sondern auch dafür, daß es wahrscheinlich die einzige Reaktion ist die zwischen TAA und diesen Ionen verläuft, daß also TAA mit den Cu^+-Ionen vermutlich nicht als Komplexbildner reagiert.

Es wurde gezeigt daß die Aktivität des TAA im Prozeß der Sulfidbildung nicht nur in ammoniakalischem[1] aber auch in saurem Milieu—in eigentlich gewählten Bedingungen—den ziemlich großen für amperometrische Bedingungen entsprechenden Wert, sogar bei der niedrigen Temperatur (25°) annehmen kann.

Anerkennung—An dieser Stelle sagen wir Frau Z. Białek und Frau E. Małkiewicz unseren Dank für Ihren Anteil im experimentellen Teil der vorliegenden Arbeit.

Institut für Allgemeine Chemie
Technische Hochschule
Mickiewicza 66
Szczecin, Polen

MARIA PRYSZCZEWSKA
EWA KRZESZOWSKA

Zusammenfassung—Es wird eine amperometrische Methode der Bestimmung von Kupfer(I) mittels Thioacetamid (TAA) in saurem pH-Gebiet beschrieben. Der Strom wird bei konstantem Potential zwischen −0,25 und 0,40 V gegen eine gesättigte Kalomelelektrode gemessen. Auch bei tausendfachemüberschuß stört die Anwesenheit von Zn^{2+}, Te^+, Pb^{2+}, Fe^{2+}, Co^{2+} und Ni^{2+} nicht. Die Reaktion verläuft bei Zimmertemperatur schnell, und der Durchschnittsfehler liegt zwischen 1 und 2%.

Summary—A method is described for the amperometric titration of copper with thioacetamide (TAA) at pH 2–6, and at room temperature. Current is recorded with a potential in the range −0·25 to −0·40 V applied across a dropping mercury and calomel electrodes. The presence of Zn^{2+}, Tl^+, Pb^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+}, even in thousandfold excess, causes no interference. The reaction is rapid at room temperature, and the mean error lies between 1 and 2%.

Résumé—On décrit une méthode pour le titrage ampérométrique du cuivre au thioacétamide (TAA) à pH 2–6 et à température ambiante. On enregistre l'intensité avec un potentiel compris entre −0,25 et −0,40 V, appliqué à travers une électrode à goutte de mercure et une électrode au calomel. La présence de Zn^{2+}, Tl^+, Pb^{2+}, Fe^{2+}, Co^{2+} et Ni^{2+}, même en quantités mille fois en excès, ne cause pas d'interférence. La réaction est rapide à température ambiante et l'erreur moyenne se situe entre 1 et 2%.

LITERATUR

1. M. Pryszczewska, *Proc. Anal. Chem. Conf., Budapest*, 1966, 256.
2. *Idem, Talanta*, 1965, **12**, 569.
3. *Idem, Acta Chem. Acad. Sci. Hung.*, 1962, **34**, 135.
4. M. Pryszczewska und L. Iwanowska, *Zeszyty Nauk. Politech. Szczec. Chemia*, 1967, **88**, 25.
5. M. Pryszczewska, *Chem. Anal. (Warsaw)*, 1960, **5**, 931.
6. *Idem, Acta Chim. Acad. Sci. Hung.*, 1962, **34**, 365.
7. *Idem, Talanta*, 1963, **10**, 135.
8. *Idem, ibid.*, 1964, **11**, 671.
9. *Idem, ibid.*, 1966, **13**, 1701.
10. J. G. Nikelly und W. D. Cooke, *Anal. Chem.*, 1956, **28**, 243.
11. N. I. Blok, *Kacestv. Chem. Analiz.*, S.405. Goschimzdat, Moskau, 1952.
12. D. F. Bowersox, D. M. Smith und E. H. Swift, *Talanta*, 1960, **3**, 282.
13. E. H. Swift und F. C. Anson, *ibid.*, 1960, **3**, 296.
14. M. Nardelli und I. Chierici, *Gazz. Chim. Ital.*, 1958, **87**, 1478.
15. E. G. Cox, W. Wardlaw und K. C. Webster, *J. Chem. Soc.*, 1936, 775.
16. T. D. Seth und R. C. Kappor, *Chem. Anal. (Warsaw)*, 1964, **9**, 651.

Talanta, 1971, Vol. 18, pp. 642 to 646. Pergamon Press. Printed in Northern Ireland

Traitement mathématique des resultats du dosage titrimétrique

(*Reçu le* 9 *octobre* 1970. *Accepté le* 29 *octobre* 1970)

L'INTERPRÉTATION objective des données titrimétriques présente parfois des difficultés, en particulier dans le cas oú les inflexions des courbes du dosage potentiométrique et conductométrique ne sont pas très bien marquées. Les inflexions peuvent apparaître comme résultat des changements physico-chimiques dans le système (la formation ou dissolution d'un précipité, le dégagement gazeux), ainsi qu'à cause des déformations accidentelles dûes aux erreurs expérimentales.

Les auteurs suédois, dans leur récente publication,[1] donnent une revue complète des programmes pour machines à calculer et des différentes méthodes applicables au calcul des courbes titrimétriques. Cependant, de pareils calculs exigent une connaissance à priori des détails du processus (des données relatives à la cinétique de l'interaction, des constante d'instabilité *etc.*). A titre d'exemple, on peut citer la méthode des surfaces potentiométriques[2] ou celle de Gran permettant de préciser les coordonnées du point d'equivalence.[3]

Il est intéressant d'étudier le cas général du titrage où, tout en ignorant le caractère exact du processus et des traits spècifiques, on a besoin de répondre à la question suivante: les inflexions sur les courbes de titrage correspondent—elles aux processus réels ayant lieu dans un système donné?

En cas de réponse positive, on peut aborder d'autres problèmes, par exemple calculer les constantes ou déterminer plus exactement les coordonnées du point d'équivalence.

Nous avons essayé d'employer les méthodes statistiques pour calculer les inflexions des courbes, en utilisant l'appareil mathématique servant à l'analyse de régression.[4] En supposant qu'en absence de l'effet en question la courbe soit linéaire, nous avons formulé une équation de régression linéaire dans la zone de l'inflexion. La validité de cette équation était vérifiée par le test *F*. Si la valeur de *F* dépasse la limite confidentielle, cela doit être considéré comme l'indication des changements qualitatifs au cours du processus. Une telle formulation du problème n'est pas suffisamment exacte, les domaines des inflexions possibles étant choisis visuellement et une réprésentation graphique étant indispensable. En outre, on risque de perdre au cours de l'examen les domaines de la courbe qui semblent visuellement linéaires, où les déviations par rapport au fond ne seraient pas assez nettement marquées (l'échelle des coordonnées n'étant pas, par exemple, bien choisie).

Dans la présente publication nous essayons d'analyser tous les points de la courbe dans leur ensemble, ce qui permet d'éviter les difficultés précédemment éxposées.

Considérons un domaine de la courbe de titrage qui comprend les points $x_1, x_2 \ldots x_n$ (le volume du titrant) auxquels correspondent les valeurs $Y_1, Y_2 \ldots Y_n$ (le paramètre de sortie) et composons une équation de régression pour ces points:

$$Y^{(1)} = a^{(1)} + b^{(1)}(x - \bar{x}). \tag{1}$$

Supposons que cette équation soit valable. Composons de la même façon une équation de régression:

$$Y^{(2)} = a^{(2)} + b^{(2)}(\hat{x} - \bar{x}) \tag{2}$$

pour un domaine voisin comprenant les points $x_{n+1}, x_{n+2} \ldots x_{n+m}$ et les valeurs $Y_{n+1}, Y_{n+2} \ldots Y_{n+m}$ respectives. Nous la supposons également vérifiée. Confrontons les pentes des droites correspondant à deux domaines choisis. La vérification de l'hypothèse selon laquelle deux courbes de régression sont équivalantes est généralement effectuée d'après le test de Student[5] en utilisant l'expression

$$\begin{gathered} t_{\mathrm{B}} = \frac{b^{(1)} - b^{(2)}}{S/Q_1 + 1/Q_2} \\ S^2 = \frac{(n-2)s_1{}^2 + (m-2)s_1{}^2}{n+m-4} \end{gathered} \tag{3}$$

représentant la variance combinée de $S_1{}^2$ et $S_2{}^2$ tandis que
$Q_1 = (x_1 - \bar{x}^{(1)})^2$ pour n points du 1er domaine et
$Q_2 = (x_1 - \bar{x}^{(2)})^2$ pour m points du 2ème domaine.

Si la grandeur n dépasse une limite confidentielle, cela signifiera qu'à l'intérieur de la région $x_1, x_2 \ldots x_n$ il y a une déviation considérable par rapport à la dépendance linéaire.

Mais le fait que n ne dépasse pas les limites confidentielles ne suffit pas pour en conclure que les deux courbes coïncident: elles peuvent aussi bien être parallèles.

La vérification de l'hypothèse selon laquelle deux courbes sont parallèles peut être effectuée en employant l'expression:

$$t_{\mathrm{A}} = \frac{\hat{b} - \bar{b}}{\dfrac{S}{(\bar{x} - \bar{x}^{(2)})^2}\left(\dfrac{1}{n} + \dfrac{1}{m}\right) + \dfrac{1}{Q_1 + Q_2}} \tag{4}$$

où

$$\bar{b} = \frac{Q_1 b^{(1)} + Q_2 b^{(2)}}{Q_1 + Q_2} \qquad \text{et} \qquad \hat{b} = \frac{a^{(1)} - a^{(2)}}{\bar{x}^{(1)} - \bar{x}^{(2)}}$$

Si le nombre des points dans la région choisie est supérieur à 30, on peut se servir de la répartition Gaussienne au lieu du test F.

Cette méthode de côntrôle de la validité statistique d'une inflexion dans une région choisie constitue une nouvelle technique par rapport à celle citée en réference 4. Maintenant la région pouvant contenir une inflexion ne sera pas délimitée d'avance et nous examinerons successivement tous les points de la courbe sans exception. Dans ce but, prenons, pour premier domaine, trois premiers points x_1, x_2, x_3 et pour second domaine les trois points voisins qui suivent, x_4, x_5, x_6. Pour chaque domaine formulons les équations de régression et calculons les grandeurs (3) et (4). Si les valeurs (3) et (4) ne dépassent pas leurs limites confidentielles, on prend, pour domaines suivants les groupes de points x_1, x_2, x_3, x_4 et x_5, x_6, x_7, c'est-à-dire qu'en cas d'équivalence les points s'accumulent jusqu'au moment où au moins une de deux grandeurs, t_{A} ou t_{B}, sort au-delà de la limite critique.

La machine enregistre ce moment et on répète le procédé à partir du point x correspondent. Ainsi, la courbe de titrage est approximativement représentée par une ligne brisée, dont les sommets correspondent aux inflexions vraies par rapport à une limite critique confidentielle, le niveau de probabilité étant erroné de 5%.

