An International Journal of Analytical Chemistry

ταλαντα

talanta

PERGAMON PRESS
LONDON NEW YORK PARIS LOS ANGELES
VOLUME 5 NUMBERS 3/4 SEPTEMBER–OCTOBER 1960

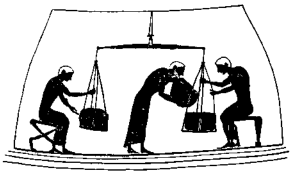
EDITOR-IN-CHIEF

Professor CECIL L. WILSON; Department of Chemistry, The Queen's University, Belfast, Northern Ireland.

ASSISTANT EDITOR

Dr. M. WILLIAMS; Department of Chemistry, College of Advanced Technology, Gosta Green, Birmingham 4, England.

REGIONAL EDITORS



Professor L. GORDON; Department of Chemistry and Chemical Engineering, Case Institute of Technology. Cleveland 6, Ohio, U.S.A.

Dr. R. PŘIBIL; Czechoslovak Academy of Sciences, Chemical Institute, Laboratory of Analytical Chemistry, Praha, I, Jilská 16, Czechoslovakia.

Professor T. TAKAHASHI; 1051 Wadahon cho, Suginami ku, Tokyo, Japan.

Professor G. GOPALA RAO; Department of Chemistry, Andhra University, Waltair, S. India

ADVISORY BOARD

Professor F. E. BEAMISH—Toronto
Professor R. BELCHER—Birmingham (Chairman of the Board)
Professor H. BODE—Hanover
Professor G. CHARLOT—Paris
Professor C. CIMERMAN—Haifa
Dr. C. E. CROUTHAMEL—Argonne, Illinois
Professor P. DELAHAY—Baton Rouge, Louisiana
Professor H. DIEHL—Ames, Iowa
Dr. C. DRĂGULESCU—Timisoara
Professor L. ERDEY—Budapest
Professor F. FEIGL—Rio de Janeiro
Professor H. FLASCHKA—Atlanta, Georgia
Professor W. GEILMANN—Mainz
Dr. J. HOSTE—Ghent
Mr. H. W. KIRBY—Miamisburg, Ohio
Professor J. J. LINGANE—Cambridge, Massachusetts
Professor F. LUCENA-CONDE—Salamanca
Dr. S. J. LYLE—Durham
Dr. R. J. MAGEE—Belfast
Professor H. MALISSA—Vienna
Professor W. WAYNE MEINKE—Ann Arbor, Michigan
Professor J. MINCZEWSKI—Warsaw
Dr. A. D. MITCHELL—London
Dr. G. H. MORRISON—Bayside, New York
Professor F. NYDAHL—Uppsala
Dr. MAURICE PESEZ—Paris
Dr. E. RANCKE-MADSEN—Copenhagen
Professor C. N. REILLEY—Chapel Hill, N. Carolina
Dr. M. L. SALUTSKY—Clarksville, Maryland
Professor E. SCHULEK—Budapest
Professor G. SEMERANO—Padova
Professor G. FREDERICK SMITH—Urbana, Illinois
Professor H. SPECKER—Dortmund-Alperbeck
Professor E. H. SWIFT—Pasadena, California
Professor P. S. TUTUNDŽIĆ—Belgrade
Professor F. L. WARREN—Pietermaritzburg
Professor H. WEISZ—Vienna
Dr. T. S. WEST—Birmingham
Dr. JAMES C. WHITE—Oak Ridge, Tennessee
Professor H. H. WILLARD—Ann Arbor, Michigan
Mr. F. J. WOODMAN—Sellafield

Publishing Offices: Headington Hill Hall, Oxford (OXFord 64881).

Published monthly – 3 Volumes per year, each of 4 issues

Subscription (including postage): (A) for Libraries, Government Establishments and Research Institutions—£7 ($20) per Volume, £21 ($60) per annum. (B) for private individuals, who place their orders with the Publisher and who certify that the Journal is for their personal use—£5.5. ($15) per annum.

Payments must be made in advance

Copyright © 1960
Pergamon Press Ltd.

Pergamon Press are also the publishers of the following journals:

JOURNAL OF NUCLEAR ENERGY (*including* THE SOVIET JOURNAL OF ATOMIC ENERGY—PART A: REACTOR SCIENCE; PART B: REACTOR TECHNOLOGY)
HEALTH PHYSICS (*The official journal of the Health Physics Society*)
JOURNAL OF INORGANIC AND NUCLEAR CHEMISTRY
TETRAHEDRON (*The International Journal of Organic Chemistry*)
INTERNATIONAL JOURNAL OF APPLIED RADIATION AND ISOTOPES
BIOCHEMICAL PHARMACOLOGY
* BIOPHYSICS
* JOURNAL OF MICROBIOLOGY, EPIDEMIOLOGY AND IMMUNOBIOLOGY
* PROBLEMS OF HEMATOLOGY AND BLOOD TRANSFUSION
* PROBLEMS OF VIROLOGY
* PROBLEMS OF ONCOLOGY
* SECHENOV PHYSIOLOGICAL JOURNAL OF THE U.S.S.R.
* BULLETIN OF THE ACADEMY OF SCIENCES OF THE U.S.S.R., GEOPHYSICS SERIES
* ELECTRIC TECHNOLOGY, U.S.S.R.
* RADIO ENGINEERING
* RADIO ENGINEERING AND ELECTRONICS
* TELECOMMUNICATIONS
* PHYSICS OF METALS AND METALLOGRAPHY
* THE ABSTRACTS JOURNAL OF METALLURGY
* APPLIED MATHEMATICS AND MECHANICS
CHEMICAL ENGINEERING SCIENCE
JOURNAL OF ATMOSPHERIC AND TERRESTRIAL PHYSICS
PLANETARY AND SPACE PHYSICS
GEOCHIMICA ET COSMOCHIMICA ACTA
BULLETIN GÉODÉSIQUE
ANNALS OF THE INTERNATIONAL GEOPHYSICAL YEAR
SPECTROCHIMICA ACTA
ACTA METALLURGICA
(*for the Board of Governors of Acta Metallurgica*)
JOURNAL OF THE MECHANICS AND PHYSICS OF SOLIDS
INTERNATIONAL JOURNAL OF THE PHYSICS AND CHEMISTRY OF SOLIDS
DEEP-SEA RESEARCH
JOURNAL OF NEUROCHEMISTRY
JOURNAL OF PSYCHOSOMATIC RESEARCH
JOURNAL OF INSECT PHYSIOLOGY
INTERNATIONAL JOURNAL OF AIR POLLUTION
INTERNATIONAL ABSTRACTS OF BIOLOGICAL SCIENCES (*for Biological and Medical Abstracts Ltd.*)
RHEOLOGY ABSTRACTS
VACUUM
OPERATIONAL RESEARCH QUARTERLY
ANNALS OF OCCUPATIONAL HYGIENE
ARCHIVES OF ORAL BIOLOGY
PLANETARY AND SPACE SCIENCE
ELECTROCHIMICA ACTA

**** Translations of Russian Journals published on behalf of Pergamon Institute, a Division of Pergamon International Corporation***

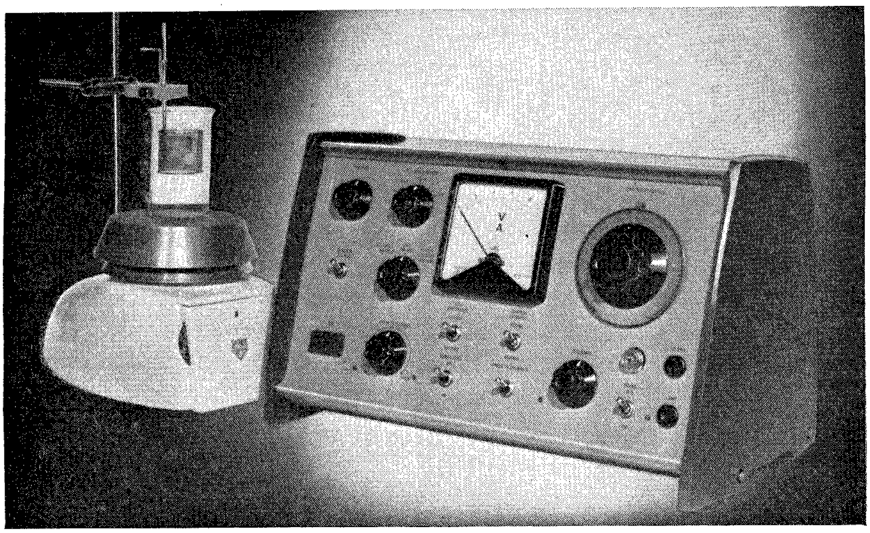
Leaflets giving further details and subscription rates of each of these Journals are available on request.

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

A 1654

Wadsworth Controlled Potential Electro-Depositor

ELECTRO-DEPOSITION has long been recognised as an analytical and separative technique for solutions containing metallic ions. The method may be applied where the ionic concentrations of the metals present in solution vary widely, separation being best achieved where the potential of the working electrode relative to the solution is controlled, using a reference electrode as described independently by Sand & Fischer. Manual control of the electrode potential, although possible, is tedious and time consuming, with the result that automatic control circuits have been developed by a number of workers.



The Southern Analytical controlled potential electro-depositor is based upon a design due to N. J. Wadsworth of R.A.E., Farnborough, and is intended primarily for use with platinum electrodes. The circuit is fully transistorised in the interests of compactness and reliability and is capable of supplying a maximum controlled current of 10 amperes to the electrolysis cell.

In operation, the required cathode potential is preset upon a built-in high grade potentiometer. Any error between the preset potential and that of a reference half-cell (e.g. saturated calomel), mounted immediately adjacent to the cathode, is applied to an amplifier which controls the current passing through the cell in such a sense that the potential error tends towards zero.

In order to ensure that thermal drift in the control amplifier is held at a very low level, a water-cooled heat sink is employed to maintain the transistors at a substantially constant temperature. The accuracy of control attained may be judged from the fact that the incremental error in electrode potential as a function of cell current has a mean value of 1.6 millivolts/ampere; thus when the electrolysis current has fallen to the low levels obtaining towards the end of a deposition, extremely close control is established. It is noteworthy that the potential defined by the built-in potentiometer cannot be exceeded as cell current cuts off at zero potential error.

The apparatus is supplied complete with leads for connection to the user's own electrode assembly. If desired however, suitable standard accessory equipment can be provided.

SOUTHERN Analytical

SOUTHERN ANALYTICAL LIMITED CAMBERLEY SURREY TELEPHONE: CAMBERLEY 3401

PERGAMON PRESS

specialized journals
for
specialized advertising!

Advertise in TALANTA

Space is available to all manufacturers of suitable products—the range which will appeal to readers of this journal is extensive and includes balances, laboratory chemicals of all kinds, filtration apparatus, ion exchange materials, absorptiometers, spectrophotometers, potentiometers, polarographs, ovens and furnaces, glass ware, platinum ware, silica apparatus, volume measuring apparatus, automatic titrators, vacuum pumps, colorimeters, fluorimeters, microscopes, gas detection and measurement apparatus, thermometers of all types, sampling apparatus . . . this list could easily be trebled!

We shall be happy to provide impartial advice as to the suitability of products not listed.

THIS IS ONE OF MORE THAN 50 INTERNATIONAL SCIENTIFIC JOURNALS. SPECIAL REDUCED "COMBINED RATES" ARE OFFERED TO MANUFACTURERS ADVERTISING IN MORE THAN ONE JOURNAL.

For details WRITE OR PHONE to

R. D. MILLER
Advertisement Manager
PERGAMON PRESS LIMITED
Pergamon House,
4 Fitzroy Square,
London W.1
Phone: EUSton 4455

H. L. WOUDHUYSEN
Advertisement Manager
PERGAMON PRESS INC.
122 East 55th Street,
New York 22, N.Y.,
U.S.A.
Phone: Plaza 3-9651

-6. ก.ค. 2504

Talanta, 1960, Vol. 5, pp. 137 to 140. Pergamon Press Ltd. Printed in Northern Ireland

AMPEROMETRIC DETERMINATION OF GLUCOSE, FRUCTOSE AND SACCHAROSE AT ZERO APPLIED POTENTIAL

E. Michalski, K. Czarnecki and M. Ignaczak
Inorganic Chemistry Department, University of Łódź, Poland

(*Received* 18 *March* 1960)

Summary—An indirect amperometric determination of glucose, fructose, and saccharose has been developed. The sugars are oxidised with cerium^{IV} perchlorate in $1N$ perchloric acid at 60°. After cooling, the excess oxidant is titrated with sodium oxalate solution. The end-point is determined amperometrically at zero applied potential.

Existing methods for the determination of sugars can be divided into two groups: physical and chemical. The former include the polarimetric, the densitometric and the refractometric methods. The chemical methods are based on the capacity of the sugar for reducing some oxidants. In most cases a base solution containing copper^{I} salts is the oxidant.[1] As a consequence, the determination of sugars is reduced to different methods of determining the resulting copper^{I} oxide. As under these conditions there is no stoichiometric dependence on the quantity of the resulting copper^{I}, oxide, it is necessary to determine it under exactly the same conditions.

It is characteristic of the methods used hitherto that comparatively weak oxidants were employed, causing only a partial oxidation of the sugar. The application of a stronger oxidant can produce a more complete oxidation of the examined compound.

A method of determining glucose, fructose, and saccharose has been developed by the authors, which consists in oxidising the sugars in an acidic medium by means of cerium^{IV} perchlorate.[4]

EXPERIMENTAL

0·1N solution of cerium^{IV} perchlorate in 1N perchloric acid: The solution of cerium^{IV} perchlorate was prepared according to the method described by Smith and Getz.[2] It was standardised potentiometrically by means of sodium oxalate. The standardised solution was kept in a dark and cool place. It has been established that the normality remains practically unchanged under these conditions.

0·15N solution of sodium oxalate in 1N perchloric acid: Sodium oxalate was obtained by the neutralisation of a solution of oxalic acid.[3] The substance obtained after drying served as the standard substance. The conventional weight was dissolved in $1N$ perchloric acid.

The solutions of glucose, fructose and saccharose used for the determinations, were prepared from weighed quantities of material recrystallised from ethyl alcohol. The quantities were dissolved in $1N$ perchloric acid.

Apparatus

In order to determine the end-point of the cerimetric titration an amperometric method at zero applied potential was employed. A saturated calomel electrode was used as reference electrode, and a wire of polished platinum (diameter 0·5 mm, length 8 mm) as an indicator electrode. The electrodes were connected with a galvanometer having a sensitivy of 3×10^{-7} A per scale division. During the determinations the indicator electrode was immovable, but the solution was vigorously stirred. The presence of oxygen was found to have no influence on the results.

The determination of sugars has also been performed by means of an amperometric "dead-stop end-point" method. The electrodes employed were made of platinum wire (diameter 1 mm, length 7 mm). The potential difference applied to the electrodes from outside amounted to 50 mV. The changes in the current intensity were observed with a galvanometer of sensitivity $7{\cdot}8 \times 10^{-8}$ A per scale division.