Pour fixer plus exactement les coordonnées de ces sommets il est recommandable de reprendre le même procédé dans le sens inverse. Le processus peut se terminer en plusieurs points contigus; cette région représente la "zone de l'effet."

Voici un exemple d'application de cette méthode, avec laquelle on traite les courbes de titrage.

On a choisi comme modèle le système Sc^{3+}–$H_2PO_2{}^-$; les hypophosphites de potassium et d'ammonium ont servi de solutions titrantes. La concentration de ces solutions était 10–20 fois plus élevée que celle de la solution titrée (perchlorate ou chlorure de scandium).* La température était maintenue dans l'interval le 20 ± 0,1°. Pour les mesures conductométriques on a utilisé le pont R-38; les mesures de pH on été effectuées à l'aide d'un pH-titrimétre LPU-OI. L'intervalle des mesures était égal à 0,1 ml.

Les Fig. 1–4 représentent les résultats partiels des déterminations effectuées. Les courbes montrent que l'intensité des effets dépend de la concentration des réactifs et de la nature des cations et des anions qui pourraient sembler indifférents ($NH_4{}^+$, K^+, Cl^-, $ClO_4{}^-$). Ce fait peut être dû à la tendance à l'hydrolyse différente dans les conditions expérimentales données.

---

* Tous les réactifs étaient de marque "pure pour analyse." Les solutions de sels de Sc ont été préparées à partir de Sc_2O_3 (contenu en impuretés 0,01%).

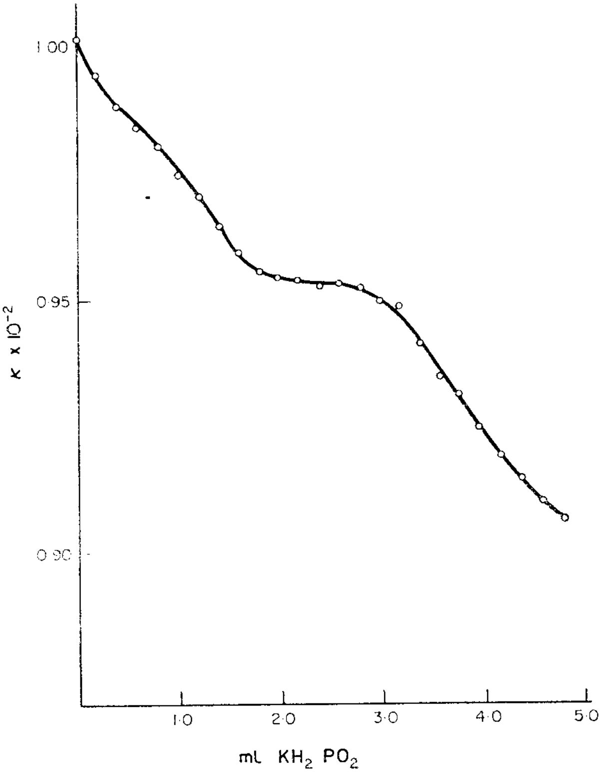


FIG. 1.—Titrage conductométrique (0,026m $ScCl_3$–1,16m KH_2PO_2).

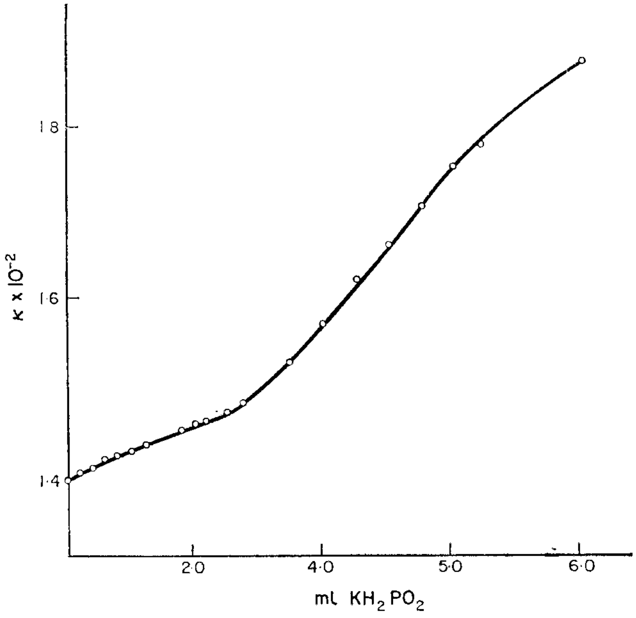


FIG. 2.—Titrage conductométrique (0,01m $Sc(ClO_4)_3$–1,16m KH_2PO_2).

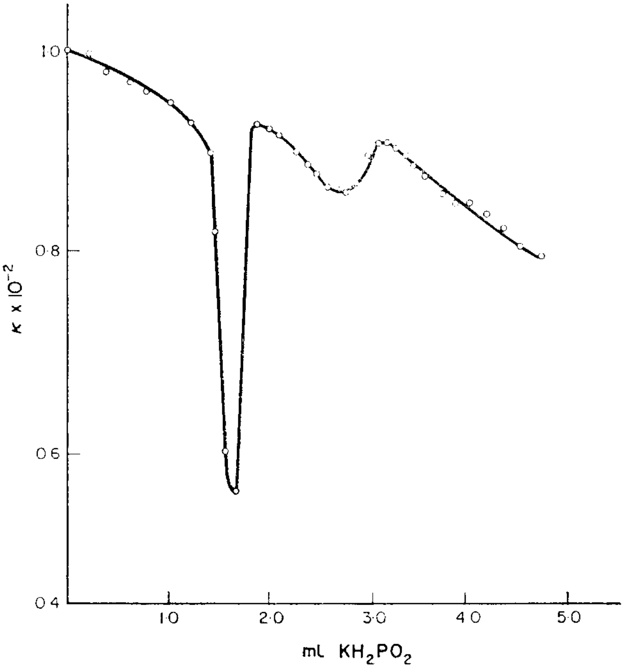


FIG. 3.—Titrage conductométrique (0,02m $Sc(ClO_4)_3$–0,90m KH_2PO_2).

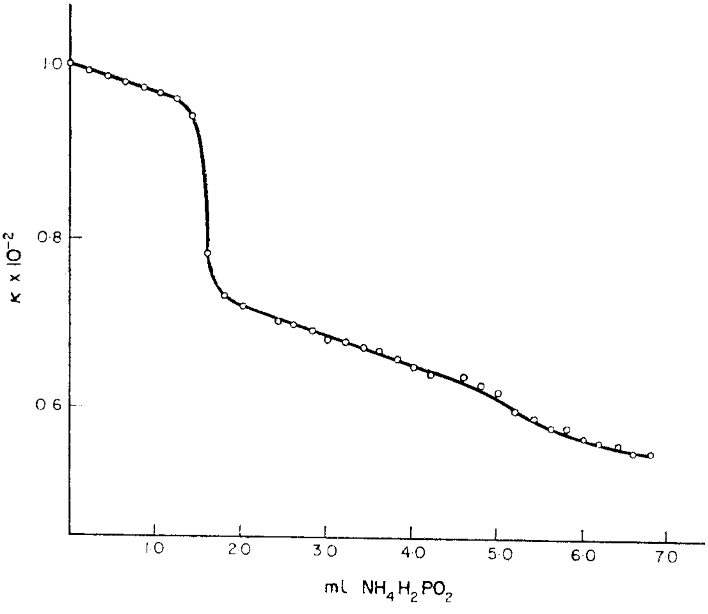


FIG. 4.—Titrage conductométrique (0,02m $Sc(ClO_4)_3$–0,90m $NH_4H_2PO_2$).

TABLEAU I.—RÉSULTATS DES TITRAGE DANS LE SYSTÉME $Sc^{3+}:H_2PO_{2-}$

Concentrations des réactifs	Titrage	S^2	Relations $Sc^{3+}:H_2PO_2^-$		
0,026m $ScCl_3$	conduct.	$0{,}29 \cdot 10^{-4}$	1:2	1:3	
1,16m KH_2PO_2	potent.	$0{,}32 \cdot 10^{-3}$		1:3	
0,01m $Sc(ClO_4)_3$ 1,16m KH_2PO_2	conduct.	$0{,}18 \cdot 10^{-4}$	1:2	1:3	1:6
0,02m $Sc(ClO_4)_3$ 0,90m KH_2PO_2	conduct.	$0{,}17 \cdot 10^{-3}$	1:2	1:3	
0,02m $Sc(ClO_4)_3$ 1,80m KH_2PO_2	conduct.	$0{,}27 \cdot 10^{-3}$			1:6
0,02m $Sc(ClO_4)_3$ 0,90m $NH_4H_2PO_2$	conduct.	$0{,}31 \cdot 10^{-4}$	1:2		1:6

Les résultats de titrage étaient traités à l'aide d'une calculatrice par un programme élaboré selon le procédé décrit ci-dessous. Pour chaque titrage, on a introduit dans la machine, une série de valeurs de x avec des valeurs respectives de Y. Les valeurs de critére t_A et t_B pour chaque point x sont obtenues à la sortie.

Le tableau représente les relations $Sc^{3+}: H_2PO_2^-$ qui se sont avérées justifiées pour le système en question. Les complexes ayant le rapport $Me^{3+}: H_2PO_2^- = 1:2$ ont été déjà décrits précédemment,[6] en particulier pour Fe. Il est naturel que pour le scandium, dont la tendence à la formation de complexes est moins bien marquée, l'isolement de tels composés doit être assez difficile et se manifester uniquement par des inflexions sur les courbes de titrage. Les composés ayant un rapport 1:3 ne sont rien d'autre que l'hypophosphite de scandium, déjà bien connu.[7] Nous avons mis à l'évidence que $Sc(H_2PO_2)_3$ se dissout dans un excès de H_3PO_2 et de solutions d'hypophosphites alcalins. On a précisé que la dissolution complète de précipité est achevée pour le rapport 1:6. Il est important de souligner que la seule méthode graphique ne permet pas de découvrir cet effet, dont la validité ne peut être mise en évidence qu'au moyen du procédé statistique.

Département de Chimie Minérale
de l'Université de Moscow
Moscow, U.R.S.S.

N. A. CHERNOVA
P. P. MEL'NIKOV
L. N. KOMISSAROVA
V. SPYTZIN

Summary—A statistical method is proposed for treatment of titrimetric results. It permits differentiation between true effects on titrimetric graphs and the effects that are the result of random scattering of the experimental points. As an example the mathematical treatment of the data for the system $Sc^{3+}:H_2PO_2^-$ is considered.