The determination of glucose

The oxidation of glucose with cerium^{IV} perchlorate may be represented by the equation:

$$CH_2OH(CHOH)_4CHO + 12Ce^{4+} + 6H_2O \rightarrow 6HCOOH + 12Ce^{3+} + 12H^+ \quad (1)$$

The reaction is relatively slow and it does not permit an immediate titration of the sugar to be made. The determination was performed by adding approximately a two-fold excess of the oxidant to a sample of the examined solution taken from the standard sugar solution with a pipette. The mixture was heated for 35 to 45 min in a water bath at 60°. When small quantities of sugar were examined the time of heating was prolonged. After cooling the solution, the excess cerium^{IV} was back-titrated by means of standard sodium oxalate. To establish the end-point an amperometric method at zero applied potential was employed. The measurement of the current was carried out towards the end of the titration when the solution became almost completely discoloured. Based on the results obtained a curve was drawn of the current intensity versus the volume of reagent added (Fig. 1).

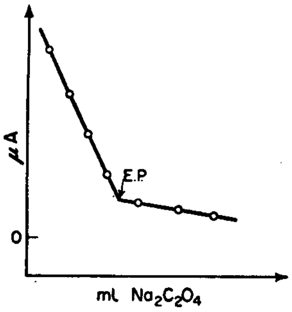


FIG. 1.

To establish the end-point of titration an amperometric "dead-stop end-point" method was also applied. The sudden fall observed in the current intensity at the end-point permits it to be determined without a diagram. The differences between the results obtained by means of both amperometric methods did not exceed experimental error.

By means of the method described 0·6–10 mg of glucose have been determined. Four series of determinations were made, each consisting of 9 to 10 determinations. The results of each series are given in Table I.

TABLE I. AMPEROMETRIC DETERMINATION OF GLUCOSE

Series	Normality of Ce^{4+} solution	Normality of $C_2O_4^{2-}$ solution	Time of heating, *min*	Glucose Present, *mg*	Glucose Found, mean, *mg*	Mean deviation from mean % error
I	0·1026	0·1487	35	8·44	8·43	0·10
II	0·1026	0·1487	40	3·44	3·43	0·18
III	0·1026	0·1487	45	1·62	1·63	0·55
IV	0·1026	0·1487	45	0·60	0·58	0·75

The determination of fructose

The oxidation of fructose by means of cerium^{IV} perchlorate is according to the equation:

$$CH_2OH(CHOH)_3COCH_2OH + 14Ce^{4+} + 6H_2O \rightarrow 5HCOOH + CO_2 + 14Ce^{3+} + 14H^+ \quad (2)$$

As in the case of glucose, a two-fold excess of cerium^{IV} perchlorate was added to the examined sugar taken from the standard sugar solution with a pipette. The mixture was heated for 45 min at a temperature of 60°, then the excess of cerium^{IV} was back-titrated with sodium oxalate.

0·6–13 mg of fructose were determined by means of this method. Four series of determinations were made, each of them consisting of 10 to 12 determinations. The results obtained are presented in Table II.

TABLE II. AMPEROMETRIC DETERMINATION OF FRUCTOSE

Series	Normality of Ce^{4+} solution	Normality of $C_2O_4^{2-}$ solution	Time of heating, *min*	Fructose		Mean deviation from mean %error
				Present, *mg*	Found, mean, *mg*	
I	0·1026	0·1487	45	12·52	12·50	0·09
II	0·1102	0·1487	45	6·57	6·58	0·12
III	0·1102	0·1487	50	2·36	2·35	0·56
IV	0·1102	0·1487	50	0·60	0·62	0·80

The determination of saccharose

Saccharose reacts in a similar way to glucose and fructose. As the reaction takes place in an acidic medium it is preceded by the process of inversion. The products obtained as a result of this process react with cerium^{IV} perchlorate according to equations (1) and (2). The process of oxidation as a whole gives the following overall equation in the case of saccharose:

$$C_{12}H_{22}O_{11} + 26Ce^{4+} + 13H_2O \rightarrow 11HCOOH + CO_2 + 26H^+ + 26Ce^{3+} \qquad (3)$$

As with glucose and fructose, the determination of saccharose was performed by adding an excess of the oxidant to a sample taken from the standard solution with a pipette. The mixture was heated for about 50 min in a water bath at 60°. Then the excess of cerium^{IV} was back-titrated amperometrically. The determination of 0·6–8 mg of saccharose has been performed. Three series of determinations were made, each of them consisting of 10 to 12 determinations. The results obtained are presented in Table III.

TABLE III. AMPEROMETRIC DETERMINATION OF SACCHAROSE

Series	Normality of Ce^{4+} solution	Normality of $C_2O_4^{2-}$ solution	Time of heating, *min*	Saccharose		Mean deviation from mean %error
				Present, *mg*	Found, mean, *mg*	
I	0·1102	0·1487	45	7·28	7·27	0·21
II	0·1102	0·1487	50	2·00	2·01	0·15
III	0·1102	0·1487	55	0·67	0·65	0·93

CONCLUSION

Milligram quantities of glucose, fructose and saccharose may be determined by oxidising them in an acidic medium with cerium^{IV} perchlorate. The end-point of the reaction has been determined by an amperometric method at zero applied potential, titrating the excess cerium^{IV} perchlorate with sodium oxalate. Several series of determinations of each sugar have been performed, each series consisting of about 10 determinations. The mean deviation from the mean % error has amounted to about 0·2% for quantities of sugar of the order of several mg, about 0·5% for quantities of sugar of the order of 1 mg, and about 0·9% for quantities smaller than 1 mg.

Zusammenfassung—Es wird eine amperometrische Methode zur Bestimmung von Glucose, Fructose und Saccharose beschrieben. Obengenante Zucker werden mit $Ce(ClO_4)_4$ Lösung in 1n Perchlorsäure bei 60°C oxydiert und der Überschuss der Oxydationsmittels durch Rücktitration mit Natriumoxalatlösung zurückgemessen. Endpunkt mit Titration bestimmt man amperometrisch ohne die Aussenspannung.

Résumé—Les auteurs ont élaboré une méthode ampérométrique du dosage de glucose, fructose et de saccharose. Les sucres nommés ont été oxidés en chauffant—environ 60°C—par une solution de perchlorate de cerium(IV) dans 1*N* l'acide perchlorique. L'excès de l'oxydant après le refroidissement a été titré à l'aide de la solution d'oxalate de sodium. Le point d'équivalent était marqué en utilisant une méthode ampérométrique sans applications du potentiel imposé de l'extérieur.

REFERENCES

[1] K. H. Bauer, *Analiza Zwiazków Organicznych*, P.W.T., Warszawa, 1957.
[2] G. F. Smith and C. Getz, *Ind. Eng. Chem. Anal.*, 1940, **12**, 339.
[3] J. W. Koriakin and I. I. Angelow, *Czistyje Chimiczeskije Reaktiwy*, G. Ch. I., Moskwa, 1955.
[4] F. Duke and G. Smith, *Ind. Eng. Chem. Anal.*, 1940, **12**, 201.

Talanta, 1960, Vol. 5, pp. 141 to 146. Pergamon Press Ltd. Printed in Northern Ireland

THE APPLICATION OF METALLOCHROMIC INDICATORS IN COLORIMETRY—I

THE SPECTROPHOTOMETRIC DETERMINATION OF MINUTE AMOUNTS OF COPPER WITH ANALOGUES OF GLYCINE THYMOL BLUE

M. Koch, V. Svoboda and J. Körbl*
Department of Chemistry, School of Agriculture, Brno
and
Spolana, N.E., Research Centre of the Lachema Plant, Brno, Czechoslovakia

(*Received* 23 *March* 1960)

Summary—The possibility of application of five different metallochromic derivatives of Thymol Blue (I–V) to the spectrophotometric determination of micro amounts of copper has been studied. The derivative of proline (I), applied in a solution buffered with hexamethylenetetramine and hydrochloric acid, has proved best for this purpose. Absorbance of its copper complex shows only insignificant changes in the pH range from 4·9 to 5·4 and it conforms to Beer's law up to 25 μg of copper^{II} at 595 mμ. Larger quantities of iron^{II}, cobalt^{II}, nickel^{II}, zinc^{II}, lead^{II}, uranium^{VI} and beryllium^{II} interfere.

With the development of chelatometry many new indicators have been recently introduced into chemical analysis, undoubtedly the most important of them being the so-called metallochromic indicators.[1] Their great sensitivity, favourable colour properties and, in some cases, good selectivity are very promising as to their potential application to other fields of analytical chemistry, *e.g.* many colorimetric methods have been developed with the use of these substances.

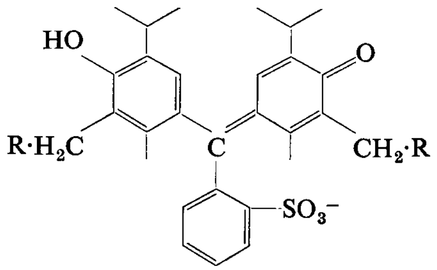
In the group of "complexone-type" metallochromic indicators only the application of Cresolphthalein Complexone[2] and recently also of Xylenol Orange[3–5] to spectrophotometry have been studied. Other analogous compounds have not been investigated from this standpoint, although many of them are capable of meeting all the requirements necessary for colorimetric reagents. One of the most promising indicators of this type is Glycine Thymol Blue, introduced in recent years into chelatometry.[6] The chelating properties of this substance, as compared with the analogous Methylthymol Blue,[7] are decreased to such an extent by eliminating one carboxymethyl group in the side-chain, that only the reaction with copper is actually applicable; other cations react only weakly or fail to react at all. Analogous condensation products of Thymol Blue with formaldehyde and other aminocarboxylic acids, prepared in connection with the systematic study of new metallochromic indicators,[8] behave similarly. By further modifying the auxiliary functional groups[9] a still higher specificity was reached as compared with Glycine Thymol Blue.

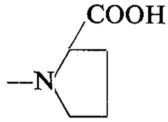
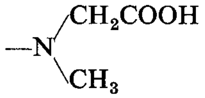
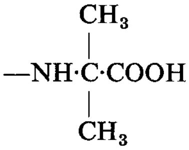
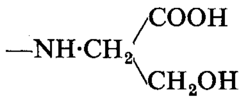
All of the prepared substances are acid-base indicators with the colour properties of the parent dye, *i.e.* Thymol Blue. In an acidic medium, where the original colour of the dye is yellow, they form blue complexes with copper^{II}.[8] The sensitivity of these

---

* Present address, Pharmaceutical and Biochemical Research Institute, Prague, Czechoslovakia.

reactions, stability of the colour formed, and sufficient selectivity promise—according to preliminary investigations—the potential use of some of these substances as chromogenic reagents for spectrophotometric determination of copper. From this viewpoint five most satisfactory reagents (I–V) have been studied; the results of this study are reported in this paper.



No.	R	Name
(I)		Proline Thymol Blue
(II)	 $-\mathrm{N}{<}^{\mathrm{CH_2COOH}}_{\mathrm{CH_3}}$	Sarcosine Thymol Blue
(III)	$-\mathrm{NH\cdot CH_2COOH}$	Glycine Thymol Blue
(IV)	 $-\mathrm{NH}\cdot\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\cdot\mathrm{COOH}$	Methylalanine Thymol Blue
(V)	 $-\mathrm{NH\cdot CH_2}{<}^{\mathrm{COOH}}_{\mathrm{CH_2OH}}$	Serine Thymol Blue

EXPERIMENTAL AND RESULTS

Apparatus and reagents

The absorption spectra of the reagents and their copper complexes were measured by means of a quartz spectrophotometer SF 4 in cells of 1-cm optical path. Other absorption measurements were made on a König-Martens spectrophotometer with an entrance and eye-piece slit width of 0·2 mm. For the pH measurements an Acidimetr AK (Kovodružstvo, Prague), with a high-resistance glass electrode, was used.

0·1% solutions of reagents (I)–(V) were prepared in double-distilled water; all of these solutions were stable for several weeks. The stock solution (0·001*M*) of copper$^{\mathrm{II}}$ was prepared by dissolving 0·2497 g of $CuSO_4 \cdot 5H_2O$ (A. R. grade) in double-distilled water and diluting to 1 litre. Working solutions were prepared by appropriate diluting of the stock solution. 0·1*M* solutions of other cations were prepared by dissolving the corresponding salts (A. R. grade). Buffer solutions for the pH range from 4·2 to 6·2 were prepared by mixing a 1*M* solution of hexamethylenetetramine (A. R. grade) and 6*N* hydrochloric acid in the appropriate proportions.

Qualitative test for copper and sensitivity of the reaction

To a 5-ml sample solution of copper buffered with hexamethylenetetramine and hydrochloric acid, 3 drops of the reagent solution were added and the colour formed was compared, after a few sec, with a blank. According to the amount of copper present, the resulting colour was either sky-blue or, with smaller quantities of copper, purple or grey. The sensitivity of the reaction at the optimal pH values is given in Table I.

TABLE I.—SENSITIVITY

Reagent	pH	pD
Proline Thymol Blue	4·9	7·6
Sarcosine Thymol Blue	4·6	7·6
Glycine Thymol Blue	5·4	7·6
Methylalanine Thymol Blue	5·1	7·4
Serine Thymol Blue	6·0	7·4

Absorption spectra

The yellow coloured, slightly acid reagent solutions show an absorption maximum at about 450 mμ. The formation of a copper complex causes a bathochromic shift of about 150 mμ. Fig. 1 shows the absorption spectrum of Proline Thymol Blue (curve 1) and of its copper complex with an excess of the reagent (curve 2) at pH 5·2. Absorption curves of the copper-complexes of all of the compounds studied (I–V) measured against the reagent blanks are illustrated in Fig. 1 and 2.

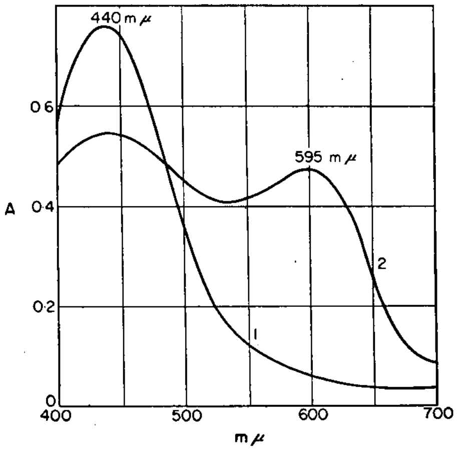


FIG. 1.

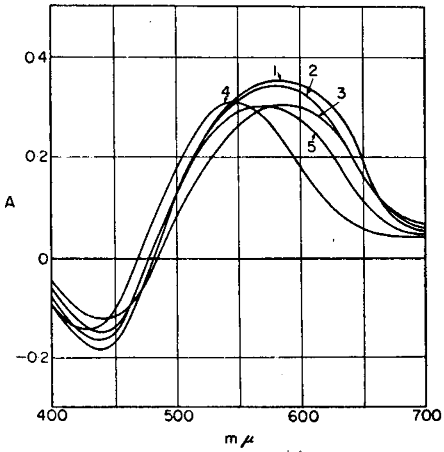


FIG. 2.

Effect of pH and choice of the appropriate buffer

The effect of pH on the sensitivity of the reaction was studied with different buffer solutions. However, their choice was restricted since some of them, *e.g.* citrate, mask the reaction. Hexamethylenetetramine was found to be the most convenient buffer. Acetate buffer is less suitable for it slightly decreases the sensitivity, and gives negative results in the presence of larger amounts of iron^{III} or tin^{II}.

The relation between the absorption of the copper complex and pH was studied in hexamethylenetetramine buffer at different wavelengths and with an excess of the reagents. Fig. 3 shows the absorbancy plotted against pH at wavelengths of absorption maxima (see Fig. 2) in the pH range from 4·2 to 6·2. All the obtained curves have two branches: the ascending one represents the successive formation of the complex up to a maximum lying at the pH at which the reaction with copper is quantitative. A moderate slope of the second branch is caused by the commencing acid-base change of the reagent blank against which the measurements have been made. From this standpoint, Proline

Thymol Blue has been found to be the most convenient reagent for the spectrophotometric determination of copper, since the pH-curve of this reagent shows only insignificant changes of absorbancy in rather broad limits around pH 5·2.

Calibration curves

The validity of Beer's law has been verified in the hexamethylenetetramine-hydrochloric acid buffer at a reagent concentration of 0·2 ml of a 0·1 % solution in a total volume of 25 ml. Measurements were made at wavelengths of the maximum difference in absorbancy of the copper complex against the reagent blank (see Fig. 2), and at two different pH values. Proline Thymol Blue follows Beer's law best of all these reagents. Calibration curves of this dye are illustrated in Fig. 4. Curves No. 1 were obtained with 5-cm cells at pH 4·9 and 5·4, respectively, and conform to Beer's law up to 10 μg of copper^{II} in 25 ml. Calibration curve No. 2 was obtained at the same pH values in 2-cm cells for amounts of copper up to 25 μg in an equal volume. A slight "gooseneck" curvature occurs but even in this case Beer's law is followed well within the limits of error of measurement.

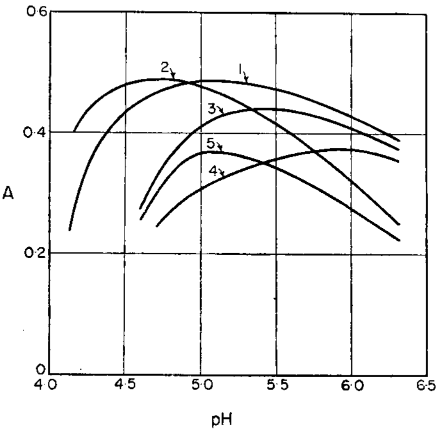


FIG. 3.

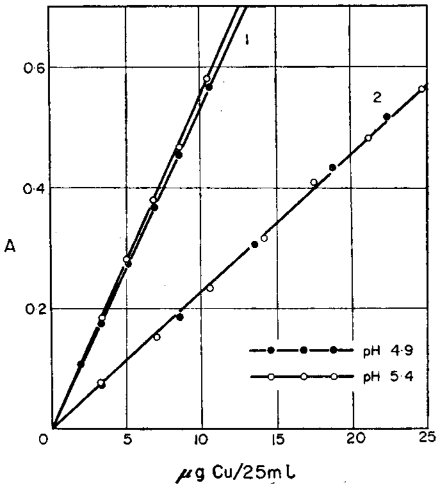


FIG. 4.

Influence of foreign ions

The effect of foreign ions was studied by absorption measurements in the solutions of copper complexes of all of the reagents with 0·2 ppm of copper^{II} at the same wavelengths as in the preceding determination. As interfering were classified those ions causing a greater difference in absorption—in comparison with the absorption of the copper complex alone—than 0·005 units. On the basis of the results obtained the reagents studied may be arranged in the following sequence of increasing sensitivity to foreign ions: Proline Thymol Blue, Methylalanine Thymol Blue, Sarcosine Thymol Blue, Serine Thymol Blue and Glycine Thymol Blue. From this viewpoint Proline Thymol Blue was again found to be the most convenient reagent for the application studied, which under the conditions used for the determination of copper reacts only with cobalt, zinc, nickel, lead, uranium and beryllium. Iron^{II} interferes if present in an approximately 2·5-fold excess; however, this interference may be easily removed by oxidation to the tervalent form and by the subsequent addition of an appropriate quantity of ammonium fluoride. Upper limits for the concentrations of all of the interfering cations allowing the determination of 0·2 ppm of copper^{II} are given in Table II. Chromium^{III} interferes by virtue of its own colour and all cations precipitated under the conditions used prevent the determination of copper.

Of the anions iodides, dithionites, ferro- and ferricyanides, oxalates, citrates, tartrates and all substances giving even weak complexes with copper, interfere.

Strong oxidants and reductants destroy the dye.

Stability of coloration

The stability of the coloured complex of copper with Proline Thymol Blue was studied at the laboratory temperature by measuring the absorption at regular time intervals. The maximal colour developed over a period of a few min and no decrease of absorbance was then observed even after several days.

TABLE II.—INTERFERING IONS

Ion	Added as	Limiting conc., *ppm*	
		pH 4·9	pH 5·4
Fe^{2+}	$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	0·5 1000*	0·5 1000*
Co^{2+}	$CoSO_4 \cdot 7H_2O$	0·8	0·7
UO_2^{2+}	$UO_2(CH_3COO)_2 \cdot 2H_2O$	1·8	0·7
Ni^{2+}	$NiSO_4 \cdot 7H_2O$	7	3
Be^{2+}	$BeSO_4 \cdot 4H_2O$	10	7
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	15	9
Pb^{2+}	$Pb(NO_3)_2$	40	10

* After oxidation to Fe^{3+} and addition of NH_4F.

DISCUSSION

A large number of reagents for the spectrophotometric determination of copper have been proposed to date, so that the addition of any new ones must be properly justified. There are, in our opinion, serious reasons for which Proline Thymol Blue should be included. Its advantages are:

1. High sensitivity, expressed by the value of pD = 7·6 and a molar extinction coefficient of 19600 at 595 mμ.
2. Absorption of its copper complex sufficiently independent of pH.
3. Favourable properties with regard to interferences from other cations.
4. Practically unlimited stability of the coloration formed.

The results presented in this paper show that only a very few of the reagents previously suggested and used for the spectrophotometric determination of copper can successfully compete with Proline Thymol Blue. By comparison with the sensitivity of other reagents, as expressed by molar extinction coefficients, it follows that only four substances (oxalyldihydrazide, Zincone, dithizone and 1:5-diphenylcarbohydrazide) are better—in this respect—than Proline Thymol Blue (*cf.* [10]). However, Zincone and dithizone show very low specifity so that in applying these reagents a tedious and time-consuming separation of copper from other interfering cations is usually indispensable. The application of diphenylcarbohydrazide is restricted by the low stability of both the reagent solution and the colour produced; it is also necessary to maintain accurately both the pH (a change of 0·01 in pH implies a 2% error in the determination) and the temperature.[10] On the other hand, the absorption of the copper complex of Proline Thymol Blue changes but negligibly over a pH range from 4·9 to 5·4, the reagent is practically of unlimited stability, and only a few cations interfere with the determination.

From this point of view Proline Thymol Blue seems to be very convenient for the determination of minute amounts of copper, especially in biological materials. In this case only the interference of iron^{II} presents a certain difficulty; this difficulty can, however, be obviated by the oxidation of the iron to the tervalent form and by the addition of a small amount of ammonium fluoride.

Zusammenfassung—Die Möglichkeit der Anwendung von fünf verschiedenen metallochromen Thymolblauderivaten /I–V/ für die spektrophotometrische Bestimmung von Cu^{2+}-Mikromengen wurde untersucht. Am besten bewährte sich das Prolinderivat /I/ in Lösungen, die mit Urotropin-Salzsäure gepuffert wurden. Die Absorption des Kupferkomplexes dieses Derivats bleibt in pH-Grenzen 4.9–5.4 praktisch konstant und folgt dem Beerschen Gesetz bis zu 25 μg Kupfer bei 595 mμ. Grössere Mengen von Fe^{2+}-, Co^{2+}-, Ni^{2+}-, Zn^{2+}-, Pb^{2+}-, Be^{2+}- und $UO_2{}^{2+}$-Ionen stören.

Résumé—Les auteurs ont étudié la possibilité d'application de cinq différents dérivés métallochromiques du bleu de thymol au dosage spectrophotométrique de micro-quantités de cuivre. Le dérivé de la proline utilisé en solution tamponnée avec l'héxaméthylènetétramine et l'acide chlorhydrique s'est révélé au mieux pour ce dosage. L'absorption de son complexe avec le cuivre montre seulement des changements insignifiants dans le domaine de pH 4,9–5,4 et obéit à la loi de Beer jusqu'à 25 μg de Cu^{2+} à 595 mμ. De plus grandes quantités de Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} Pb^{2+}, UO_2^{2+} et Be^{2+} gênent.

REFERENCES

[1] J. Körbl and R. Přibil, *Coll. Czech. Chem. Comm.*, 1957, **22,** 1122.
[2] F. H. Pollard and J. V. Martin, *Analyst*, 1956, **81,** 348.
[3] K. L. Cheng, *Talanta*, 1959, **2,** 61, 186, 266.
[4] *Idem, ibid.*, 1959, **3,** 81.
[5] *Idem, ibid.*, 1959, **3,** 147.
[6] J. Körbl, E. Kraus and R. Přibil, *Coll. Czech. Chem. Comm.*, 1958, **23,** 1218.
[7] J. Körbl and R. Přibil, *ibid.*, 1958, **23,** 873.
[8] J. Körbl, V. Svoboda, D. Terzijská and R. Přibil, *Chem. and Ind.*, 1957, 1624.
[9] J. Körbl and R. Přibil, *Ind. Chemist*, 1958, **34,** 616.
[10] R. W. Turkington and F. M. Tracy, *Analyt. Chem.*, 1958, **30,** 1699.

Talanta, 1960, Vol. 5, pp. 147 to 153. Pergamon Press Ltd. Printed in Northern Ireland

THE DETERMINATION OF GALLIUM IN ROCKS BY NEUTRON-ACTIVATION ANALYSIS

D. F. C. MORRIS and Miss M. E. CHAMBERS
Department of Chemistry, Brunel College of Technology, London, W.3, England

(*Received* 6 *June* 1960)

Summary—Neutron-activation analysis has been applied to the determination of gallium in rocks. The Harwell Pile BEPO has been used as the source of neutrons, and a radiochemical procedure employing carrier chemistry has been utilised to separate the induced gallium activity.

Neutron-activation analyses of gallium in the standard rocks G1 and W1 are reported and compared with results obtained by other analytical methods.

INTRODUCTION

THE geochemistry of gallium has been reviewed by Shaw,[1] and an extensive study of the distribution of the element in rocks, minerals, sediments, and sea water has been reported recently by Burton, Culkin, and Riley.[2]

Various analytical procedures have been employed for the determination of gallium in rocks; spectrographic,[3] spectrophotometric,[4] fluorimetric,[5] and fluorescent X-ray spectrographic[6] methods have been used. Neutron-activation analysis has been successfully employed for the determination of gallium in iron meteorites[7] and in blende,[8] and it was decided to apply this technique to the determination of gallium in rocks.

The principles of neutron-activation analysis have been extensively discussed elsewhere, and the subject has been reviewed recently by Atkins and Smales.[9] Advantages of the method for determining trace elements may be summarised as follows:

Sensitivity. With the advent of high-flux atomic piles, neutron-activation analysis has, for many elements, represented the ultimate in practical sensitivity.

Specificity. The identity of the radionuclide used for the determination can be confirmed by measurements of the decay and energy of its radioactivity, in addition to radiochemical separation.

Contamination. A feature of the neutron-activation method is that analytical samples generally require little pre-treatment before irradiation. Since carriers are usually employed in radiochemical separations, the method is free from difficulties caused by reagent blanks or by contamination from traces of inactive material during radiochemical operations after irradiation.

Separation. If carrier chemistry is used there is no need for radiochemical separation steps to be quantitative, as a correction is made for losses by measurement of chemical yield.

Scale of operation. The use of carriers avoids the difficulties of chemical operations with ultramicro quantities, such as problems of co-precipitation and adsorption.

Standards. It is usually easier to prepare satisfactory comparison standards for neutron-activation analysis than for spectrochemical analysis.

Neutron activation of gallium

Naturally occurring gallium consists of two isotopes, ^{69}Ga(% abundance, $\theta = 60{\cdot}2$) and ^{71}Ga($\theta = 39{\cdot}8\,\%$). On irradiation with neutrons of thermal energies, radioisotopes of gallium are produced by the following nuclear reactions:

$$^{69}\mathrm{Ga} \xrightarrow{n,\gamma} {}^{70}\mathrm{Ga}(t\tfrac{1}{2} = 21{\cdot}1 \text{ min}) \xrightarrow{\beta^-} {}^{70}\mathrm{Ge} \text{ (stable)}$$

$$^{71}\mathrm{Ga} \xrightarrow{n,\gamma} {}^{72}\mathrm{Ga}(t\tfrac{1}{2} = 14{\cdot}3 \text{ hr}) \xrightarrow{\beta^-} {}^{72}\mathrm{Ge} \text{ (stable)}$$

Isotopic thermal neutron activation cross-sections, σ, for the nuclear reactions are:

^{69}Ga(n,γ)^{70}Ga $\sigma = 1{\cdot}4$ barns

^{71}Ga(n,γ)^{72}Ga $\sigma = 3{\cdot}4$ barns

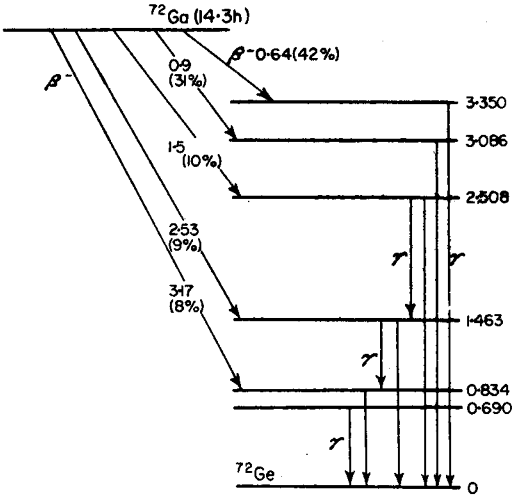


FIG. 1. Decay scheme for ^{72}gallium. Energies in MeV.

The radionuclide 14·3-hour ^{72}Ga was used in the present study. With a neutron flux of 10^{12} neutrons. cm^{-2}. sec^{-1} available in the Harwell Pile BEPO, it has been estimated by Jenkins and Smales[10] that *ca.* 1×10^{-10} g of gallium may be determined under ideal conditions. Since the average abundance of gallium in igneous rocks is about 19 ppm, neutron-activation analysis may be applied in cases where only very small samples of the material are available.

The decay scheme[11] for ^{72}Ga is shown in Fig. 1.