Zussammenfassung—Es wird die statistische Methode der titrometrischen Bearbeitung betrachtet, der Angaben die die Möglichkeit geben die wahren Effekte an den Kurven der Titration von den Knicken zu unterschieden, die vom zufäligen Zerstreuen der experimentellen Punkte hervorgerufen werden. Als Beispiel die Bearbeitung der Angaben für das System $Sc^{3+}:H_2PO_2^-$ angeführt.

Résumé—On propose une méthode statistique pour le traitement des résultats titrimétriques. Elle permet la différenciation entre les influences vraies sur les graphiques titrimétriques et les influences qui sont le résultat de la dispersion due au hasard des points expérimentaux. A titre d'exemple, on considère le traitement mathématique des données pour le système $Sc^{3+}:H_2PO_2^-$.

BIBLIOGRAPHIE

1. D. Dyrssen, D. Jagner et W. Wengelin, *Computer Calculation of Ionic Equilibria and Titration Curves*, Almqvist and Wiksell, Stockholm; Wiley, New York, 1968.
2. V. Gran, *Analyst*, 1952, 77, 661.
3. G. Léfèvre, *Compt. Rend.*, 1955, **241,** 1037.
4. L. N. Komissarova, P. P. Mel'nikov et N. A. Chernova, *J. Less-Comm. Met.*, 1967, **13,** 253.
5. A. Hald, *Statistical Theory with Engineering Applications*, London, 1952.
6. R. E. Weinland et W. Hieber, *Z. Anorg. Allgem. Chem.*, 1919, **106,** 15.
7. L. N. Komissarova et P. P. Mel'nikov, *Zh. Neorgan. Chim.*, 1966, **11,** 1262.

Talanta, 1971, Vol. 18, pp. 647 to 649. Pergamon Press. Printed in Northern Ireland

Spectrophotometric study and analytical application of rare-earth Tiron complexes—II
Determination of europium

(*Received* 7 *September* 1970. *Accepted* 19 *October* 1970)

In the previous paper,[1] it was reported that europium interfered in the determination of holmium and erbium with Tiron (disodium 1, 2-dihydroxybenzene-3,5-disulphonate) because the yellow-brown solution containing the Tiron complex had a broad absorption band below 550 nm. In the present paper, results are given that suggest that the absorption band arises from a charge-transfer complex between europium(III) and Tiron. The analytical application of the system is also given. Although the spectrophotometry of rare earths with organic reagents is often non-selective, the absorption band of the europium–Tiron complex is remarkably different from that of the other rare earth complexes and its analytical application is selective for europium.

EXPERIMENTAL

Reagents

As in the previous paper.[1]

Procedure

Transfer to a beaker a hydrochloric acid solution containing less than about 8 mg of europium and evaporate it to near dryness on a water-bath. Dissolve the residue by adding 1 ml of 0·25*M* Tiron. Then add 1 ml of 5% hexamine solution and adjust the pH to 6·5–6·7 with dilute hydrochloric acid and sodium hydroxide solution. Transfer the solution to a 10-ml volumetric flask and dilute to volume with water. Measure the absorbance at 390 or 420 nm against water as reference.

RESULTS AND DISCUSSION

Absorption spectra of aqueous solutions (pH 6·4–6·6) containing individual rare-earth–Tiron complexes (metal concentration $3{\cdot}29 \times 10^{-3}M$) were measured between 340 and 650 nm and are shown in Fig. 1. The particular absorption bands of praseodymium, neodymium, samarium, holmium and

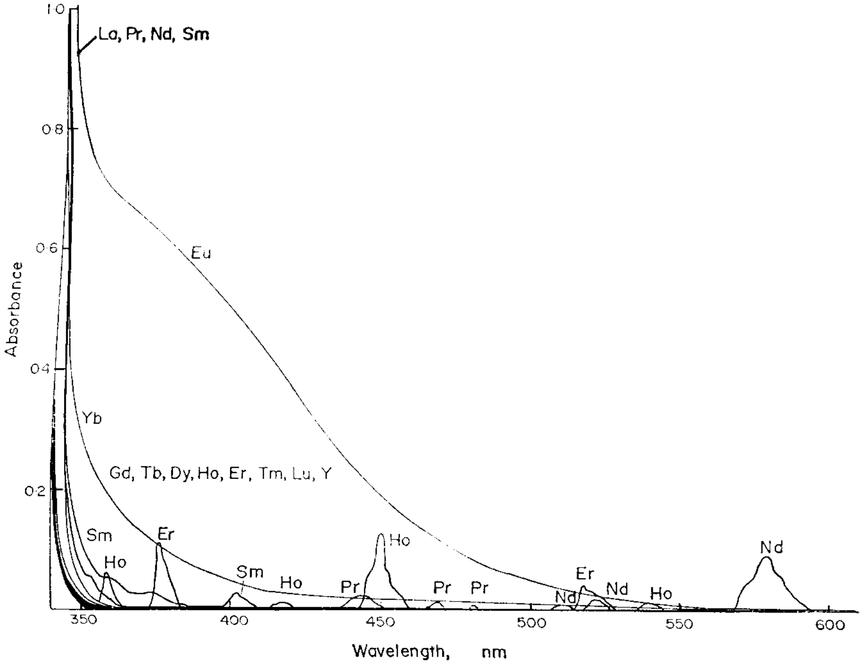


FIG. 1.—Absorption spectra of various rare-earth–Tiron complexed. (Rare earth $3{\cdot}3 \times 10^{-3}M$, Tiron $3 \times 10^{-2}M$, pH 6·4–6·6.)

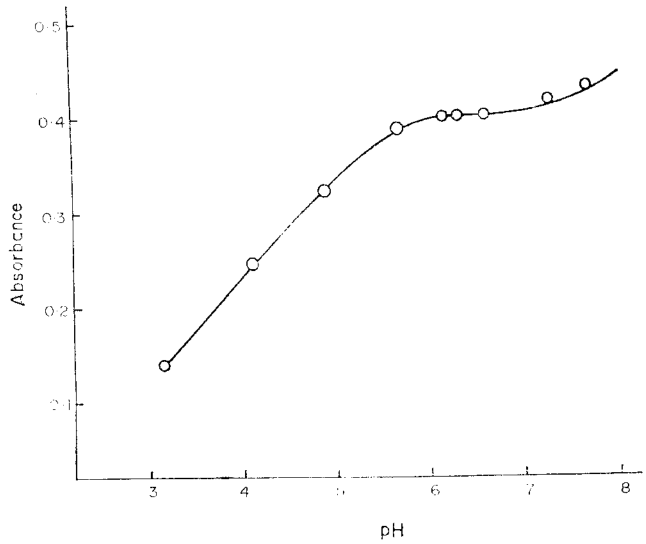


FIG. 2.—Variation of absorbance with pH. (Eu 3·3 × $10^{-3}M$; Tiron 2 × $10^{-2}M$; 420 nm.)

TABLE I.—INTERFERENCES IN THE DETERMINATION OF EUROPIUM IN SYNTHETIC SAMPLES (MEASUREMENT AT 420 nm)

Metal ion	Metal ion added, *mg*	Europium ion, *mg* Taken	Europium ion, *mg* Found
La	3·60	2·50	2·53
Ce	4·56	2·50	2·60*
Ce	9·12	2·50	2·70*
Pr	4·43	2·50	2·52
Nd	3·14	2·50	2·60
Sm	3·21	2·50	2·54
Sm	6·41	2·50	2·70
Gd	3·73	2·50	2·52
Gd	7·45	2·50	2·54
Tb	2·70	2·50	2·48
Dy	6·04	2·50	2·48
Ho	6·11	2·50	2·58
Er	4·56	2·50	2·48
Tm	8·75	2·50	2·52
Yb	3·78	2·50	2·57
Lu	6·82	2·50	2·57
Y	6·47	2·50	2·56

* In the presence of ascorbic acid.

erbium complexes arise from electronic transitions within the 4*f* subshell. The cerium(IV)–Tiron complex gives a strong absorption band over all wavelengths used, and is not shown in the figure. On the other hand, it is suggested that the broad absorption bands of the europium and ytterbium complexes arise from charge-transfer bands. The possibility of the absorption bands being due to an oxidation product of Tiron is not supported, because there is an obvious difference between the absorption bands of the europium and ytterbium complexes, and the yellow-brown colour of the europium–Tiron complex is immediately discharged on addition of an equivalent amount of EDTA. It is therefore also unlikely that europium is reduced to the bivalent state.

Figure 2 shows the variation of absorbance at 420 nm as a function of pH. The absorbance is almost constant over the pH range 6·2–6·6. A 2-fold excess or more of Tiron gives a constant absorbance for a fixed europium concentration. For determination of europium, a tenfold excess was used. The absorbance is almost constant over a period of 1–7 hr after the reaction begins, and follows Beer's law in the range of 0–0·7 mg of europium per ml both at 390 and 420 nm. The continuous-variation method showed that the complex has 1:1 stoichiometry.

The effects of other rare earths are shown in Table I. Although cerium seriously interferes, the effect can be completely removed by adding ascorbic acid.

In the previous paper it was reported that the combining ratio of neodymium, holmium and erbium with Tiron in weakly acidic and neutral media was 2:3 metal:ligand. In order to confirm the difference between the europium and other rare earth complexes, the method of continuous variation was used again with lower concentrations of samarium, europium and gadolinium. The results showed the combining ratio of the europium complex to be 1:1 and of the samarium and gadolinium complexes 2:3, metal:ligand.

College of General Education
Kyushu University
Fukuoka, Japan

Tomitsugu Taketatsu
Taeko Yamauchi

Summary—The absorption spectra of europium–Tiron complexes in aqueous solution have been measured from 340 to 600 nm. The absorbance at 390 and 420 nm follows Beer's law up to 0·8 mg/ml (pH 6·2–6·6). Other rare earths except for cerium(III) did not interfere. The interference of cerium could be removed by addition of ascorbic acid. The combining ratio of Tiron to europium has been found to be 1:1.

Zusammenfassung—Die Absorptionsspektren von Europium-Tiron-Komplexen wurden in wäßriger Lösung von 340 bis 600 nm gemessen. Die Extinktion bei 390 und 420 nm genügt dem Beerschen Gesetz bis 0,8 mg/ml (pH 6,2–6,6). Andere seltene Erden außer Cer(III) störten nicht. Die Störung durch Cer konnte durch Zugabe von Ascorbinsäure beseitigt werden. Es wurde gefunden, daß Tiron und Europium sich im Verhültnis 1:1 verbinden.

Résumé—On a mesuré les spectres d'absorption de complexes europium-Tiron en solution aqueuse de 340 à 600 nm. L'absorption à 390 et 420 nm suit la loi de Beer jusqu'à 0,8 mg/ml (pH 6,2–6,6). Les autres terres rares à l'exception du cérium(III) n'interfèrent pas. L'interférence du cérium peut être éliminée par addition d'acide ascorbique. On a trouvé que le rapport de combinaison du Tiron à l'europium est de 1:1.