EXPERIMENTAL

Irradiation

All rock samples were available in a finely powdered condition, and were given no preliminary treatment before neutron-irradiation. Suitable quantities, usually about 0·5 g, of the powdered material were weighed out accurately into silica tubes of internal diameter 6 mm, and the tubes were immediately sealed. Standards were prepared by weighing out 0·1–0·2-ml aliquots of a dilute standard solution of gallium (100 mg of Ga/litre in 1*M* HNO_3) into silica tubes of internal diameter 4 mm. Samples and standards were packed side by side, with silica wool, in a standard screw-top aluminium can 3 in. long by 1 in. diameter, and were sent to the Atomic Energy Research Establishment, Harwell, for irradiation. Irradiation was in the Pile BEPO at pile factor 10, and was for 15 hr.

On delivery from Harwell after irradiation, the samples and standards were allowed to "cool" for 1 day and then were analysed radiochemically for ^{72}Ga.

Radiochemical separation

The radiogallium was separated from other elements in the irradiated rock samples by a modification of the procedure of Morris and Brewer.[8] The rock samples were dissolved by digesting with hydrofluoric acid and fuming with perchloric acid. Carrier chemistry was used in the separation procedure, and an excellent first decontamination step involved the extraction of gallium into ether from 5·5*M* hydrochloric acid. The relatively few elements extracted along with the gallium were then removed by scavenging with antimony trisulphide and ferric hydroxide. The gallium was finally precipitated and weighed as the 8-hydroxyquinolate.

A rather similar procedure has been employed recently by Bowen[12] in the analysis of biological material.

Reagents

Ga carrier: 10 mg of Ga/ml (added as $GaCl_3$ in dilute HCl)—standardised.
Fe carrier: 2 mg of Fe/ml (added as $FeCl_3{\cdot}6H_2O$ in very dilute HCl).
Sb carrier: 10 mg of Sb/ml (added as $SbCl_3$ in sufficient HCl to give a clear solution).

HF: 40%.
$HClO_4$: 9*M*.
HNO_3: 16*M*.
HNO_3: 6*M*.
HCl: 6*M*.
HCl: 1*M*.
Ether: pre-treated with 5·5*M* HCl.
HCl: 5·5*M* pre-treated with ether.
NH_4OH: 6*M*.
NaOH: 6*M*.
H_2S: generator.
Manoxol OT (British Drug Houses): 0·1% aqueous solution.
8-Hydroxyquinoline: 1% solution in 2*M* CH_3CO_2H.
$CH_3CO_2NH_4$: 6*M*.

Preparation and standardisation of the gallium carrier

Dissolve 5 g of pure gallium metal in dilute HCl and dilute to 500 ml.

Pipette 5 ml of the carrier solution into a 500-ml beaker, add 200 ml of H_2O, and warm to 70°. Add 35 ml of the 1% 8-hydroxyquinoline reagent, followed by the dropwise addition of 6*M* $CH_3CO_2NH_4$ with continuous swirling until a permanent yellow precipitate is formed. Add a further 1 ml of 6*M* $CH_3CO_2NH_4$ and continue swirling for 1 min, then allow to cool. Filter the granular precipitate through a sintered-glass crucible of medium porosity and wash with hot water. Dry to constant weight in an oven at 110°, and weigh.

Standardisations as the 8-hydroxyquinolate give results which are reproducible, but which may be a little higher[13] than the values obtained by standardisation as Ga_2O_3. Since gallium is finally weighed as the 8-hydroxyquinolate in the radiochemical procedure, the carrier is standardised gravimetrically through this compound.

Radiochemical separation procedure for the rock samples

Step 1: Remove the silica irradiation tubes containing the rock samples from the can, open them at the constriction, and transfer the contents to 60-ml platinum crucibles. Wash out the tubes with a little warm 6*M* HNO_3 and transfer the washings quantitatively to the crucibles. To a sample in a platinum crucible add 2 ml of standard Ga carrier. Cover loosely with a platinum lid and gently warm for a few min.

Step 2: Add 10 ml of 40% HF, cover the crucible with the platinum lid, and digest on a steam-bath until the sample is dissolved. Add 3 ml of 9*M* $HClO_4$ and 2 ml of 16*M* HNO_3, and heat the mixture till white fumes of $HClO_4$ begin to be given off, taking care to avoid spattering. Replace the cover loosely, and continue to heat for 5 min at a temperature such that the $HClO_4$ fumes moderately, but does not evaporate rapidly. Heat for 5–10 min longer, adding 1 ml of 9*M* $HClO_4$. Finally evaporate carefully almost to dryness. Extract the residue with hot water. Filter and discard any residue. Collect the filtrate in a 50-ml centrifuge tube and precipitate hydroxides by addition of 6*M* NH_4OH. Centrifuge and discard the supernate.

Step 3: Take up the residue in 15 ml of 6*M* HCl and filter, collecting the filtrate in a 50-ml centrifuge tube. Extract the gallium from the solution by agitating with 15 ml of ether pre-treated with 5·5*M* HCl. Transfer the ether phase to a clean 50-ml tube and wash it twice with 10-ml portions of 5·5*M* HCl saturated with ether. Discard the aqueous phases. Extract the gallium from the ether phase by equilibrating with an equal volume of H_2O. Draw off and retain the aqueous phase.

Step 4: Remove ether from the final solution by heating on a water-bath. Add 1 ml of Sb carrier and acidify with 6*M* HCl until the solution is clear. Boil and pass H_2S through the hot solution. Centrifuge and decant the clear supernatant solution into a clean 50-ml centrifuge tube. Boil to expel H_2S.

Step 5: Add 6*M* NaOH until the solution has a hydroxide concentration of 1-2*M*. Add 1 drop of Manoxol OT solution, heat to boiling, and add 1 ml of Fe carrier dropwise. Digest for 30 min. Filter through a Whatman No. 541 filter paper and discard the precipitate.

Step 6: Just acidify the solution with 1*M* HCl and dilute to 20 ml with H_2O. Heat to 70° and add 12 ml of 1% 8-hydroxyquinoline reagent. Add 6*M* $CH_3CO_2NH_4$ drop by drop with continuous stirring until a permanent yellow precipitate is formed, and then add 1 ml more. Continue stirring for 1 min. Wash the precipitate with 10 ml of warm H_2O and two 5-ml portions of cold water. Slurry the precipitate with H_2O on to a weighed aluminium counting tray (A.E.R.E. Cat. No. 4-3/1068), using a transfer pipette. Ensure that the distribution of the precipitate on the tray is uniform. Dry at 110° for 30 min and weigh.

Treatment of the irradiated gallium standards

At a suitable time open the irradiation tubes containing the standards. By means of a drop-pipette drawn out almost to a point, transfer the gallium solution quantitatively to a 50-ml centrifuge tube and rinse thoroughly with hot 2*M* HCl. Add 2 ml of standard Ga carrier and mix thoroughly. Dilute to about 35 ml with H_2O and adjust to pH 1. Precipitate gallium with 8-hydroxyquinoline and mount for counting as in *Step 6* above.

Measurement of radioactivity of the final precipitates

The final precipitates of gallium 8-hydroxyquinolate from the rock samples and the standards were counted under similar conditions with a Geiger-Müller counter of the EHM 2/S type, associated with conventional electronic equipment. At least 10^4 counts were recorded when possible. All measured counting rates were corrected for paralysis, background, and chemical yield. No self-absorption corrections were necessary with the range of weights of gallium 8-hydroxyquinolate obtained in the radio-chemical procedure. Decay curves of samples and standards were measured and corresponded with the published half-life of ^{72}Ga, so confirming the radiochemical purity of the gallium—*e.g.* see Fig. 2. Extrapolation of the decay curves to zero time or to any arbitrary time, gave activity values for sample and standard from which the gallium content of the original material could be found.

RESULTS

The results of neutron-activation analyses of the granite G1 and the diabase W1, which have been suggested as international standards for the determination of both major and minor constituents of igneous rocks,[14] are given in Table I. The results may be compared with those obtained by other workers using different analytical methods (Table II.)

DISCUSSION

In the neutron-activation analysis of gallium in rocks consideration must be given to the fact that elements other than gallium, on irradiation, undergo nuclear reactions

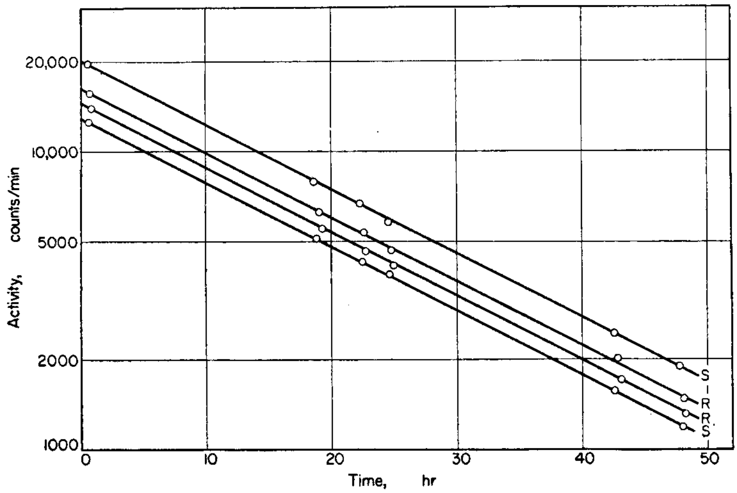


FIG. 2. Decay curves of final precipitates: S, from gallium standards. R, from samples of rock.

TABLE I. GALLIUM CONTENTS OF THE STANDARD GRANITE G1 AND THE STANDARD DIABASE W1 DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

G 1, *ppm*	W 1, *ppm*
21·2	17·5
21·2	18·4
19·5	
21·6	

TABLE II. OTHER RESULTS FOR THE GALLIUM CONTENTS OF THE STANDARD ROCKS G1 AND W1

Method	G1, *ppm* Ga	W1, *ppm* Ga	Analysts	
Spectrographic	20	15	Mitchell	see Ahrens[3]
Spectrographic	18	12	Murata	
Spectrographic	19	13	Gorfinkle and Ahrens	
Spectrographic	15	20	Nockolds	
Spectrographic	18	11	Shaw and Webber	
Spectrographic	23	23	McKenzie *et al.*[6]	
Chemical and fluorimetric	15	15	Hey, see Ahrens[3]	
Spectrophotometric	21·3	21·5	Culkin and Riley[4]	
Fluorescent X-ray spectrographic	20	24	McKenzie *et al.*[6]	
	av. 19 ± 3	av. 17 ± 5		

In addition to the above results, Hamaguchi *et al.*[15] have obtained the value 13·6 ± 1·2 ppm for the gallium content of W1 by a spectrographic method. Semi-quantitative spectrographic analyses by Harvey (see Ahrens[3]) give for G1 10 ppm Ga and for W1 20 ppm Ga.

leading to the formation of gallium isotopes. The elements germanium, arsenic, zinc, and uranium need consideration in this respect.

Germanium may give rise to ^{72}Ga on irradiation with fast neutrons (of which there is a proportion, about 17% of the thermal neutron flux,[16] under the irradiation conditions employed in BEPO) by the reaction ^{72}Ge(n,p)^{72}Ga. The mean cross-section for this reaction with the pile distribution of fast neutrons may be estimated theoretically[17] to be 0·42 millibarns. Taking this value for the cross section, it may be calculated that if a rock contains 7 ppm of germanium* the apparent gallium content due to this secondary transformation is only *ca.* 10^{-4} ppm. Germanium may also give rise to ^{72}Ga from the thermal neutron irradiation by the process

$$^{70}\text{Ge}(n,\gamma)^{71}\text{Ge} \xrightarrow{\text{EC}} {}^{71}\text{Ga}(n,\gamma)^{72}\text{Ga}.$$

A previous study of this sequence[19] shows that it is of no consequence in the analysis of gallium in rocks. Yet a further nuclear reaction whereby germanium may yield ^{72}Ga is ^{72}Ge(γ,p)^{72}Ga, but this is unlikely to be significant.

Arsenic may yield ^{72}Ga with fast neutrons by the reaction ^{75}As(n,α)^{72}Ga. Taking a theoretically calculated value of the cross-section for this reaction, 0·04 barns, and assuming[18] that the average arsenic content of a rock is 5 ppm, it can be calculated that the spurious gallium content due to this reaction is 0·02 ppm.

The formation of ^{72}Ga from zinc in rocks by the process

$$^{70}\text{Zn}(n,\gamma)^{71}\text{Zn} \xrightarrow{\beta^-} {}^{71}\text{Ga}(n,\gamma)^{72}\text{Ga}$$

can be shown by calculation to be negligible.[19]

Another possible mode of formation of ^{72}Ga is by the slow-neutron fission of uranium. The fission yield of ^{72}Ga is very low, however, and since there is only about 4 ppm of uranium in an average rock,[18] interference with the activation analysis of gallium is negligible.

Any interference of importance due to the production of gallium radio-isotopes other than ^{72}Ga would have been apparent from the decay measurements made on the counted samples from rock specimens.

Zusammenfassung—Neutronenaktivierungsanalyse wurde zur Bestimmung von Gallium in Gestein herangezogen. Der Harwell-Reaktor BEPO wurde als Neutronenquelle verwendet und radiochemische Methoden, wie Trägerfällungen wurden herangezogen um die erzeugte Galliumaktivität zu isolieren. Resultate nach dem neuen Verfahren wurden mit denen nach anderenAnalysenmethoden erhaltenen für Standardgesteinsproben G1 und W1 verglichen.

Résumé—L'analyse par activation par les neutrons a été appliquée au dosage du gallium dans les roches, la pile BEPO de Harwell a été utilisée comme source de neutrons et un procédé radiochimique employant la chimie des entraîneurs a été utilisé pour séparer l'activité induite du gallium. Les analyses par activation par les neutrons du gallium dans les roches étalons G1 et W1 sont décrites et comparées avec les résultats obtenus par d'autres méthodes analytiques.

REFERENCES

[1] D. M. Shaw, *Progr. Phys. Chem. Earth*, 1957, **2**, 164.
[2] J. D. Burton, F. Culkin and J. P. Riley, *Geochim. Cosmochim. Acta*, 1959, **16**, 151.
[3] L. H. Ahrens, *Quantitative spectrochemical analysis of silicates*. Pergamon Press, London, 1954.
[4] F. Culkin and J. P. Riley, *Analyst*, 1958, **83**, 208.

---

* This is the figure quoted by Rankama and Sahama[18] for the average abundance of germanium in igneous rocks. A more recent value for the crustal abundance, due to Burton *et al.*,[2] is 1·7 ppm Ge.

[5] E. B. Sandell, *Analyt. Chem.*, 1947, **19**, 63.

[6] R. M. McKenzie, A. C. Oertel and K. G. Tiller, *Geochim. Cosmochim. Acta*, 1958, **14**, 68.

[7] H. Brown and E. Goldberg, *Science*, 1949, **109**, 347.

[8] D. F. C. Morris and F. M. Brewer, *Geochim. Cosmochim. Acta*, 1954, **5**, 134.

[9] D. H. F. Atkins and A. A. Smales, *Adv. Inorg. Chem. and Radiochem.*, 1959, **1**, 315.

[10] E. N. Jenkins and A. A. Smales, *Quart. Rev.*, 1956, **10**, 83.

[11] D. Strominger, J. M. Hollander and G. T. Seaborg, *Rev. Mod. Phys.*, 1958, **30**, 585.

[12] H. J. M. Bowen, *Int. J. Applied Radiation Isotopes*, 1959, **5**, 227.

[13] J. M. Siegel and L. E. Glendenin, *Radiochemical studies: the fission products.* Ed. C. D. Coryell and N. Sugarman. McGraw-Hill, 1951, Paper 227.

[14] H. W. Fairbairn, W. G. Schlect, R. E. Stevens, W. H. Dennen, L. H. Ahrens and F. Chayes, *U.S. Geological Survey Bull.* No. 980, 1951.

[15] H. Hamaguchi, R. Kuroda and R. Negishi, *Talanta*, 1959, **3**, 207.

[16] C. E. Mellish, J. A. Payne and R. L. Otlet, *Radioisotopes in Scientific Research*, 1958, **1**, 35.

[17] D. J. Hughes, *Pile neutron research*, Addison-Wesley, Cambridge, Mass., 1953.

[18] K. Rankama and T. G. Sahama, *Geochemistry.* University of Chicago Press, 1950.

[19] D. F. C. Morris, D.Phil. thesis (Oxon), 1952.

Talanta, 1960, Vol. 5, pp. 154 to 161. Pergamon Press Ltd. Printed in Northern Ireland

FERRIMETRIC DETERMINATION OF URANIUM^{IV} USING RHODAMINE 6G AS FLUORESCENT INDICATOR

SEETARAMARAJU SAGI and G. GOPALA RAO
Chemistry Department, Andhra University, Waltair, India

(*Received* 6 *June* 1960)

Summary—Experimental conditions have been developed for the titration of uranium^{IV} with iron^{III} alum solution, using Rhodamine 6G as a fluorescent indicator. The titration is best carried out at 98–100° in a 2-3*N* hydrochloric acid medium, under filtered ultraviolet light, using 2·0 ml of 0·05% Rhodamine 6G solution for 30 ml of the titration mixture. A slight excess of iron^{III} solution quenches the greenish-yellow fluorescence of the dye through inner filter action. With the titration assembly described here, it is possible to determine uranium^{IV} with an accuracy of about 0·4%. This method appears to be more convenient than the potentiometric titration or the method employing potassium thiocyanate as internal indicator.

Evidence is also presented to show that the reaction between uranium^{IV} and iron^{III} is slow at room temperature.

FROM a consideration of redox potentials, iron^{III} sulphate and iron^{III} chloride are much less powerful oxidising agents than cerium^{IV} salts, potassium permanganate, potassium dichromate, or even sodium vanadate. It is, therefore, obvious that iron^{III} salts have not been widely employed as oxidants in titrimetric analysis. However, they have been so used in a few instances by employing higher temperatures. The determination of tin^{II} chloride with iron^{III} chloride is perhaps the earliest example of the analytical applications of iron^{III} chloride as a titrimetric reagent.[1,2,3] Next in importance are to be mentioned the determination of titanium^{III} and chromium^{II}.[4,5,6,7,8] Bradbury and Edwards[9] employed the direct titration between mercury^{I} nitrate and iron^{III} alum in the presence of excess thiocyanate for analytical purposes. A more detailed examination of this reaction was made by Belcher and West[10] and by Burriel and Lucena.[11] Pugh[12] has recommended mercury^{I} perchlorate in place of mercury^{I} nitrate. Uranium^{IV} has also been determined by titration with iron^{III} at 98–100°.

The indicators that have so far been used in titrations with iron^{III} include thiocyanate, methylene blue, indigo carmine, phenosafranine and cacotheline. No one appears to have so far used Rhodamine 6G as a fluorescent indicator in titrations involving iron^{III} as an oxidant. The present investigation is concerned with the titration of uranium^{IV} with iron^{III} in a hydrochloric acid medium.

Auger[13] appears to have been the earliest person to propose the titrimetric determination of uranium^{IV} with iron^{III} using potassium thiocyanate as indicator. Vortmann and Binder[14] determined iron^{III} with uranium^{IV} sulphate by titration to the disappearance of the colour of ferrithiocyanate. Weiss and Blum[15] carried out the titration of uranium^{IV} with iron^{III} potentiometrically at an elevated temperature, not exceeding 70°, in an atmosphere of carbon dioxide. They stated that the addition of ammonium thiocyanate to the mixture is essential, believing that ammonium thiocyanate does not alter the potential of the system but acts as a catalyst. Belcher, Gibbons and West[16] found that the reverse titration of iron^{III} with uranium^{IV} gives trouble at 60° and they preferred a slow titration in the cold with a potentiometric end-point. In the potentiometric titration, Issa and Elsherif[17] found that it is necessary to wait for 11–14 min at the end-point if the titration is performed in a 5–7N overall hydrochloric acid concentration at 20°, but only for 1 min if the titration is carried out at 60°. Cellini and Lopez[18] determined uranium^{IV} by titration with iron^{III} sulphate in a 0·1N sulphuric acid medium at room temperature, in an inert atmosphere. Rodden[19] recommended the titration of uranium^{IV} to be carried out below 90° using either ammonium thiocyanate as internal indicator or by potentiometry or by amperometry. Korach, Nessle, Sinclair and Casto[21] have studied the rate of oxidation of uranium^{IV} with iron^{III} by means of the absorption maximum of uranium^{IV} at 650 mμ, and believe that the rate of oxidation of uranium^{IV} by iron^{III} in 5% sulphuric acid is rapid at room temperature. They expressed the opinion that the electrometric titration of uranium^{IV} with iron^{III} should be feasible at room temperature, if some way could be found of speeding up the rate of establishment of potential equilibrium at the electrode. But the results cited by Rodden[20] on the amperometric titration of uranium^{IV} with iron^{III} indicate that the reaction is rather slow. It is stated that the errors obtained are "due to incomplete attainment of chemical equilibrium" and that the percentage error increases with the use of more and more dilute solutions.

EXPERIMENTS AND OBSERVATIONS

Preparation of Reagents: (*a*) The uranium^{IV} solution used in this investigation is prepared by reducing uranium^{VI} acetate in a Jones reductor and passing air through the reduced solution for 10 min to oxidise any uranium^{III} formed to uranium^{IV}. The strength of the uranium^{IV} solution is adjusted to be about 0·05N, with the concentration of sulphuric acid remaining at about 1·0N. (*b*) About 0·05N solution of iron^{III} is prepared from an AnalaR B.D.H. sample of ferric alum dissolved in 2–3N hydrochloric acid and standardised by reduction in a Jones reductor and titration with standard ceric sulphate solution. (*c*) A 0·05% solution of B.D.H. Rhodamine 6G is prepared in water. The solution has been found to be quite stable for 1 week, and for longer periods if treated with a drop or two of chloroform.

In view of the above, it appears that the question remains unsettled, whether the reaction between uranium^{IV} and iron^{III} is sufficiently rapid for analytical purposes. We have made a study of the problem by two methods.

In the first method we have made use of a very dilute solution of ferriin (oxidised ferroin) to indicate the progress of the reaction. In a blank experiment, 50 ml of $10^{-5}M$ ferriin solution (containing sulphuric acid at a 2N overall concentration) is treated with 1·0 ml of $5 \times 10^{-4}N$ uranium^{IV} solution (in 2N sulphuric acid). It is noted that in 10 min, the mixture develops a very slight red colour due to the reduction of ferriin. In another experiment the same mixture of ferriin and uranium^{IV} is treated with 1·0 ml of $5 \times 10^{-2}N$ iron^{III} sulphate solution (in 2N sulphuric acid). This mixture is found to develop a strong red colour in 10 sec. The first experiment shows that the reduction of ferriin by uranium^{IV} is *very* slow. This result, taken along with the result of the second experiment, shows that the strong red colour appearing in the second experiment is due to the formation of iron^{II} by the interaction of uranium^{IV} and iron^{III}. It is well known that even a trace of iron^{II} gives an intense red colour with ferriin. The speed of the development of the red colour in the second experiment will, therefore, be an indication of the speed of interaction of uranium^{IV} and iron^{III}. A large number of such experiments have been made with varying concentrations of uranium^{IV} and iron^{III}; the results are given in Tables I and II.

From Tables I and II, it is seen that the speed of the reaction is dependent on the concentrations of both uranium^{IV} and iron^{III}. It will also be evident that the reaction is very slow at concentrations of uranium^{IV} and iron^{III} encountered near the equivalence point of a volumetric titration.

The second method employed by us to obtain qualitative information on the speed of the reaction between uranium^{IV} and iron^{III} consists in the use of a fluorescent indicator, namely Rhodamine 6G.

TABLE I

Volume of uranium^{IV} solution, X *ml*	Time required for the development of a red colour, *sec*
1·0	10
0·50	25
0·25	35

50 ml of $10^{-5}M$ ferriin in $2N$ sulphuric acid
+1 ml of $5 \times 10^{-2}N$ iron^{III} in $2N$ sulphuric acid.
+X ml of $5 \times 10^{-4}N$ uranium^{IV} in $2N$ sulphuric acid.

TABLE II

Volume of iron^{III} solution, X *ml*	Time required for the development of a red colour, *sec*
1·0	10
0·5	30
0·2	60
0·1	90
0·05	140

50 ml of $10^{-5}M$ ferriin in $2N$ sulphuric acid
+1 ml of $5 \times 10^{-4}N$ uranium^{IV} in $2N$ sulphuric acid
+X ml of $5 \times 10^{-2}N$ iron^{III} in $2N$ sulphuric acid

From preliminary experiments with a 0·0005% solution of Rhodamine 6G, we have made the following observations:

(1) It has a greenish-yellow fluorescence in a 1–4*N* hydrochloric acid medium in the diffused light of the laboratory.

(2) If the acid concentration is increased beyond 4*N*, the fluorescence intensity decreases but it is still marked under filtered ultraviolet light (<400 mμ).

(3) The intensity of fluorescence appears to be lower at 90° than at 28° in a 3–6*N* hydrochloric acid medium, while a rise of temperature appears to be without much effect on the fluorescence intensity in a 1–3*N* hydrochloric acid medium.

(4) The intensity of fluorescence in filtered ultraviolet light is not affected by fairly large concentrations of sodium chloride (1–4 g of salt per 100 ml).

(5) The addition of a small quantity of iron^{III} markedly quenches the greenish-yellow fluorescence of the dye in filtered ultraviolet light, but not the greenish-yellow fluorescence of the dye in daylight.

(6) The quenching effect of iron^{III} is much more pronounced in a hydrochloric acid medium than in a sulphuric acid medium. The minimum amount of iron^{III} required to effect complete quenching of the greenish-yellow fluorescence in a 30-ml volume of a 0·0005% solution of the dye in 6*N* hydrochloric acid has been found to correspond to 0·12 ml of 0·05*N* iron^{III} solution, when the flask containing the mixture is kept at a distance of 20 in. from the lamp in the apparatus described here. With a 2*N* hydrochloric acid solution of the dye, the minimum amount of iron^{III} required to produce complete quenching corresponds to 0·16 ml of the same iron^{III} solution. Working with sulphuric acid solutions of the dye, we have found that the minimum amounts of iron^{III} required to produce complete quenching correspond to 4 ml and 5 ml of the same iron^{III} in 6*N* and 2*N* sulphuric acid solutions, respectively. These observations can be explained from the optical absorption curves of iron^{III} in hydrochloric acid and sulphuric acid, respectively. The optical absorption for iron^{III} in the region 340–400 mμ is much greater in an hydrochloric acid medium than in a sulphuric acid medium. This difference is more and more accentuated as the acid concentration is increased up to 6*N*.

We have made the interesting observation that the quenching action of iron^{III} can be counteracted by the addition of a suitable quantity of uranium^{IV} and allowing to stand for sufficient time. This indicates that (1) the quenching action of iron^{III} is due to a physical effect, (2) the fluorescence re-appears when the iron^{III} is destroyed by reaction with uranium^{IV}, and (3) the reaction between iron^{III} and uranium^{IV} is slow, as the restoration of fluorescence requires time and is not instantaneous after the addition of uranium^{IV}.

The following experiments have been conducted to ascertain, qualitatively, the speed of the reaction between uranium^{IV} and iron^{III} in a hydrochloric acid medium. Five ml of 0·04*N* uranium^{IV} solution are mixed with 15 ml of concentrated hydrochloric acid and 1·0 ml of 0·05 % Rhodamine 6G and the mixture diluted to 40 ml. This solution is treated with varying volumes (X ml) of 0·05*N* iron^{III} solution. It was noticed that, in each case, the fluorescence of the mixture was quenched immediately after the addition of the iron^{III} solution but it reappeared after some time. The time required for re-appearance of the fluorescence was noted in each case. The results are presented in Table III.

TABLE III

Volume of iron^{III} solution, X *ml*	Time required for the re-appearance of a fluorescence, *min*
2·0	11
1·0	8
0·8	6
0·6	5
0·4	4
0·2	3

Temperature 28°

In the above experiments, the time required for the re-appearance of fluorescence is evidently the time required for the reduction of iron^{III} by uranium^{IV}. These experiments, therefore, lead us to the conclusion that the reaction between iron^{III} and uranium^{IV} is slow at 28°. In another set of experiments, 0·4 ml of iron^{III} solution is mixed with 15 ml of concentrated hydrochloric acid and 1 ml of 0·05 % Rhodamine 6G and the mixture diluted to 40 ml. This mixture (which does not show any fluorescence) is treated with varying volumes (Y ml) of 0·04*N* uranium^{IV} solution in 2*N* sulphuric acid. A fluorescence appears in the mixture after some time. The time required for the appearance of the bright fluorescence of the dye is noted in each case. The results are given in Table IV.

TABLE IV

Volume of uranium^{IV} solution, Y *ml*	Time required for the appearance of a fluorescence, *min*
1·0	14
2·0	9
3·0	7
5·0	4

The results in Table IV also show that the reaction between iron^{III} and uranium^{IV} is slow at room temperature and that the speed of the reaction increases as the uranium^{IV} concentration is increased, while keeping the concentration of iron^{III} constant.

Experiments similar to those involved in Tables III and IV, but conducted at 98–100°, lead us to the conclusion that the reaction between uranium^{IV} and iron^{III} is very fast at that temperature. Hence it is possible to carry out the titration of iron^{III} with uranium^{IV} or *vice versa* using Rhodamine 6G as a fluorescent indicator.

The apparatus employed by us in the fluorimetric titration has been assembled as shown in Fig. 1. Light from a Philips 125 W "Germicidal lamp" U (run on 220 V, a. c. mains), mounted horizontally, passes through an iris diaphram D on to a condensing lens L_1. After passing through L_1 it is rendered parallel by lens L_2. A narrow pencil of light from this lens passes through a second iris diaphram D_2 and falls on the titration mixture contained in a 100-ml Pyrex glass beaker V mounted on a B.T.L. magnetic stirrer hot plate H (P is the paddle). The entire assembly is enclosed in a box painted black on the inside and provided with suitable shutters. The side of the box opposite the titration beaker at A has a small aperture, which enables the fluorescent light from the beaker to be observed in a direction perpendicular to the incident light, by a person sitting in a comfortable position. The neck of the beaker passes through a hole in the right-end top of the box, as shown in the figure. The mouth of the beaker is fitted with a stopper having three holes. Through two holes of this stopper are fitted the inlet and exit tubes for passage of carbon dioxide, while through the middle hole passes the nozzle of a micro burette B. The Philips "Germicidal lamp" transmits mostly ultraviolet light with a trace of violet radiation.