REFERENCE

1. T. Taketatsu and N. Toriumi, *Talanta*, 1970, **17**, 465.

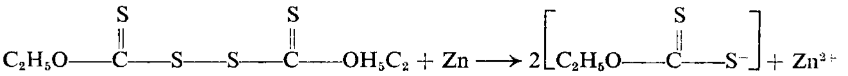
Talanta, 1971, Vol. 18, pp. 649 to 652. Pergamon Press. Printed in Northern Ireland

Reduction and determination of dixanthogens

(*Received* 30 *April* 1970. *Revised* 19 *September* 1970. *Accepted* 11 *October* 1970)

Xanthates of the alkali metals and dixanthogens are well known for their application as mineral collectors in the flotation of sulphide minerals. Though xanthate can be determined by several methods,[1–4] dixanthogen is seldom determined, very few methods being available. Shankarnarayana and Patel[5] suggested reaction of dixanthogen with potassium cyanide to form xanthogen monosulphide and potassium thiocyanate. Later, Rao[6] suggested the use of chloramine-T. Both these methods are of limited value. The first is tedious and uses poisonous potassium cyanide. The method based on chloramine-T is applicable only to the estimation of dixanthogen alone, and not of dixanthogen in presence of xanthate. It was therefore thought that the development of a quick and accurate method for the determination of dixanthogens along with xanthates would be potentially useful in the analysis of flotation liquors and of technical samples of xanthates, which invariably contain dixanthogen as an impurity.

This paper describes the use of liquid zinc amalgam to reduce dixanthogen to xanthate, which can be titrated with standard iodine, with starch as indicator.



$$C_2H_5O-\overset{\overset{S}{\|}}{C}-S-S-\overset{\overset{S}{\|}}{C}-OH_5C_2 + Zn \longrightarrow 2\left[C_2H_5O-\overset{\overset{S}{\|}}{C}-S^-\right] + Zn^{2+}$$

The method can be applied to the determination of dixanthogen in mixtures containing xanthate.

EXPERIMENTAL

Reagents

Xanthate. Potassium ethyl xanthate was prepared by Foster's method[7] and purified by the method described by Dewitt and Roper.[8] The purity was >99%, as determined by iodine titration.[2]

Dixanthogen. Pure potassium ethyl xanthate was oxidized by iodine to yield an insoluble oily diethyl dixanthogen as described by Whitby and Greenberg.[9] The oil was extracted with petroleum ether and the solvent evaporated under a current of air. The dixanthogen is obtained as a yellow oil and can be distilled under vacuum. Analysis: S 53·2%; theory 52·93%. Alcoholic solutions of known concentration were used.

Zinc amalgam, 3% *w/w.* Stored under dilute sulphuric acid.

Procedure

Take 50 ml of dixanthogen solution in a separating funnel. Add 20–30 ml of zinc amalgam and shake thoroughly for an appropriate time (see Fig. 1). Separate the solution from the amalgam and titrate the xanthate with $10^{-2}M$ iodine (starch as indicator), or potentiometrically with silver nitrate solution, or measure its concentration spectrophotometrically at 310 mμ. The choice of method is discussed below.

RESULTS AND DISCUSSION

Time of shaking

The time required for complete reduction of dixanthogen by zinc amalgam was found experimentally, and the results are shown in Fig. 1. Curve 1 shows that shaking for 10 min is necessary for 100% reduction of $10^{-3}M$ dixanthogen and curve 2 shows that 60 min are needed for $10^{-1}M$ dixanthogen.

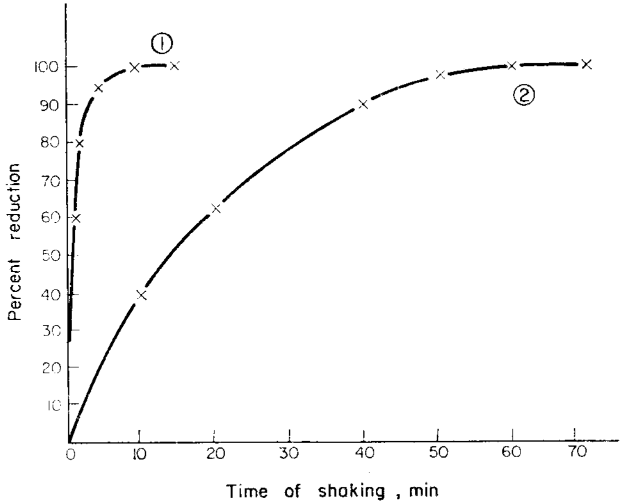


FIG. 1.—Reduction of dixanthogen as a function of time of shaking. (1) $1 \times 10^{-3}M$ dixanthogen (2) $1 \times 10^{-1}M$ dixanthogen.

Determination of dixanthogen

Dixanthogen solutions of different concentrations were analysed and the results are shown in Table I. It can be seen that dixanthogen is completely reduced for all concentrations from $10^{-2}M$ to $10^{-5}M$. Iodine titration is satisfactory for xanthate concentrations down to $2{\cdot}5 \times 10^{-4}M$, but for lower concentrations is not suitable, because of the difficulty in locating the end-point. For concentrations lower than $2{\cdot}5 \times 10^{-4}M$ the spectrophotometric method[3] is used.

TABLE I.—REDUCTION OF DIXANTHOGEN SOLUTIONS OF DIFFERENT CONCENTRATIONS

[Diethyl dixanthogen], M	
Present	Found
$1{\cdot}05 \times 10^{-2}$	$1{\cdot}04 \times 10^{-2}$*
$5{\cdot}25 \times 10^{-3}$	$5{\cdot}10 \times 10^{-3}$*
$1{\cdot}05 \times 10^{-3}$	$1{\cdot}06 \times 10^{-3}$*
$0{\cdot}525 \times 10^{-3}$	$0{\cdot}530 \times 10^{-3}$*
$0{\cdot}2625 \times 10^{-3}$	$0{\cdot}270 \times 10^{-3}$*
$1{\cdot}00 \times 10^{-4}$	$1{\cdot}02 \times 10^{-4}$†
$1{\cdot}00 \times 10^{-5}$	$1{\cdot}042 \times 10^{-5}$†

* Determined by iodine titration.
† Determined by spectrophotometry.

Determination of dixanthogen in mixtures containing xanthate

Mixtures of various amounts of xanthate and dixanthogen were prepared. The xanthate was determined first and the dixanthogen in another aliquot was reduced to xanthate by the proposed method and the total xanthate determined. The difference between the two values gives the amount of dixanthogen. The results shown in Table II were obtained for mixtures containing xanthate and dixanthogen in molar ratios ranging from 3:1 to 1:3; iodine titration[2] was used for the higher concentrations, and potentiometric titration with silver[4] for the lower.

TABLE II.—REDUCTION AND ESTIMATION OF DIXANTHOGEN IN SOLUTIONS CONTAINING MIXTURES OF ETHYL XANTHATE AND DIETHYL DIXANTHOGEN

	[Xanthate], M		[Dixanthogen], M	
	Present	Found	Present	Found
Iodine titration	$0{\cdot}50 \times 10^{-3}$	$0{\cdot}56 \times 10^{-3}$	$0{\cdot}50 \times 10^{-3}$	$0{\cdot}510 \times 10^{-3}$
	$0{\cdot}335 \times 10^{-3}$	$0{\cdot}336 \times 10^{-3}$	$0{\cdot}665 \times 10^{-3}$	$0{\cdot}684 \times 10^{-3}$
	$0{\cdot}25 \times 10^{-3}$	$0{\cdot}251 \times 10^{-3}$	$0{\cdot}75 \times 10^{-3}$	$0{\cdot}740 \times 10^{-3}$
	$0{\cdot}665 \times 10^{-3}$	$0{\cdot}680 \times 10^{-3}$	$0{\cdot}335 \times 10^{-3}$	$0{\cdot}320 \times 10^{-3}$
	$0{\cdot}75 \times 10^{-3}$	$0{\cdot}74 \times 10^{-3}$	$0{\cdot}25 \times 10^{-3}$	$0{\cdot}240 \times 10^{-3}$
Silver nitrate titration	1×10^{-5}	1×10^{-5}	—	—
	$0{\cdot}5 \times 10^{-5}$	$0{\cdot}49 \times 10^{-5}$	$0{\cdot}50 \times 10^{-5}$	$0{\cdot}48 \times 10^{-5}$
	$0{\cdot}335 \times 10^{-5}$	$0{\cdot}350 \times 10^{-5}$	$0{\cdot}665 \times 10^{-5}$	$0{\cdot}64 \times 10^{-5}$
	$0{\cdot}25 \times 10^{-5}$	$0{\cdot}24 \times 10^{-5}$	$0{\cdot}75 \times 10^{-5}$	$0{\cdot}78 \times 10^{-5}$
	$0{\cdot}75 \times 10^{-5}$	$0{\cdot}76 \times 10^{-5}$	$6{\cdot}25 \times 10^{-5}$	$0{\cdot}29 \times 10^{-5}$
	—	—	$1{\cdot}00 \times 10^{-5}$	$1{\cdot}05 \times 10^{-5}$

The potentiometric method is useful for determination of dixanthogen in flotation liquors, which cannot be conveniently handled by iodimetry or spectrophotometry.

Determination of higher dixanthogens

Reduction of higher dixanthogens also takes place quantitatively. Isopropyl and amyl dixanthogens were determined successfully by iodine titration, with an error of ~4% at the $10^{-3}M$ level. Naturally, the method does not work if more than one dixanthogen is present.

Acknowledgement—The author gratefully acknowledges the financial support provided by the Council of Scientific and Industrial Research, New Delhi, under the scheme "Collector Action in the Flotation of Sulphide Minerals". He is also thankful to Dr. S. R. Rao for his interest in this work.

Department of Chemistry
Indian Institute of Technology
New Delhi-29, India

M. S. PRASAD

Summary—A convenient method for the reduction and determination of dixanthogen has been developed. It is based on the quantitative reaction of dixanthogen with zinc amalgam to form xanthate; the latter can be determined by iodine titration, potentiometric titration with silver nitrate or by spectrophotometry at 310 mμ. Dixanthogen can be determined in mixtures containing xanthate, by titration of aliquots with and without reduction. Higher dixanthogens can also be determined, and flotation liquors analysed.

Zusammenfassung—Ein bequemes Verfahren zur Reduktion und Bestimmung von Dixanthogen wurde entwickelt. Es beruht auf der quantitativen Reaktion von Dixanthogen mit Zinkamalgam zu Xanthat; letzteres kann durch Jodtitration, potentiometrische Titration mit Silbernitrat oder durch Spektralphotometrie bei 310 nm bestimmt werden. In Xanthat enthaltenden Mischungen kann Dixanthogen durch Titration aliquoter Teile mit und ohne Reduktion bestimmt werden. Höhere Homologe von Dixanthogen können ebenfalls bestimmt werden; die Analyse von Flotationslargen ist möglich.

Résumé—On a élaboré une méthode convenable pour la réduction et le dosage du dixanthogène. Elle est basée sur la réaction quantitative du dixanthogène avec l'amalgame de zinc pour former le xanthate; on peut doser ce dernier par titrage à l'iode, titrage potentiométrique au nitrate d'argent, ou par spectrophotométrie à 310 nm. On peut déterminer le dixanthogène dans des mélanges contenant du xanthate, par titrage de parties aliquotes avec et sans réduction. On peut aussi doser des dixanthogènes supérieurs, et analyser des liqueurs de flottation.

REFERENCES

1. W. Hirschkind, *Eng. Mining J.*, 1925, **119**, 968.
2. M. P. Matuszak, *Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 98.
3. C. H. G. Bushell and M. Malnarich, *Mining Eng.*, 1956, **8**, 734.
4. C. Du Rietz, *Svensk Kem. Tidskr.*, 1957, **69**, 310.
5. M. L. Shankaranarayana and C. C. Patel, *Analyst*, 1961, **86**, 98.
6. S. R. Rao, *Talanta*, 1961, **8**, 746.
7. L. S. Foster, *Mineral Metallurgical Res. Techn. Paper No.* 2, University of Utah, 1927.
8. C. C. Dewitt and E. E. Roper, *J. Am. Chem. Soc.*, 1932, **54**, 445.
9. G. S. Whitby and H. Greenberg, *Trans. Roy. Soc. Canada*, 1929, **23**, 21.

Talanta, 1971, Vol 18, pp. 653 to 654. Pergamon Press. Printed in Northern Ireland

LETTER TO THE EDITOR

Computer calculation of equilibrium constants by use of the program SCOGS; a correction

SIR,

Since the publication of the computer program SCOGS,[1] a general program for the calculation of equilibrium constants of species present in mixtures of metal ions and complexing agents (pK_a's, stability constants *etc*), a number of workers have used the program in interpreting their results. Under most conditions the results obtained do not differ significantly from those obtained by using alternative calculation methods, but under certain circumstances differing results have been obtained. These have shown up an error in the derivation of one of the equations used.

The equation for the calculated titre is

1. CTITR = [VOL1*TURM(K) + V(K)*AC(K) − VOL 1*HO]/BA(K) or in simpler terms
2. CTITR = [A + D − (X + f(β_i))]/BA

where A = moles of H^+ contributed by ligand(s)
D = moles of H^+ added as strong acid
X = moles of free H^+ as measured by pH meter
f(β_i) = moles of H^+ bound to various species (a function of the various constants β_i), making allowances for hydrolysed species
BA = concentration of base

In the original program equation (1) was used to derive the equation (card no. 158, Statement no. 150)

3. CTITR = V(K)*(TURM(K) + AC(K) − HO)/(BA(K) − TURM(K) + HO)

which was obtained by assuming VOL1 = VOL + CTITR and bringing terms in CTITR to the left-hand side of the equation.

This procedure has now been shown to be in error,[2] and the error may be significant if volumes of titrant >2% of total volume are used. The form of equation (1) is in fact correct and the experimental value VOL1 should be retained. However, in order that the program should function correctly the following changes are necessary.

(1) Dimension VOL1 as VOL1(60).
(2) Dimension new variable VOX1(200), *i.e.*, volume at point K.
(3) Card no. 70, VOL1(K) = VOL + TITRE(K)
(4) Card no. 72, ZB(I, K) = TM(I)*VOL/VOL1(K)
(5) Card no. 73, 119 ZL(I, K) = TL(I)*VOL/VOL1(K)
(6) Insert new card, between cards 82, 83, VOX1(K) = VOL1(MTN)
(7) Card no. 158

```
150 CTITR = (VOX1(K)*TURM(K) + V(K)*AC(K) − VOX1(K)*HO)/BA(K)
```

With these changes the program functions satisfactorily when used with titrant volumes of the order of 10–15% of total volume, in excellent agreement with those obtained by using alternative calculation methods.

The program was originally developed, and has been mainly used, for titrations in which the volume of titrant was low (~1% of total volume) and it should be noted that under these circumstances the changes above cause no significant alteration to the values of constants obtained[3–5]. For such titrations the errors in constants calculated with the original program will be negligible. However, it is recommended that constants calculated from titrant volumes >2% of total volume be revised by use of the modified program.

I am indebted to Dr. R. Cassidy of McMaster University for pointing out this error, and the required corrections, also to Dr. C. W. Childs, of Canada Centre for Inland Waters, for testing the alterations on systems with small titrant volume.

Division of Inorganic and Metallic Structure
National Physical Laboratory, Teddington, Middlesex, U.K.
13 *August* 1970

I. G. SAYCE

REFERENCES

1. I. G. Sayce, *Talanta*, 1968, **15**, 1397.
2. R. Cassidy, private communication.
3. C. W. Childs and D. D. Perrin, *J. Chem. Soc.* (*A*), 1969, 1039.
4. C. W. Childs, *J. Phys. Chem.*, 1969, **73**, 2956.
5. *Idem*, *Inorg. Chem.*, in the press.

Talanta, 1971, Vol. 18, p. i. Pergamon Press. Printed in Northern Ireland

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY (IUPAC)

COMMISSION ON ELECTROANALYTICAL CHEMISTRY (V.5)

The IUPAC Commission on Electroanalytical Chemistry deals with all aspects of electrochemical measurements used for and aimed at analytical methods. To ensure that the Commission represents the views of electroanalytical chemists, comments on present projects, suggestions of new topics, and active participation of societies, groups and individuals are invited. The current programme of the Commission deals with critical compilations of reference data, with standardization of procedures, and with nomenclature.

(1) *Tables of Dissociation Constants* of Inorganic Acids and Bases in Aqueous Solutions, collected by D. D. Perrin, are being printed. Tables of Dissociation Constants of Organic Bases in Aqueous Solutions are being revised by D. D. Perrin and the manuscript will be submitted before July 1971.

(2) *Polarographic Data.* A list of half-wave potentials, based on a linear free energy treatment, is being prepared.

(3) *Oxidation–Reduction Potentials.* A revised critical compilation by G. Charlot, A. Collumeau and J. C. Marchon has been approved for publication. Further electrochemical thermodynamic data are being compiled.

(4) *Electrochemical Data for Non-Aqueous Solvents.* Tables of dissociation constants of acids and salts in non-aqueous solvents are being collected. Inorganic half-wave potentials in dimethylformamide have been collected. *A Symposium on Non-Aqueous Electrochemistry held in Paris, 8–10 July, 1970*, was sponsored by this Commission and the Commission on Electrochemistry of the Physical Chemistry Division.

(5) *Purification of Solvents.* A number of reports on purification of solvents for electrochemical purposes have been published and more reports are in preparation.

(6) *Purification and Purity of Reagents.* Procedures used for purification of reagents used in electroanalytical chemistry together with tests for purity are being critically examined. The most suitable methods for purification of metallic mercury, sulphuric and hydrochloric acids, and ammonia are currently under consideration.

(7) *Solid Electrodes.* A report on the effect of pretreatment of solid electrodes used for analytical purposes in characterization of analytically important electrode reactions is under consideration. Compilation of chronopotentiometric data is under consideration. The possibilities of using the Coulomb for standardization of solutions is being reinvestigated.

(8) *Nomenclature.* The 1959 report on classification and nomenclature of electroanalytical methods is being revised and expanded to include definitions.

(9) *General Co-operation.* The Commission has offered its services in the exchange of information on bibliographic projects and in organization of meetings between national bodies. Reports on progress in electroanalytical chemistry in various regions are being considered: a report on activities in India is already being prepared.

Inquiries and communications may be directed to the Secretary of the Commission on Electroanalytical Chemistry: Prof. P. Zuman, Department of Chemistry, Clarkson College of Technology, Potsdam, N.Y. 13676, U.S.A. Other Members and Associate Members of the Commission are: E. Bishop (U.K.), S. Bruckenstein (U.S.A.), J. F. Coetzee (U.S.A.), T. Fujinaga (Japan), Z. Galus (Poland), R. C. Kapoor (India), I. M. Kolthoff, Chairman (U.S.A.), H. A. Laitinen (U.S.A.), L. Meites (U.S.A.), H. W. Nürnberg (Germany), D. D. Perrin (Australia), J. K. Taylor (U.S.A.), B. Trémillon (France).

The Commission is co-operating with other appropriate IUPAC Commissions, *viz.* with the Commission on Electrochemistry (J. Jordan, Chairman) in items (3), (4), and (8); with the Commission on Physicochemical Symbols, Terminology and Units (M. L. McGlashan, Chairman) and the Interdivisional Committee on Nomenclature and Symbols (K. A. Jensen, Chairman) on item (8); and with the Commission on Microchemical Techniques and Trace Analysis on item (6).

Talanta, 1971, Vol. 18, p. ii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Determination of indium and thallium in indium–thallium alloys: Melvin J. Tschetter, Robert Z. Bachman and Charles V. Banks. (28 *January* 1971)

Synthetic inorganic ion exchangers—I. Hydrous oxides and acidic salts of multivalent metals: V. Veselý and V. Pekárek. (22 *March* 1971)

New masking procedure for selective complexometric determination of copper(II): Rajinder Pal Singh. (22 *March* 1971)

Spectrophotometric determination of dimethylsulphoxide: Z. Dizdar and Z. Idjaković. (22 *March* 1971)

The effect of precipitate and complex formation on the determination of silver by atomic-absorption spectroscopy: R. F. Lee and W. F. Pickering. (22 *March* 1971)

Choice of standard samples and precision of analysis in emission spectroscopy by statistical means: Allan Danielsson, Kurt Johansson, Folke Ingman and Rolf Sundberg. (26 *March* 1971)

The use of triethanolamine in a buffer system for the determination of fluoride in calcium and transition metal orthophosphates by use of a fluoride-selective electrode: Edward J. Duff and J. L. Stuart. (26 *March* 1971)

A spectrophotometric method for the determination of copper ions and its application for the co-precipitation of Cu^{2+} with crystallizing NaCl: A. Glasner, S. Sarig, D. Weiss and M. Zidon. (29 *March* 1971)

Analytical applications of ion-association complexes—II. Determination of Alizarin-S: V. Pandu Rao, K. Venugopala Rao, B.S.R. Sarma and V. V. Rama Sastry. (29 *March* 1971)

Studies on the extraction and determination of metals—I. Extraction of hafnium into isobutyl methyl ketone and tributyl phosphate: Norio Ichinose. (30 *March* 1971)

Determination of platinum-group metals, gold and silver by the tin-collection scheme: G. H. Faye and P. E. Moloughney. (30 *March* 1971)

Iodometric microdetermination of sulphur in organic compounsd by an amplification reaction: Y. A. Gawargious and A. B. Farag. (31 *March* 1971)