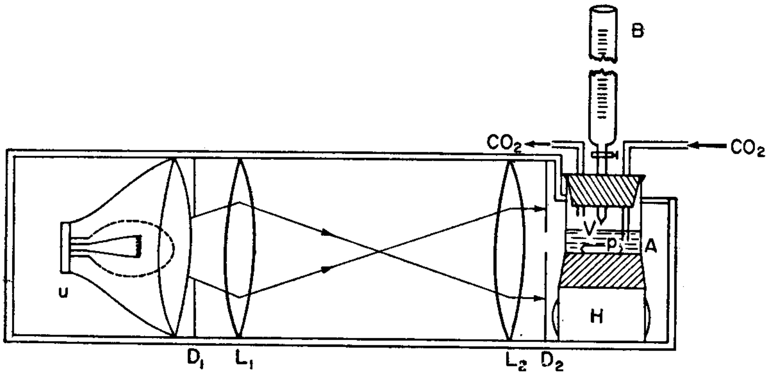


FIG. 1.—Titration assembly.

Both Rhodamine 6G and iron^{III} chloride strongly absorb the light emitted by the germicidal lamp. The fluorescence emitted by Rhodamine 6G in a 5–6N hydrochloric acid solution appears greenish-yellow under this light, both at room temperature and also at 98°. When 1 drop of 0·05N iron^{III} solution is added to 30–40 ml of the mixture, containing Rhodamine 6G, the fluorescence is noticed to disappear at A, while the fluorescence is still observable in the solution near the point of entry of the light.

For the fluorescence to disappear throughout the entire mixture, the addition of 3 drops (about 0·12 ml) of 0·05N iron^{III} solution is necessary under the experimental conditions described above. Hence, 0·12 ml of 0·05N iron^{III} solution may be taken as the blank correction in a fluorimetric titration if one takes the end-point as the disappearance of fluorescence throughout the entire solution, but 0·04 ml as the correction if one takes the disappearance of the fluorescence at A. The blank correction depends upon the concentration of the iron^{III} solution, the intensity of the light, the distance of the flask from the light source and the volume of the titration mixture, as well as the acidity of the solution. If the titration is carried out in 2–3N hydrochloric acid, a correction of 0·16 ml of 0·05N iron^{III} solution is necessary if one takes the quenching of fluorescence throughout the mixture as the end-point, and a correction of 0·04 ml if one takes the quenching at A as the end-point. In actual practice, titrations in a 2–3N hydrochloric acid medium have been found more convenient, taking the quenching of the fluorescence at A as indicating the end-point of the titration.

Influence of hydrochloric acid concentration

We have noticed that the titration becomes increasingly difficult as the acid concentration is increased beyond 5–6N. This is presumably due to the fact that the speed of the reaction diminishes with an increase in hydrochloric acid concentration. At hydrochloric acid concentrations higher than 5–6N, the quenching of fluorescence is noted at a titre lower than the theoretical. The difference in the observed and theoretical titres increases with increasing acid concentration. Moreover, it has been noticed that the fluorescence does not return, even after standing for 10 to 15 min in spite of the low titres. These results could be understood in the light of the fact that the potential of the U_{N}/U^{VI} system increases with an increase in the concentration of hydrochloric acid. The experimentally observed titres and the corresponding uranium potentials for different hydrochloric acid concentrations are given in Table V.

TABLE V

Concentration of hydrochloric acid, *moles/l*	U^{IV}/U^{VI} potentials, *mV*	Fe^{III}/Fe^{II} potentials, *mV*	Observed titre, *ml*	Blank correction for overall quenching, *ml*	Correct titre, *ml*
2	530*	680†	4·02	0·16	3·86
3	530*	670†	4·01	0·16	3·85
4	530*	660†	4·01	0·16	3·85
5	535*	—	3·98	0·12	3·86
6	535*	—	3·97	0·12	3·85
7	560*	—	3·78	0·08	3·70

* Computed from the graph given by Issa and Elsherif[17]
† Smith and Richter[22]

The hydrochloric acid concentrations given here can only be approximate as the mixture loses hydrochloric acid when heated at the higher acid concentrations.

It has been observed by us that when the acid concentration is below 2*N*, the quenching effect is not very prominent, with the result that slightly higher titres are obtained. In solutions which are more than 4*N* in hydrochloric acid, the end-point detection is somewhat less sharp, although accurate titres can be obtained with practice.

Prescribed procedure

Using the apparatus described above, in which the distance of the flask from the lamp is about 20 in., we have found that it is convenient to carry out the titration of uranium^{IV} with iron^{III} in a 2–3*N* hydrochloric acid medium at 98–100°. It is also convenient to take the quenching at A to indicate the end-point of the titration. In such titrations, the blank correction corresponds to 0·04 ml of 0·05*N* iron^{III} solution for a titration mixture of 30 ml. Some typical results are given in Table VI. These show that the error of determination is within 0·4%. It is recommended that 2·0 ml of 0·05% aqueous solution of Rhodamine 6G are added to 30 ml of the titration mixture.

TABLE VI

Amount of uranium^{IV} taken, *millimoles*	Amount of uranium^{IV} found, *millimoles*
0·250	0·248
0·375	0·374
0·500	0·502
0·560	0·558
0·780	0·778
0·805	0·808

Interferences

Since uranium^{IV} prepared by reduction of a uranium^{VI} salt in the Jones reductor is contaminated with zinc sulphate, we have studied the interference of zinc sulphate in the fluorimetric titration procedure here proposed. A number of titrations have been made with varying quantities of zinc sulphate added in addition to what has already been introduced in the Jones reductor. The results presented in Table VII show that zinc sulphate does not interfere.

Similar studies with chrome alum showed that the addition of 0·02–0·2 g of chrome alum does not interfere with the titration, but it has been observed that when a larger amount (0·5 to 1·0 g) is present, the dark green colour of chromium^{III} masks the greenish-yellow fluorescence of the dye.

TABLE VII

Amount of $ZnSO_4 \cdot 7H_2O$ added, *g*	Volume of iron^{III} solution required, *ml*
1·0	4·15
2·0	4·16
3·0	4·16
4·0	4·13
5·0	4·15

5 ml U^{IV} solution ≡ 4·16 ml of Fe^{III} solution

Metals like vanadium and molybdenum, which are reduced in the Jones reductor to lower oxidation states oxidisable by iron^{III}, should be absent.

Zusammenfassung—Experimentelle Bedingungen zur Titration von Uran(VI) mit Eisenalaunlösung unter Verwendung von Rodamin-6G als Fluorescenz-indicator wurden ausgearbeitet. Die Titration wird am besten bei 98–100°C in 2–3n Salzsäure, unter filtriertem UV-Licht, nach zusatz von 2·0 ml einer 0·05% Rodamin-6G-Lösung für je 30 ml Titrationslösung, vollzogen. Ein geringer Überschuss von Eisen(III) lösung löscht die grünlichgelbe Fluorescenz des Indicators. Mit der beschriebenen Titrationsanordnung ist es möglich Uran mit einer Genauigkeit von etwa 0·4% zu bestimmen. Die Methode ist besser geeignet als das übliche Verfahren mit Thiocyanat als Indicator. Es wird gezeigt, dass die Reaktion zwischen Uran(VI) und Eisen(III) bei Zimmertemperatur nur langsam verläuft.

Résumé—Les auteurs ont élaboré les conditions expérimentales de titrage de l'uranium (VI) avec une solution d'alun ferrique en utilisant la rhodamine 6G comme indicateur fluorescent. Le titrage est effectué à 98°–100° en milieu acide chlorhydrique 2N–3N, sous lumière ultra-violette filtrée, en utilisant 2,0 ml de la solution de rhodamine 6G à 0,05 pour cent pour 30 ml du mélange de titrage. Un faible excès de la solution de fer (III) fait disparaître la fluorescence jaune verdâtre du colorant par action de filtre interne. Avec le montage décrit, il est possible de doser l'uranium (VI) avec une précision d'environ 0,4 pour cent. Cette méthode paraît être plus commode que le titrage potentiométrique ou la méthode employant du thiocyanate de potassium comme indicateur interne. Les auteurs démontrent aussi que la réaction entre l'uranium (VI) et le fer (III) est lente à la température ordinaire.

REFERENCES

[1] R. Fresenius, *Z. analyt. Chem.*, 1862, **1**, 26, 32.
[2] Z. G. Szabó and E. Sugar, *Analyt. Chem.*, 1950, **22**, 361.
[3] *Idem, Analyt. Chim. Acta*, 1952, **6**, 293.
[4] E. Knecht, *Ber.*, 1903, **36**, 166; E. Knecht and E. Hibbert; *ibid.*, 1903, **36**, 1549.
[5] J. L. Henry and R. W. Grelbach, *Ind. Eng. Chem. Anal.*, 1944, **16**, 49.
[6] F. M. Burriel and F. Pinoperez, *Anales Fis. Quim*, 1951, **47B**, 305.
[7] J. L. P. Wyndham, *S. African Ind. Chemist*, 1951, **5**, 73.
[8] V. S. Syrokomskii and K. N. Zhukova, *Zavodskaya Lab.*, 1945, **11**, 373.
[9] F. R. Bradbury and E. G. Edwards, *J. Soc. Chem. Ind.*, 1940, **59**, 96T.
[10] R. Belcher and T. S. West, *Analyt. Chim. Acta*, 1951, **5**, 260, 268, 272.
[11] F. M. Burriel and F. C. Lucena, *Anales Fis. Quim.*, 1951, **47B**, 257; 1953, **49B**, 45.
[12] W. Pugh, *J. Chem. Soc.*, 1954, 588.
[13] V. Auger, *Compt. rend.*, 1912, **155**, 647–9; *Chem. Abs.*, 1913, **7**, 313.
[14] G. Vortmann and F. Binder, *Z. analyt. Chem.*, 1925, **67**, 269.

[15] G. Weiss and P. Blum, *Bull. Soc. chim., France*, 1947, 735; *Chem. Abs.*, 1948, **42,** 482.
[16] R. Belcher, D. Gibbons and T. S. West, *Analyt. Chem.*, 1954, **26,** 1025.
[17] I. M. Issa and I. M. Elsherif, *Analyt. Chim. Acta*, 1956, **14,** 466.
[18] R. Fernandez Cellini and J. Alonso Lopez, *Anales Fis. Quim*, 1956, **52B,** 163; *Analyt. Abs.*, 1957, **4,** 97.
[19] C. J. Rodden, *Analytical Chemistry of the Manhattan Project*, McGraw-Hill Book Co. Inc., New York, 1950, p. 70.
[20] *Idem., ibid.*, p. 71–72.
[21] M. Korach, G. Nessle, E. E. Sinclair and G. C. Casto, Report C-4. 100, 19, Aug. **11,** 1945, p. 2.
[22] G. F. Smith and F. P. Richter, *Ind. Eng. Chem. Anal.*, 1944, **16,** 580.

Talanta, 1960, Vol. 5, pp. 162 to 167. Pergamon Press Ltd. Printed in Northern Ireland

THE PHOTOMETRIC DETERMINATION OF ALCOHOLS BY MEANS OF VANADIUM OXINATE

MOTOHARU TANAKA
Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University
Nagoya, Japan

(*Received* 10 *February* 1960)

Summary—Vanadium oxinate dissolved in such organic solvents as chloroform and nitrobenzene can be successfully used for the photometric determination of micromolar quantities of various alcohols. The sensitivity depends upon the dielectric constant of the solvent and the concentration of the reagent. Suggestions are made for using the reaction to estimate the relative reactivity of a given alcohol and the steric effect about the alcoholic OH. The reaction can also be used to differentiate alcohol isomers.

INTRODUCTION

VANADIUM oxinate dissolves to give solutions of different colours in different solvents. In solvents such as acetic anhydride, amyl acetate, benzene, toluene, the solutions, like the solid, are dark violet, while in acidic solvents such as acetic acid and phenol they are blue. Furthermore, a red colour is characteristic of hydroxylic solvents. Therefore the red colour which vanadium oxinate produces in commercial chloroform is due to ethyl alcohol which has been added to the chloroform as stabiliser. This was pointed out by Buscarons and others,[1] who proved that a chloroform preparation which has been purified by repeated washing with water is coloured dark violet instead of red on addition of the oxinate. It has also been shown by the present author that while, by the addition of vanadium oxinate, a pure sample of an ester such as amyl acetate or benzyl acetate is coloured dark violet without any shade of red, some samples of the same esters are coloured red by the same oxinate, undoubtedly due to the presence of alcoholic impurity.

These facts suggest that the functional group of an alcohol has a specific affinity for vanadium oxinate, an affinity which is strong enough to produce an alcohol-vanadium oxinate association characterised by a red colour.

It has proved possible to utilise this red colour for detecting and even for determining alcohols. Thus in 1949 Buscarons *et al.*[1,2] demonstrated the usefulness of vanadium oxinate as a reagent for detecting a small amount of alcohol. In 1957 Kudo and Aoki[3] proposed vanadium oxinate in xylene-acetic acid as a reagent for alcohol detection and actually detected the alcoholic OH present in sterols such as testosterone and œstradiol. Furthermore, Maruta and Iwama[4] were able to determine photometrically aliphatic alcohols higher than hexyl alcohol by using Kudo and Iwama's reagent with slight modification.

The aim of the present investigation was to establish more elaborate methods for alcohol determination, using the same colour reaction. The nature of the colour of the alcohol–vanadium oxinate associate was therefore critically examined to find the factors and conditions which determine or control its development and stability.

REAGENTS AND APPARATUS

Vanadium oxinate: Precipitated from an acetic acid-acetate medium and washed with water and finally recrystallised from chloroform.

Oxine: GR.

Chloroform: Shake 500 ml of chloroform with 100 ml of 1*N* sulphuric acid containing 1 g of potassium chromate. Wash the organic layer, first with 100 ml of 1*N* sodium hydroxide and then 4 times with distilled water. The purified chloroform is dehydrated and is kept in a dark bottle, preferably in a dark cold place.

Other organic solvents: GR. If necessary, shake the solvent with distilled water to eliminate any alcoholic impurity and dehydrate.

*Vanadium oxinate solution:** In the case of chloroform and nitrobenzene, 1 μmol of vanadium oxinate per ml of solvent, containing about 1 mg of oxine per ml of solution, is used. In the case of the other solvents, which dissolve a smaller amount of vanadium oxinate, saturated vanadium oxinate solution, containing about 1 mg of oxine per ml of solution, is used.

Beckman DU spectrophotometer.

EXPERIMENTAL AND DISCUSSION

Spectrum of alcohol-vanadium oxinate associate

The first approach was to establish the difference spectrum between the absorption curve for the oxinate in an indifferent solvent (E_1) and that for the same solution to which an excess of an alcohol has been added (E_2).

The tested alcohols were those from ethyl alcohol to amyl alcohol and the indifferent solvents tested were benzene, toluene, xylene, nitrobenzene and chloroform.

The difference spectrum of the amyl alcohol-chloroform system (Fig. 1), representing an absolute value of $E_1 - E_2$, is characterised by two maxima with peaks at 470 mμ and 635 mμ. It is important that irrespective of the nature of the alcohol and the solvent, the positions of these two maxima remain unchanged, while the value $E_1 - E_2$ varies greatly with the amounts of alcohol added and the kind of solvent used. The value increases with the amount of alcohol and decreases with increase in the dielectric constant of the solvent.

This suggests the existence of the equilibrium:

$$\text{Vanadium oxinate} + \text{Alcohol} \rightleftharpoons \text{Vanadium oxinate-alcohol.}$$

Increase of the dielectric constant of the medium would favour dissociation, the point of equilibrium shifting to the left, to produce a decrease in the value of $E_1 - E_2$; while increase of the concentration of alcohol or vanadium oxinate would cause the equilibrium to move to the right, with an increase in $E_1 - E_2$ value. This view is supported by Fig. 2, in which are shown some examples of standard curves for amyl alcohol.

Calculation of the $\Delta\varepsilon_{635}$ value, defined as

$$\Delta\varepsilon_{635} = \frac{E_1 - E_2}{c \cdot d}$$

---

* A solution of vanadium oxinate in xylene-acetic acid[3,4] is blue and is best for the qualitative test for alcohols, because the colour change from blue to red can be more easily observed than the colour change from dark violet to red. On the other hand, the stability of the reagent is not so great in an acidic medium and fading of the reagent occurs to some extent even in the course of the reaction between alcohol and the reagent, thus producing a larger blank value. In the present study, vanadium oxinate is dissolved in various inert solvents containing some oxine in excess. The reagent thus prepared is very stable and no appreciable change in colour is observed at least for several days at room temperature, and even at 70° it is stable for more than 12 min.

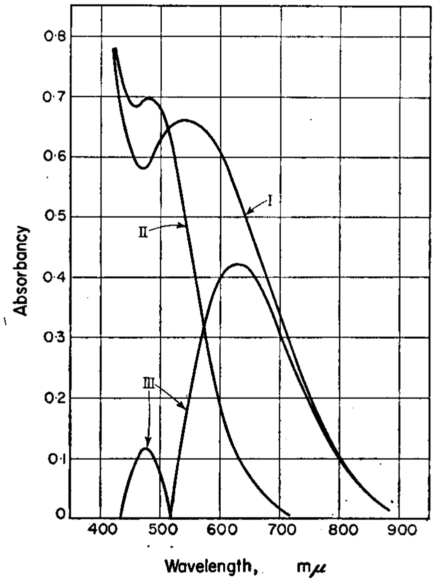


FIG. 1.—Absorption spectra of vanadium oxinate in chloroform (cell depth: 1·0 cm)
I—2 × $10^{-4}M$ vanadium oxinate in the absence of alcohol.
II—2 × $10^{-4}M$ vanadium oxinate in the presence of excess amyl alcohol.
III—Absolute value of (I—II).

in which c is the molar concentration of alcohol and d is cell depth in cm, and E_1 and E_2 are absorbancies at 635 mμ of reagent itself and of reagent in the presence of alcohol respectively, is also important.

In Table I are listed the values as determined for several alcohols. The values vary over a short range from 43·7 for benzyl alcohol to 95 for *n*-octyl alcohol, apart from 10·5 for *tert*butyl alcohol. The exceptionally low $\Delta\varepsilon_{635}$ value for *tert*butyl alcohol reflects the weak reactivity of the OH group of this alcohol.

This relationship appears to hold widely and the measurement of $\Delta\varepsilon_{635}$ for various

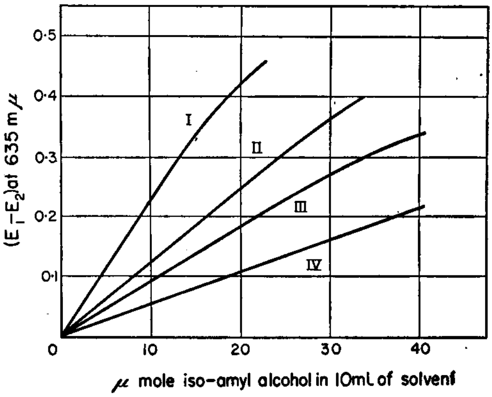


FIG. 2.—Influence of reagent concentration and solvent on the colour
I—4 μmol of vanadium oxinate in 10 ml of chloroform.
II—2 μmol of vanadium oxinate in 10 ml of chloroform.
III—5 μmol of vanadium oxinate in 10 ml of nitrobenzene.
IV—2·5 μmol of vanadium oxinate in 10 ml of nitrobenzene.

TABLE I.—$\Delta\varepsilon_{635}$ OF SOME ALCOHOLS AND ALCOHOL–ETHERS*

5 μmol of vanadium oxinate in 10 ml of nitrobenzene; heating at 70° for 10 min.

Compound	$\Delta\varepsilon_{635}$
Methyl alcohol	60·0
Ethyl alcohol	59·3
n-Propyl alcohol	65·3
n-Butyl alcohol	94·3
tert-Butyl alcohol	10·5
iso-Amyl alcohol	94·9
n-Octyl alcohol	95·0
Benzyl alcohol	43·7
Ethyleneglycolmonobutylether	37·8
Ethyleneglycolmonomethylether	34·0

* Mean values of the results obtained for 10, 20 and 40 μmol of each alcohol in 10 ml of nitrobenzene.

alcohols offers a basis for ascertaining the reactivity of the OH group of these organic substances and the steric hindrance around their OH group. Moreover it is noteworthy that knowledge of molecular weight, together with the $\Delta\varepsilon_{635}$ value, allows differentiation of alcohol isomers. For example, *n*-butyl alcohol can be thus easily distinguished from *tert*-butyl alcohol.

Of special interest is the fact that the value is nearly constant for normal alcohols with more than four carbon atoms, showing the possibility of determining collectively the quantity of alcohol, in moles, in a mixed sample of these different kinds of alcohols.

Colour development and stability

The development of the colour is complete within about 3 hours at room temperature irrespective of the solvent. As shown by nitrobenzene (Fig. 3), heating

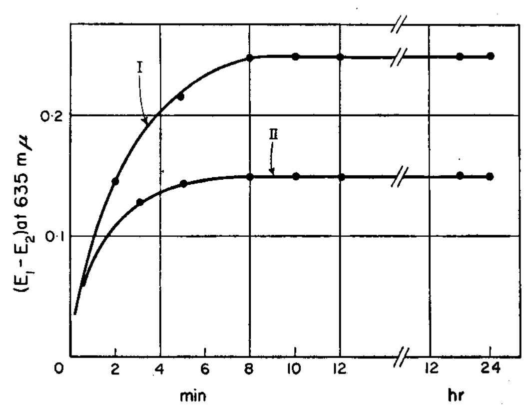


FIG. 3.—Time necessary for complete colour development for *n*-propyl alcohol at 70° and colour stability at room temperature.

I—5 μmol of vanadium oxinate and 40 μmol of *n*-propyl alcohol in 10 ml of nitrobenzene, cell depth: 1·0 cm.

II—2·5 μmol of vanadium oxinate and 40 μmol of *n*-propyl alcohol in 10 ml of nitrobenzene, cell depth: 1·0 cm.

shortens the time. Thus 8 min are sufficient for full development of colour at 70° and 12 min heating at this temperature causes no deterioration of the colour. Therefore for rapid determination a solvent with a high boiling point such as toluene, xylene or nitrobenzene is preferable. Of these, nitrobenzene is best, since it dissolves a greater amount of vanadium oxinate, thereby ensuring the determination of a wider range of alcohol concentration.

The colour developed is stable for at least 24 hours after development if excess oxine protects the colour; this otherwise tends to fade because of deterioration of the vanadium oxinate used as the reagent.

From these results the principles to be taken into consideration for a satisfactory alcohol determination would appear to be:

(1) A solvent with a low dielectric constant is preferable for the determination of smaller amounts of alcohol.

(2) Excess oxine favours stability both of the reagent and of the colour developed.

(3) For a rapid determination a solvent with a high boiling point is more satisfactory.

RECOMMENDED PROCEDURES

Based on the above considerations three photometric methods for determining alcoholic OH content by using vanadium oxinate have been established. The appropriate one may be chosen to suit the requirements.

1. *Rapid method*

Add 5–50 μmol of alcohol to 5 ml of a nitrobenzene solution of vanadium oxinate. Add nitrobenzene to give a total volume of 10 ml. Heat the solution for 10 minutes in a water bath at 70°. Cool with tap water. Measure the absorbancy at 635 mμ, and obtain the equivalence of alcoholic OH, from a previously constructed standard curve.

2. *Sensitive method*

Add 1–20 μmol of alcohol to 5 ml of chloroform solution of vanadium oxinate. Add chloroform to give a total volume of 10 ml. Set aside for 3 hours at 30°. Measure the absorbancy at 635 mμ. Determine the OH content from a previously constructed standard curve.

3. *Determination of alcohols dissolved in organic solvents*

(*a*) *Alcohols in a solvent with high boiling point:* Construct a standard curve using a 1:1 mixture of the solvent in question and nitrobenzene. Add 5 ml of a nitrobenzene solution of vanadium oxinate to 5 ml of sample solution containing 5–50 μmol of alcohol. Heat for 10 minutes at 70°. Then proceed as given in method 1.

(*b*) *Alcohols in a solvent with low boiling point:* Proceed as in (*a*), but use a chloroform solution of vanadium oxinate and do not heat: maintain for 3 hours at 30° before measuring the absorbancy at 635 mμ.

Acknowledgement—The author would like to express his thanks to Professor K. Sugawara and Mr. N. Nakagawa for their valuable disscussion.

Zusammenfassung—Für der photometrischen Bestimmung der Mikromolmenge verschiedener Alkoholen vorschlagt man das in solchen organischen Lösungsmittel wie Chloroform und Nitrobenzol gelöste Vanadinoxinat. Die Empfindlichkeit hängt von der Dielektrizitätskonstante des solvents und der Konzentration des Reagenses ab. Diese Reaktion gewährt eine Methode zur Abschätzung der relativen Reaktivität des gegebenen Alkohols und des sterischen Effeckts um OH des Alkohols. Die Reaktion kann auch zur Differenzierung zwischen isomeren Alkoholen verwendet werden.

Résumé—Pour le dosage photométrique d'une quantité micromole de divers alcools, on propose l'emploi de l'oxinate de vanadium dissous dans des solvants organiques tels que le chloroforme et le

nitrobenzène. La sensibilité dépend de la constante diélectrique du solvant et de la concentration du réactif. Cette reaction donne un moyen d'évaluer la réactivité relative d'un alcool et l'effet stérique au voisinage de OH alcoolique. La réaction peut aussi être utilisée pour différencier des alcools isomères.

REFERENCES

[1] F. Buscarons, J. L. Marin and J. Claver, *Analyt. Chim. Acta*, 1949, **3**, 310.
[2] *Idem, ibid.*, 417.
[3] I. Kudo and I. Aoki, *Japan Analyst*, 1957, **6**, 791.
[4] S. Maruta and F. Iwama, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80**, 1131.

Talanta, 1960, Vol. 5, pp. 168 to 178. Pergamon Press Ltd. Printed in Northern Ireland

THE SEQUENTIAL ANALYSIS OF LONG RANGE FALLOUT DEBRIS

GEORGE A. WELFORD, WILLIAM R. COLLINS JR., ROBERT S. MORSE
and DORIS C. SUTTON
Health and Safety Laboratory, United States Atomic Energy Commission, New York, N.Y., U.S.A.

(*Received* 21 *April* 1960)

Summary—A method for the determination of the principal radionuclides of Sr, Ba, Ce, Cs, Y, Zr, Nb, and W in single fallout samples containing bulk Si, Fe, and Ca is presented. The sample and added carriers are dissolved by fusion with sodium carbonate. The melt is leached first with hot water and then with hydrochloric acid. W and Cs are recovered from the water leach. Sr, Ba, Y, and the heavier rare earths appear in the hydrochloric acid leach. Ce is found in the leach residue and Nb in both the residue and the hydrochloric acid leach. The Zr and Nb in the residue are separated from Ce by absorption on an anion-exchanger from hydrochloric acid. The Zr and Nb in the hydrochloric acid leach are separated from Sr and Ba by precipitation of Sr and Ba as nitrates and then separated from Y and the heavier rare earths by absorption on the anion-exchanger. The combined Zr fractions are eluted with dilute hydrochloric acid and Nb with a hydrochloric-hydrofluoric acid mixture.

INTRODUCTION

THE chief mechanism by which radiation doses are delivered to the general population from detonations of nuclear weapons is the off-site deposition of radioactive debris. This hazard has been studied by many means, including an extensive empirical method based on gross β-activity monitoring.[1] The final practical approach, however, is the radiochemical determination of each nuclide. Many authors have summarised techniques for individual fission and neutron irradiation products.[2-4] Others have devised schemes for the determination of groups of these nuclides from single samples.[5-8] In general, all are based on specialised innovations of classical, ion-exchange, and solvent extraction chemistry used in conjunction with radiometric techniques.

A majority of these methods are limited to relatively simple sample matrices or consider only long-lived fission products. However, recent fallout distribution theory[9] suggests the presence of many shorter lived nuclides in long range fallout and the most widely used sampling systems[10,11] collect considerable quantities of insoluble silicon, iron, sulphate and phosphate compounds in the time and space necessary for the accumulation of detectable activities. The method presented is an integration of many reported techniques and several newer procedures, which permits the joint assay of the radionuclides of strontium, caesium, barium, tungsten, zirconium, niobium, and the rare earths from single samples containing up to ten grams of inert substances.

The nuclides listed are determined in association with milligram quantities of inactive carriers to provide media for chemical operations and recovery determinations. Interchange between radioactive and carrier atoms in their respective molecules is achieved by fusion with sodium carbonate. Compounds which are not attacked in the melt are then equilibrated by digestion with mineral acids.