Détermination de l'or réaction d'échange de complexes triples à association ionique: N. Gantchev and A. Dimitrova. (31 *March* 1971)

Neutron-activation determination of vanadium in oils and catalysts: Alfredo Arroyo and Dag Brune. (1 *April* 1971)

Epithermal neutron activation determination of uranium in rocks: Alfredo Arroyo and Dag Brune. (1 *April* 1971)

Chromatographic separation of copper with an α-hydroxyoxime: James S. Fritz, Donald R. Beuerman and John J. Richard. (1 *April* 1971)

The thermodynamics of the partition of 8-quinolinol between several organic solvents and aqueous buffers: J. G. Mason and I. Lipschitz. (8 *April* 1971)

Spectrophotometric determination of calcium in zirconium powder by use of Murexide: Herman Gordon and George Norwitz. (16 *April* 1971)

Cation-exchange separation and determination of silver in admixture with mercury(II): R. L. Shrimal. (16 *April* 1971)

Spektralchemische Analysenmethoden unter Benutzung der Dreiphasensysteme der Extraktion: A. I. Busev, W. P. Shiwopiszew, B. I. Petrow and J. A. Machnew. (16 *April* 1971)

Determination of vanadate in aqueous trichloroacetic acid medium with phenol as indicator: Sarjit Singh Sandhu and Dula Singh. (16 *April* 1971)

Titrimetric determination of arsenic(III) with potassium dichromate and redox indicators: G. Gopala Rao, B. Sarojini and Muralikrishna Gandikota. (16 *April* 1971)

Microdetermination of α-amino acids by spectrophotometric and titrimetric methods: W. I. Awad, S. Nashed, S. S. M. Hassan and R. F. Zakhary. (16 *April* 1971)

The possibilities of using sulphonated derivatives of diphenylcarbazone and diphenylthiocarbazone in analytical chemistry: Josef Jenik and František Renger. (16 *April* 1971)

Niederschlagsbildung—III. Kristallwachstum und Einfluss der Fremdionenkonzentration in der Bariumsulfatfällung: Candin Liteanu and Harald Lingner. (20 *April* 1971)

Spektrophotometrische Bestimmung des Wismut(III)/Thoron-Komplexes: M. Elenkova and D. Kostov. (20 *April* 1971)

Oxidimetric determination of ascorbic acid with potassium hexacyanoferrate(III) in acid medium: G. Sitaramasastry and G. Gopala Rao. (21 *April* 1971)

Electronic modulation of microwave-excited electrodeless discharge-lamps for use in atomic-fluorescence spectrometry: R. M. Dagnall, M. A. Silvester and T. S. West. (21 *April* 1971)

Sequential separation of chromium, cobalt, iron, tin, zinc and cadmium by ion-exchange chromatography: T. Z. Bishay. (21 *April* 1971)

Rapid successive complexometric determination of thorium and uranium from sulphuric acid media: M. M. L. Khosla and S. P. Rao. (22 *April* 1971)

A neutron-activation scheme for the determination of 42 elements in lunar material: A. O. Brunfelt and E. Steinnes. (23 *April* 1971)

Talanta, 1971, Vol. 18, p. iii. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Metals: HAZEL ROSSOTTI, Oxford University Press, Oxford, 1971. Pp. 96. £1.25.

A companion volume to the same author's book on water ("H_2O") this book gives an account of the physics, chemistry and metallurgy of metals, written to interest children in the age range 10–14, and covering the history of the subject from ancient times to the space age. Like its predecessor, it manages to convey a great deal of information in short space, and to do so in a most interesting way. Some out of the way bits of information will come as a surprise to many people, and the book can confidently be recommended to all with a thirst for knowledge.

National Bureau of Standards Organic Chemistry Section: Summary of Activities July 1969 to June 1970, N.B.S. Technical Note 547, National Technical Information Service, Springfield, Va. 22151. Pp. xii + 122. $1.25.

This report deals mainly with development of standard reference materials for clinical chemistry, and partly with developments in carbohydrate research and miscellaneous topics.

Status of Thermal Analysis: edited by OSCAR MENIS, NBS Special Publication 338, National Bureau of Standards, Washington, 1970, Pp. iv + 185. $1.00.

This report gives the papers presented at a Symposium on the Current Status of Thermal Analysis, and covers standardization, differential thermal analysis, differential scanning calorimetry, macrocalorimetry, rate studies, and thermogravimetry of vulcanized materials. Several specific applications of thermal analysis are mentioned, and the report is a very useful one.

Quantitative Analysis: Elementary Principles and Practice: HARVEY DIEHL, Oakland Street Science Press, Ames, Iowa, 1970. Pp. 454. $12.50.

This book is most interesting, combining sound fundamental instruction in gravimetric, titrimetric and photometric methods of analysis with some history and a good deal of philosophy of science. It is profusely illustrated with well chosen (and sometimes very amusing) figures, is handsomely produced and bound, and at the price represents a remarkable bargain. It can be recommended to students for use and to analysts for reading with profit.

The Analysis of Elemental Boron: MORRIS W. LERNER, U.S. Atomic Energy Commission, Oak Ridge, 1970. Pp. ix + 125. $3.00.

This paperback gives a thorough and up-to-date account of the determination of boron itself and the analysis of boron for impurities. It covers all major techniques of trace analysis, discusses boron standards, methods of dissolution of boron, separations and losses, contamination, and the results of a co-operative study of boron analysis. It is a most useful addition to the literature on boron chemistry, and well worth its price.

Applied Gamma-Ray Spectrometry, 2nd Ed.: C. E. CROUTHAMEL, F. ADAMS and R. DAMS, Pergamon, Oxford, 1970. Pp. xviii + 752, £12, $32.00.

This second edition of Crouthamel's well-known work has been completely revised and enlarged by Adams and Dams. There are new chapters on semiconductor gamma detectors, instrumentation and the determination of identity, purity and quantity of radionuclides. The other chapters have been revised. The appendices (430 pp) have been greatly extended, notably by the gamma-ray spectra of 46 short-lived or neutron-deficient isotopes, 220 gamma-ray spectra taken with a lithium drifted germanium detector, and tabulations of the sequence of precisely determined photon energies of nuclides formed by neutron-activation. The comparison of the spectra obtained by sodium iodide and lithium drifted germanium detectors shows sharply the tremendous advances made in nuclear instrumentation during the last decade. The text also faithfully reflects these developments. Like the 1st edition, it is still heavy going for those not at work in the field but even more indispensible for those who are.

Table of Ion Energies for Metastable Transitions in Mass Spectrometry: J. H. BEYNON, R. M. CAPRIOLI, A. W. KUNDERD and R. B. SPENCER. Elsevier, Amsterdam, 1970. Pp. 2 + 499. £8.25.

This computer print-out of metastable ion energies will be of considerable value in the interpretation of ion kinetic energy spectra and, in this connection, should be a useful addition to the "Table of Metastable Transitions for Use in Mass Spectrometry" by J. H. Beynon, R. A. Saunders and A. E. Williams (Elsevier, Amsterdam, 1965). The legibility of the tables is good for this method of reproduction and presentation.

SUMMARIES FOR CARD INDEXES

Properties and analytical applications of the heteropolymolybdates of phosphorus, arsenic, silicon and germanium—I. Spectrophotometric examination of the heteropoly acids: A. HALÁSZ and E. PUNGOR, *Talanta*, 1971, **18,** 557. (Institute of Analytical Chemistry, University for Chemical Engineering, Veszprém, Hungary.)

Summary—Spectrophotometric studies have been made of the heteropoly acids of phosphorus, arsenic, silicon and germanium, formed at molybdate concentrations of 10^{-1}–10^{-3} *M*. It was found that the heteropoly anion is quantitatively produced at a *Z*-value of 1·60 in the case of a quinquevalent central atom and 1·50 for a quadrivalent central atom, if the amount of the latter is not higher than 50% of the stoichiometric (*Z* is the number of moles of protons taken up by one mole of molybdenum). On addition of further acid the anion takes up protons, but its absorbance remains unchanged if measured at a wavelength at which the isopolymolybdates show no absorption. At *Z*-values higher than 2·2–2·3, *i.e.*, in highly acidic media, a decomposition reaction starts; its products are octamolybdate and molybdenyl ions. The different molar absorptivities and other "irregularities" found in the various analytical procedures in the literature are due not to the heteropoly acids but to the isopolymolybdate formed together with the former.

Properties and analytical applications of the heteropolymolybdates of phosphorus, arsenic, silicon and germanium—II. Modifications of the heteropoly acids: A. HALÁSZ and E. PUNGOR, *Talanta*, 1971, **18,** 569. (Institute for Analytical Chemistry, University for Chemical Engineering, Veszprém, Hungary.)

Summary—Phospho-, arseno-, silico- and germanomolybdic acids may all exist in an α- and a β-modification. α-Silicomolybdic acid is formed if the degree of acidification is below $[H^+]/[Mo] = 1{\cdot}5$. At higher acid concentrations the β-modification is formed, and spontaneously transformed into the α-form. Germanomolybdic acid behaves similarly, but the transformation is much faster. Arsenomolybdic acid is always formed as the α-modification and is transformed into the β-modification only later and in a very slow reaction if the pH of the solution is below 1. Formation of the two modifications is also dependent on acid concentration in the case of phosphomolybdic acid, but both modifications are stable and no spontaneous transformation occurs. Compounds similar to the β-modifications but showing different molar absorptivities are formed in acetone-containing solution.

Properties and analytical applications of the heteropolymolybdates of phosphorus, arsenic, silicon and germanium—III. Examination of two- and three-component systems without separation: A. HALÁSZ, E. PUNGOR and K. POLYÁK *Talanta*, 1971, **18,** 577. (Institute for Analytical Chemistry, University for Chemical Engineering, Veszprém, Hungary.)

Summary—By taking advantage of the possible variations in acid and molybdenum concentration, wavelength of measurement, α- and β-modifications, and media, P, As, Si and Ge can be determined spectrophotometrically as the heteropolymolybdates without separation. Rapid procedures are proposed for the analysis of two- and three-component mixtures of these elements.

ХАРАКТЕРИСТИКА И ПРИМЕНЕНИЕ В АНАЛИЗЕ ГЕТЕРОПОЛИМОЛИБДАТОВ ФОСФОРА, МЫШЬЯКА, КРЕМНИЯ И ГЕРМАНИЯ—I. ИСПЫТАНИЕ ГЕТЕРОПОЛИКИСЛОТ СПЕКТРОФОТОМЕТРИЧЕСКИМ МЕТОДОМ:

A. Halász and E. Pungor, *Talanta*, 1971, **18**, 557.

Резюме—Изучены спектрофотометрическим методом гетерополикислоты фосфора, мышьяка, кремния и германия, образующиеся при концентрациях молибдата 10^{-1}–$10^{-3}M$. Найдено что гетерополианион образуется колическвенно при $Z = 1{,}60$ в случае пятивалентного центрального атома, а при $Z = 1{,}50$ в случае четырехвалентного центрального атома, если количество последного не превышает 50% стехиометрического количества (Z представляет собой молярное число протонов поглощенных одним молем молибдена). Добавлением дальнейших количеств кислоты анион поглощает протоны но его светоплощение не изменяется если измеряют его при длины волн при которой изополимолибдаты не поглощают. При величинах Z выше 2,2–2,3, т.е. в сильнокислых средах начинает реакция разложения; продуктами этой реакции являются октамолибдат- и молибдениллионы. Различные молярные светопоглощения и другие «неправильности», обнаруженные в различных аналитических методах в литературе, вызваны не гетерополикислотами но изополимолибдатом, образующимся вместе с этими кислотами.

ХАРАКТЕРИСТИКА И ПРИМЕНЕНИЕ В АНАЛИЗЕ ГЕТЕРОПОЛИМОЛИБДАТОВ ФОСФОРА, МЫШЬЯКА, КРЕМНИЯ И ГЕРМАНИЯ—II. МОДИФИКАЦИИ ГЕТЕРОПОЛИКИСЛОТ:

A. Halász and E. Pungor, *Talanta*, 1971, **18**, 569.

Резюме—Фосфорно-, арсено, кремне- и германомолибденовые кислоты могут существовать в двух модификациях: α и β. α-Кремнемолибденовая кислота образуется если степень кислотности ниже $[H^+]/[Mo] = 1{,}5$. При высших концентрациях кислоты образуется β-модификация, которая самопроизвольно превращается в α-форму. Германомолибденовая кислота показывает похожее поведение, но превращение значительно быстрее. Арсеномолибденовая кислотъ образуется всегда в α-форме, а превращается в β-модификацию в весьма медленной реакции если pH раствора ниже I. Образование обеих модификаций зависит от концентрации кислоты также с случае фосфорномолибденовой кислоты, но обе модификации устойчивы и самопроизвольное превращение не появляется. В содержащем ацетон растворе образуются соединения подобные β-модификациями но имеющие различные молярные светопоглощения.

ХАРАКТЕРИСТИКА И ПРИМЕНЕНИЕ В АНАЛИЗЕ ГЕТЕРОПОЛИМОЛИБДАТОВ ФОСФОРА, МЫШЬЯКА, КРЕМНИЯ И ГЕРМАНИЯ—III. ИСПЫТАНИЕ ДВУХ- И ТРЕХКОМПОНЕНТНЫХ СИСТЕМ БЕЗ РАЗДЕЛЕНИЯ:

A. Halász, E. Pungor and K. Polyák, *Talanta*, 1971, **18**, 577.

Резюме—Пользуясь возможными вариациями концентраций кислоты и молибдена, длины волны измерения, сред и α- и β-модификациями, возможно определять P, As, Si и Ge спектрофотометрическим методом в форме гетерополимолибдатов без разделения. Предложены быстрые процедуры для анализа двух- или трехкомпонентных смесей этих элементов.

Determination of noble metals by neutron-activation analysis: R. Gijbels, *Talanta*, 1971, **18**, 587. (Institute of Nuclear Chemistry, State University of Ghent, Belgium.)

Summary—The scope and limitations of neutron-activation analysis in the field of the platinum metals are discussed. Special attention is given to interferences that occur in determination of noble metals in platinum metals and in natural samples. The problem of standards, carriers and chemical yield determination is emphasised. A recommendation is given of modern techniques for counting radionuclides formed by neutron activation of the platinum metals.

A contribution to the use of chelating agents in anodic stripping voltammetry: Ludmila Zieglerová, Karel Štulík and Jan Doležal, *Talanta* 1971, **18**, 603. (Department of Analytical Chemistry, Charles University, Prague, Czechoslovakia.)

Summary—The $E_{p/2}$ values of the ions Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, Tl^{+} were determined by means of cyclic voltammetry in solutions of acetate and Britton–Robinson buffers and in solutions containing EDTA and DCTA. DCTA was then utilized in the determination of small amounts of bismuth, down to $10^{-7}M$, in the presence of 10^4 times as much lead, and of traces of thallium down to $5 \times 10^{-9}M$ in the presence of 2×10^5 times as much cadmium by anodic stripping voltammetry. The precision was good. Further, the trace copper concentration in analytical grade DCTA was determined. A new flow-through vessel for stripping analysis with solution exchange is also described and the reproducibility of results without solution exchange, with manual solution exchange, and with the flow-through vessel is evaluated for a model determination of thallium in a DCTA solution.

Verwendung von mässig dissoziierten Komplexen bei spektralphotometrischen Bestimmungen—III. Auswertung linearer photometrischer Titrationskurven ohne Indikator: J. Fischer, Z. Slovák and J. Borák, *Talanta*, 1971, **18**, 615. (Forschungsinstitut für reine Chemikalien, Lachema, Brno, Tschechoslowakei.)

Summary—Photometric titration curves have been analysed in terms of the hyperbola form derived from a plot of a linearly related variable, in the absence of an indicator. Titration curves can be evaluated for the formation of ML-type complexes even when these are considerably dissociated, *i.e.*, when the product of the formation constant and the concentration of the species being determined falls as low as unity. Limiting conditions for the successful evaluation of curves are discussed. The applicability of the method has been checked on practical systems.

ОПРЕДЕЛЕНИЕ БЛАГОРОДНЫХ МЕТАЛЛОВ МЕТОДОМ НЕЙТРОННОАКТИВАЦИОННОГО АНАЛИЗА:

R. Gijbels, *Talanta*, 1971, **18**, 587.

Резюме—Обсуждены применимость и недостатки метода нейтронноактивационного анализа в случае платиновых металлов. Особенное внимание посвящено мешающим влияниям при определении благородных металлов в платиновых металлах и природных образцах. Подчеркнута проблема эталонов, носителей и определения химического выхода. Предложены современные методы счета радионуклидов образованных активацией нейтронами платиновых металлов.

ВКЛАД В ПРИМЕНЕНИЕ ХЕЛАТООБРАЗУЮЩИХ АГЕНТОВ В ВОЛЬТАМПЕРОМЕТРИИ С АНОДНЫМ СНИМАНИЕМ:

Ludmila Zieglerova, Karel Stulik and Jan Dolezal, *Talanta*, 1971, **18**, 603.

Резюме—Определены величины $E_{p/2}$ ионов Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, Tl^{+} применением циклической вольтамперометрии в растворах ацетата и буфферов Бриттона-Робинсона, и в растворах содержащих ЭДТА и ДЦТА. Затем использовали ДЦТА для определения небольших количеств висмута—до $10^{-7}M$, в присутствии 10^{4}-кратного количества свинца—и следов таллия, до $5 \times 10^{-9}M$ в присутствии 2×10^{5}-кратного количества кадмия, методом вольтамперометрии с анодним сниманием. Получена удовлетворительная воспроизводимость. Кроме того определяли следовие количества меди в ДЦТА аналитической чистоты. Также описана новая ячейка с протеканием для снимающего анализа, с изменением раствора. Воспроизводимость резульататов без изменения раствора, с ручним изменением раствора и с использованием ячейки с протеканием испытаны на определении таллия в растворе ДЦТА в качестве модели.

ПРИМЕНЕНИЕ УМЕРЕННО ДИССОЦИИРОВАННЫХ КОМПЛЕКСОВ В СПЕКТРОФОТОМЕТРИЧЕСКОМ АНАЛИЗЕ—III. ОЦЕНКА ЛИНЕЙНЫХ КРИВЫХ ФОТОМЕТРИЧЕСКОГО ТИТРОВАНИЯ без ИСПОЛЬЗОВАНИЯ ИНДИКАТОРА:

J. Fischer, Z. Slovak and J. Borak, *Talanta*, 1971, **18**, 615.

Резюме—Кривые фотометрических титрований анализированы в форме гиперболы появляющейся в зависимости от линейной переменной, в отсутствии индикатора. Возможно оценить титрационные кривые образования комплексов типа ML даже если они диссоциированы в значительной мере, т.е. когда продукт константы образования и концентрации определяемого становится близким единице. Обсуждены пределные условия удачнойооценки кривых. Применимость метода испытана на практических системах.

Chelating properties of α-oximinocarboxamides—I. α-Oximinophenylacetamide isomers: Dominick A. Coviello and Hamed M. El-Fatatry, *Talanta*, 1971, **18**, 631. (Department of Chemistry, College of Pharmacy, University of Illinois at the Medical Center, Chicago, Illinois 60612, U.S.A.)

Summary—Various polyfunctional oximes chelate with metals provided that the other functional group is proximal to the oxime and contains a good donor atom or is a good donor itself. Thus α-oximinocarboxamides are potential chelating agents of analytical value since the amide function attached to the carbon atom bearing the oxime has two groups capable of functioning as donors (ketone and amine). Two isomers of α-oximinophenylacetamide (AOPA) were obtained by two different synthetic routes, and structures were assigned by spectrometric methods. *syn*-AOPA was found to have chelating properties, but the *anti*-isomer did not. The synthesis and details of structure assignments are reported here.

Rapid polarographic method for the microdetermination of organically-bound phosphorus: S. W. Bishara and M. E. Attia, *Talanta*, 1971, **18**, 634. (National Research Centre, Dokki, Cairo, U.A.R.)

Summary—An indirect polarographic method for the microdetermination of phosphorus in organophosphorus compounds is described. Alkaline hypobromite is used as oxidizing absorbent. Quinoline phosphomolybdate is precipitated with a measured excess of standard molybdate solution. The unreacted Mo(VI) is determined polarographically. Nitrogen, chlorine, bromine and sulphur do not interfere. One determination takes 40 min. The results obtained fall generally within the acceptable limits of error.

Amperometrische Bestimmung der Metalle unter Anwendung von Thioacetamid—X. Bestimmung von Kupfer in saurem pH-Gebiet: Maria Pryszczewska and Ewa Krzeszowska, *Talanta*, 1971, **18**, 638. (Institut für Allgemeine Chemie der Technischen Hochschule, Mickiewicza 66, Szczecin, Polen.)

Summary—A method is described for the amperometric titration of copper with thioacetamide (TAA) at pH 2–6, and at room temperature. Current is recorded with a potential in the range −0·25 to −0·40 V applied across a dropping mercury and calomel electrodes. The presence of Zn^{2+}, Tl^{+}, Pb^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+}, even in thousandfold excess, causes no interference. The reaction is rapid at room temperature, and the mean error lies between 1 and 2%.

ХЕЛАТООБРАЗУЮЩИЕ ХАРАКТЕРИСТИКИ α-ОКСИИМИНОКАРБОКСАМИДОВ—I. ИЗОМЕРЫ α-ОКСИИМИНОФЕНИЛАЦЕТАМИДА:

DOMINICK A. COVIELLO and HAMED M. EL-FATATRY, *Talanta*, 1971, **18**, 631.

Резюме—Различные многофункциональные оксимы образуют хелаты с металлами если другая функциональная группа проксимальная оксиму и если содержает хороший этом-донор или представляет собой хороший донор. Этим образом α-оскииминокарбоксамиды представляют собой применимые в анализе хелатообразующие агенты, так как амидная функция, присоединенная несущему оксим атому углерода имеет две группы способные служить в качестве донора (кетон и амин). Два изомера α-оксииминофенилацетамида (АОФА) получены двумя различными синтезами а их структуры проверены спектроскопическими методами. Син-АОФА показал хелатообразующие характеристики, но анти-изомер—не показал. В настоящей статье приведены синтез и детали обозначения структуры изомеров.

БЫСТРЫЙ ПОЛЯРОГРАФИЧЕСКИЙ МЕТОД МИКРООПРЕДЕЛЕНИЯ ФОСФОРА В ОРГАНИЧЕСКОЙ СВЯЗИ:

S. W. BISHARA and M. E. ATTIA, *Talanta*, 1971, **18**, 634.

Резюме—Описан косвенный полярографический метод микроопределения фосфора в фосфоро-органических соединениях. Щелочный гипобромит использован в качестве окисляющего абсорбента. Хинолинфосфомолибдат осаждают известным избытком стандартного раствора молибдата, а нереагированный Mo(VI) определяют полярографическим методом. Азот, хлор, бром и сера не мешают определению. Продолжительность одного определения 40 мин. В большинстве случаев полученные результаты в приемлемых пределах ошибки.

АМПЕРОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МЕТАЛЛОВ С ПРИМЕНЕНИЕМ ТИОАЦЕТАМИДА—X. ОПРЕДЕЛЕНИЕ МЕДИ ПРИ НИЗКИХ ЗНАЧЕНИЯХ pH:

MARIA PRYSZCZEWSKA and EWA KRZESZOWSKA, *Talanta*, 1971, **18**, 638.

Резюме—Описан метод амперометрического титрования меди с тиоацетамидом (ТАА) при низких значениях pH и при комнатной температуре. Ток записывают потенциалом в пределах −0,25 до −0, 40в, примененном через капельного ртутного и каломелеього электродов. Присутствие Zn^{2+}, Tl^{+}, Pb^{2+}, Fe^{2+}, Co^{2+} и Ni^{2+} даже в 1000-кратном избытке не мешает определению. Реакция быстрая при комнатной температуре, а средная ошибка равна 1–2 %.

Traitement mathématique des resultats du dosage titrimétrique: N. A CHERNOVA, P. P. MEL'NIKOV, L. N. KOMISSAROVA and V. I. SPYTZIN, *Talanta*, 1971, **18**, 642. (Département de Chimie Minérale de l'Université de Moscou, Moscou, U.R.S.S.)

Summary—A statistical method is proposed for treatment of the titrimetric results. It permits differentiation between true effets on titrimetric graphs and the effects that are the result of random scattering of the experimental points. As an example the mathematical treatment of the data for the system $Sc^{3+}:H_2PO_2^-$ is considered.

Spectrophotometric study and analytical application of rare-earth Tiron complexes—II. Determination of europium: TOMITSUGU TAKETATSU and TAEKO YAMAUCHI, *Talanta*, 1971, **18**, 647. (College of General Education, Kyushu University, Fukuoka, Japan.)

Summary—The absorption spectra of europium–Tiron complexes in aqueous solution have been measured from 340 to 600 nm. The absorbance at 390 and 420 nm follows Beer's law up to 0·8 mg/ml (pH 6·2–6·6). Other rare earths except for cerium(III) did not interfere. The interference of cerium could be removed by addition of ascorbic acid. The combining ratio of Tiron to europium has been found to be 1:1.

Reduction and determination of dixanthogens: M. S. PRASAD, *Talanta*, 1971, **18**, 649. (Department of Chemistry, Indian Institute of Technology, New Delhi-29, India.)

Summary—A convenient method for the reduction and determination of dixanthogen has been developed. It is based on the quantitative reaction of dixanthogen with zinc amalgam to form xanthate; the latter can be determined by iodine titration, potentiometric titration with silver nitrate, or by spectrophotometry at 310 mμ. Dixanthogen can be determined in mixtures containing xanthate, by titration of aliquots with and without reduction. Higher dixanthogens can also be determined, and flotation liquors analysed.

МАТЕМАТИЧЕСКАЯ ОБРАБОТКА РЕЗУЛЬТАТОВ ТИТРИМЕТРИЧЕСКОГО АНАЛИЗА:

N. A. CHERNOVA, P. P. MEL'NIKOV, L. N. KOMISSANOVA and V. I. SPYTZIN, *Talanta*, 1971, **18**, 642.

Резюме—Предложен статистический метод обработки результатов титриметрического анализа. Метод позволяет различать между истинными эффектами на титриметрические крывы и эффектами появляющимися в результате случайного рассеяния опытных данных. В качестве примера обсуждена математическая обработка данных системы $Sc^{3+}:H_2PO_2^-$.

ИЗУЧЕНИЕ СПЕКТРОФОТОМЕТРИЧЕСКИМ МЕТОДОМ И ПРИМЕНЕНИЕ В АНАЛИЗЕ КОМПЛЕКСОВ ТИРОНА С РЕДКОЗЕМЕЛЬНЫМИ ЭЛЕМЕНТАМИ:—II. ОПРЕЛЕЛЕНИЕ ЕВРОПИЯ:

TOMITSUGU TAKETATSU and TAEKO YAMAUCHI, *Talanta*, 1971, **18**, 647.

Резюме—Измерены спектры светопоглощения комплексов тирона с европием в водном растворе от 340 до 600 нм. Светопоглощение при 390 и 420 нм повинуется закону Бера до 0,8 мг/мл (при pH 6,2–6,6). Другие редкоземельные элементы за исключением церия(III) не мешают. Влияние церия может быть исключено добавлением аскорбиновой кислоты. Отношение тирона и европия в комплексе было 1:1.

ВОССТАНОВЛЕНИЕ И ОПРЕДЕЛЕНИЕ ДИКСАНТОГЕНОВ:

M. S. PRASAD, *Talanta*, 1971, **18**, 649.

Резюме—Разработан пригодный метод восстановления и определения диксантогена. Метод основан на количественном образовании ксантата реакцией диксантогена с амальгамой цинка. Ксантат затем определяют титрованием иодом, потенциометрическим титрованием нитратом серебра или измерением светопоглощения при 310 нм. Диксантоген в ксантатсодержащих смесях можно определять титрованием аликвотных частей с восстановлением и без восстановления. Метод также позволяет определять высшие диксантогены и анализировать флотационные жидкости.

Journal of Inorganic and Nuclear Chemistry

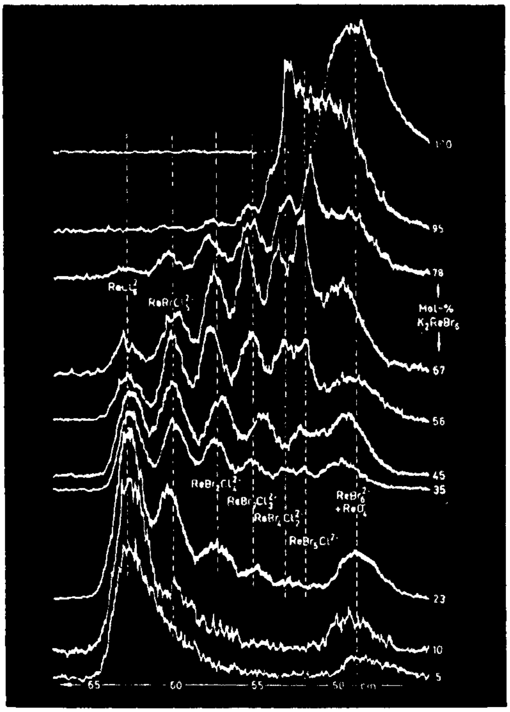
Editors

J. J. Katz *Argonne National Laboratory Illinois USA*
A. G. Maddock *University Chemical Laboratory Cambridge England*
C. B. Amphlett *Atomic Energy Research Establishment Didcot England*
G. Blasse *Physical Laboratory Solid State Department Utrecht The Netherlands*

Published Monthly

The Journal of Inorganic and Nuclear Chemistry provides an international medium for communication in the broad areas of inorganic and nuclear chemistry, including synthetic and structural inorganic chemistry, co-ordination chemistry, kinetics and mechanisms of inorganic reactions, nuclear properties and reactions.

This monthly journal publishes original research papers, both experimental and theoretical in the inorganic field. Emphasis is primarily on such topics as new compounds and reactions, structures, solution complexes, reaction mechanisms, preparation and application of stable and radioactive isotopes, including the fission products and the actinide elements.



Manuscripts are accepted in English, French or German. Short communications are published on the basis of originality, interest and timeliness. All papers should be directed to a chemical audience, and chemical aspects and principles should be emphasised.

A companion to this journal is Inorganic and Nuclear Chemistry Letters, with Joseph J. Katz as the editor-in-chief. This journal provides a medium for the very prompt communication of papers in the same areas of inorganic and nuclear chemistry.

Some recent papers from the Journal:

P. GÜTLICH, K. FRÖHLICH & S. ODAR: Polymere Chrom (III)–komplexe als folge der Neutronenbestrahlung von Kristallinem Kaliumchromat—I. Trennungs–methode und einige chemische Eigenschaften der Mehrkernigen Rückstossprodukte.

T. N. WATERS & P. E. WRIGHT: Electronic absorption band assignments for copper (II) salicylaldimine complexes.

T. B. BRILL & Z. Z. HUGUS JNR: Studies of mercuric halide donor–acceptor complexes by nuclear quadrupole resonance spectroscopy.

C. L. GARG, K. V. NARASIMHAM & B. N. TRIPATHI: The i.r. spectra and structure of some rare earth chelates of 2-hydroxy-5-methyl acetophenone.

A. KLEINSTEIN & G. A. WEBB: Spectroscopic, thermogravimetric and magnetic studies on some metal complexes with pyridine carboxylic acids.

Subscription: £70/$175 per annum

Pergamon Press

OXFORD · NEW YORK · SYDNEY · TORONTO

5/71

Volume 18, No. 6 June 1971

Contents

Short Communications

Letter to the Editor

Talanta Annual Subscription Rates (including postage)

$10 (£3.50)—*Bona fide* students

$90 (£36)—Multiple-reader institutions

Private individuals whose departmental libraries subscribe, may obtain this journal for their use at a reduced rate of $25 (£8) per annum.

Printed in Northern Ireland at The Universities Press, Belfast