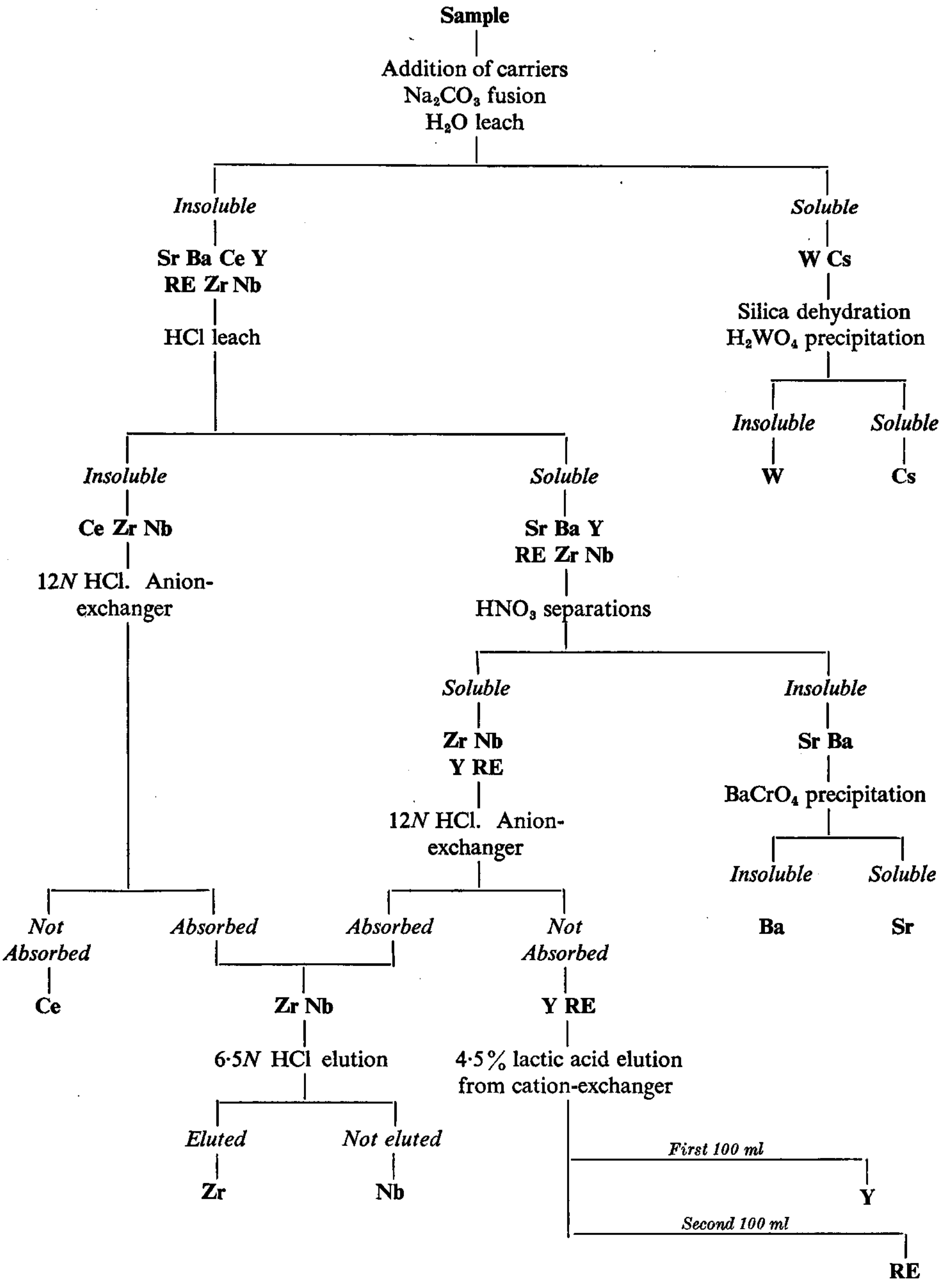


FIG. 1.—Flow chart.

The fundamental separations are illustrated in Fig. 1. Most of the precipitations shown are drawn from adaptations of classical procedures compiled by many authors.[12–15] The radiochemical separation of strontium and barium with 75% nitric acid was discussed by Fresco, Hardy and Welford.[16] The separations based on exchange of anionic chloride complexes were described by Kraus and Moore.[17] The cation-exchange separation of the rare earths was suggested by Cuninghame *et al.*[18]

Final purifications are performed by routine procedures in use in many laboratories.[2,3] Tungsten is purified by an anion-exchange method developed from work reported by Collins and Welford.[19] Caesium is collected by the method of Ewing.[20] Radiometric determinations are carried out with standard β- and γ- radiation detector techniques.[3,4]

EXPERIMENTAL

Reagents

Mineral acids—Unless otherwise noted, acid volumes cited refer to concentrated analytical grades.

Strontium carrier solution—Dissolve 24·2 g of $Sr(NO_3)_2$ in 1% HCl. Dilute solution to 1 litre with 1% HCl. Standardise by gravimetric determination of strontium as the oxide.

Barium carrier solution—Dissolve 15·2 g $BaCl_2$ in 1% HCl. Dilute solution to 1 litre with 1% HCl. Standardise by gravimetric determination of barium as the sulphate.

Cerium carrier solution—Dissolve 31·0 g $Ce(NO_3)_3.6H_2O$ in 1% HCl. Dilute solution to 1 litre with 1% HCl. Standardise by gravimetric determination of cerium as the oxide.

Zirconium carrier solution—Dissolve 3·53 g $ZrOCl_2.8H_2O$ in 1% HCl. Dilute solution to 1 litre with 1% HCl. Standardise by gravimetric determination of zirconium as the oxide.

Tungsten carrier solution—Dissolve 16·0 g Na_2WO_4 in H_2O. Dilute solution to 1 litre with H_2O. Standardise by gravimetric determination of tungsten as the 8-hydroxyquinolate.

Caesium carrier solution—Dissolve 25·4 g CsCl in 1% HCl. Dilute solution to 1 litre with 1% HCl. Standardise by gravimetric determination of caesium as the chloroplatinate.

Lanthanum carrier solution—Dissolve 31·2 g $La(NO_3)_3$ in 1% HCl. Dilute solution to 1 litre with 1% HCl. Standardise by gravimetric determination of lanthanum as the oxalate.

Yttrium carrier solution—Dissolve 21·6 g of $Y(NO_3)_3.6H_2O$ in H_2O. Dilute solution to 500 ml with H_2O. (Decontaminate by TBP extraction, if necessary.)[4] Standardise by gravimetric determination of yttrium as the oxalate.

Niobium carrier solution—Dissolve 1 g Nb metal in saturated aqueous oxalic acid solution. Dilute solution to 1 litre with saturated aqueous oxalic acid solution. Standardise by gravimetric determination of niobium as the oxide.

Sodium carbonate wash solution—Dissolve 50 g Na_2CO_3 in H_2O. Dilute solution to 1 litre with H_2O.

Cinchonine solution—Dissolve 125 g cinchonine in 6*N* HCl. Dilute solution to 1 litre with 6*N* HCl.

Cinchonine wash solution—Dilute 10 ml of cinchonine solution to 1 litre with H_2O.

Acetic acid solution—Dilute 345 ml glacial acetic acid to 1 litre with H_2O.

Ammonium acetate solution—Dissolve 463 g ammonium acetate in H_2O. Dilute solution to 1 litre with H_2O.

8-*Hydroxyquinoline solution*—Dissolve 50 g 8-hydroxyquinoline in 2*M* acetic acid. Dilute solution to 1 litre with 2*M* acetic acid.

8-*Hydroxyquinoline wash solution*—Add 50 ml of ammonium acetate solution and 25 ml of acetic acid solution to 10 ml of 8-hydroxyquinoline solution. Dilute mixture to 1 litre with H_2O.

Sodium chromate solution—Dissolve 48·6 g Na_2CrO_4 in H_2O. Dilute solution to 1 litre with H_2O.

Mandelic acid solution—Dissolve 160 g mandelic acid in H_2O. Dilute solution to 1 litre with H_2O.

Mandelic acid wash solution—Dissolve 50 g mandelic acid in 20 ml of HCl. Dilute solution to 1 litre with H_2O.

Iodic acid solution—Dissolve 61·6 g of HIO_3 in H_2O. Dilute solution to 1 litre with H_2O.

Iodic acid wash solution—Dilute 50 ml of iodic acid solution to 100 ml with 20% HNO_3.

Lactic acid solution I—Dilute commercial grade lactic acid (85%) to 4·25% with H_2O. Titrate to pH 3·5 with NH_4OH using pH meter. (For solutions that must be stored, 19 ml of phenol per litre is added to prevent deterioration oflactic acid.)

Lactic acid solution II—Titrate lactic acid solution I to pH 3·7 with NH_4OH.

Citric acid solution—Dissolve 50 g citric acid in H_2O. Titrate to pH 7·0 with NH_4OH using pH meter. Dilute solution to 1 litre with H_2O.

Chloroplatinic acid solution—Dissolve 10 g of chloroplatinic acid in H_2O. Dilute solution to 100 ml with H_2O.

Aerosol solution—Dissolve 1 g of Aerosol OT in H_2O. Dilute solution to 1 litre with H_2O.

Special apparatus

Sample mounting—Final precipitates are filtered through tared glass-fibre filter paper for weighing. The samples are then mounted on plastic discs, covered with Mylar film and secured with plastic rings. Specifications are given in USAEC Report No. NYO-4700.[4]

β- and γ-Counters—Standard mica windowed Geiger-Müller tubes are used for β-counting and the Baird well-type scintillation counter for γ-counting.[4]

Ion-exchange columns

The ion-exchange column vessel used is shown in Fig. 2. The dimensions are given in inches. A wad of glass wool is used to support the resin bed. Resins are wet-sieved, aqueous and non-aqueous extracted on receipt and stored in distilled water until required.[4]

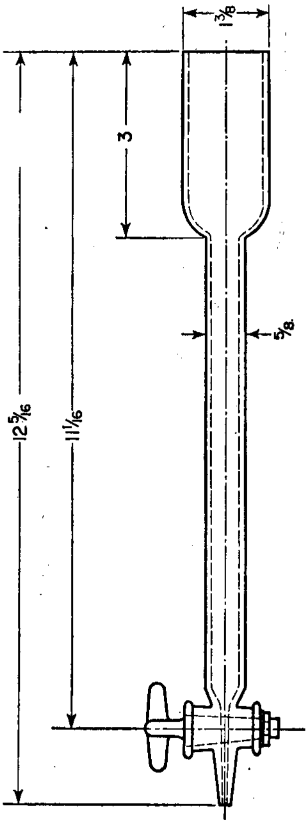


FIG. 2.—Ion exchange column.

Tungsten column—Transfer 10 ml of wet settled Dowex 1 X-4 (50–100 mesh) Cl^- form to the column. Allow the resin bed to settle, and pass 100 ml of 1*N* HCl at a flow-rate not exceeding 5 ml per min through the bed. Pass the sample solution through.

Zirconium column—Transfer 20 ml of wet-settled Dowex 1 X-2 (50–100 mesh) Cl^- form to the ion-exchange column. Allow the resin bed to settle, and pass 150 ml of HCl through at a flow-rate not exceeding 3 ml per min. Add 1 ml of Nb carrier solution directly to the resin bed and wash with 100 ml of HCl. Pass the sample solution through. To regenerate, pass 250 ml of 0·5*N* HCl through the resin bed at a flow-rate not exceeding 5 ml per min.

Yttrium column—Transfer 10 ml of wet-settled Dowex 50 X-8 (200–400 mesh) H^+ form to the ion-exchange column. Allow the resin bed to settle, and pass 100 ml of lactic acid solution I through the resin bed at a flow-rate not exceeding 3 ml per min. Pass the sample through. To regenerate, pass 100 ml of citric acid solution and 100 ml of water through the resin bed at flow-rates no exceeding 5 ml per min.

PROCEDURES

Section 1A—*Group separations*

Procedure	*Remarks*
1. Transfer the sample to a platinum dish and ignite at 500°.	Destruction of organic material.
2. Add 1 ml of Sr, Ba, Ce, Zr, W, and Cs carrier solutions and 2 ml of NH_4OH.	
3. Dry at 110°, weigh and fuse with five times the sample weight of Na_2CO_3.	Dissolution and equilibration of sample and carriers.
4. Grind the melt thoroughly and transfer to a 600-ml beaker. Dissolve any remaining material in hot water and wash into the beaker.	
5. Add 200 ml of water, digest with stirring for 1 hr. Cool and filter over Whatman No. 42 filter paper.	H_2O extraction of W and Cs.
6. Wash with sodium carbonate wash solution. Collect filtrate and washings in a 600-ml beaker and reserve for step 1, Section 3A.	Filtrate is reserved for W and Cs analysis.
7. Dissolve the precipitate on the filter paper with 1 : 1 HCl and collect the solution in a 400-ml beaker. Transfer the paper and insoluble material to a platinum crucible and reserve for step 1, Section 1B.	HCl dissolution of carbonate. Precipitate reserved for insoluble residue treatment.
8. To the filtrate, add 25 ml of HCl and evaporate to dryness. Add 10 ml of HCl to the residue. Heat on hot plate for 5 min. Add 100 ml of distilled water, heat to boiling, cool and filter over Whatman No. 40 filter paper. Wash thoroughly with hot 1 : 9 HCl. Add the paper and residue to the platinum crucible from step 7. Collect filtrate and washings in a 250-ml beaker and reserve for step 1, Section 2A.	Dehydration of silica. Combination of insoluble residues. Filtrate and washings reserved for strontium separations.

Section 1B—*Treatment of insoluble residues*

1. Dry the papers and residues from steps 7 and 8, Section 1A, at 110° and ash at 500°.	Destruction of filter paper.
2. Add 2 ml of H_2SO_4 and 10 ml of HF and evaporate to SO_3 fumes.	Volatilisation of silica.
3. Transfer to a 100-ml beaker and add 10 ml of HCl and 10 ml of HNO_3. Evaporate to SO_3 fumes. Transfer to a 40-ml centrifuge tube and dilute to 20 ml. Cool and centrifuge. Decant supernate into a 40-ml centrifuge tube and discard precipitate.	Dissolution of insoluble oxides.
4. Adjust to pH 10 with NH_4OH. Digest, cool and centrifuge. Discard supernate.	Collection of Zr and Ce.
5. To the precipitate add 10 ml of HCl and reserve for step 4, Section 4A.	

Section 2A—*Strontium*

1. Add 1 ml of yttrium carrier and evaporate the solution from step 8, Section 1A to less than 20 ml. Add 10 ml of distilled water.

Procedure	*Remarks*
2. With mechanical stirring, slowly add 100 ml of fuming nitric acid. Stir for 45 minutes. Cool and filter over glass-fibre filter paper.	Collection of Sr and Ba as nitrates.
3. Collect the filtrate in a 250-ml beaker and reserve for step 1, Section 4A. Dissolve the precipitate with distilled water and collect in a 150-ml beaker.	Reserve filtrate for Zr, Y, and Nb analysis.
4. Evaporate to dryness. Add 12 ml of distilled water and with constant stirring add 40 ml of fuming nitric acid.	
5. Cool and filter over glass-fibre filter paper. Combine filtrate with filtrate from step 3.	Separation of Sr and Ba from Ca.
6. Dissolve the nitrate precipitate with distilled water, collect in a 40-ml centrifuge tube and add 1 ml of yttrium carrier.	
7. Heat in a water bath at 90°. Adjust to pH 8 with NH_4OH. Cool, centrifuge, and decant the supernate into a centrifuge tube. Record the time.	First milking of ^{90}Y and ^{140}La
8. Dissolve the precipitate with 3–5 drops of HCl. Add 10 ml of distilled water and repeat step 7. Combine supernates. Discard the precipitate.	
9. To the combined supernates, add 1 ml of 6*M* acetic acid and 2 ml of 6*M* ammonium acetate solution. Adjust to pH 5·5 with HCl or NH_4OH. Heat in a water bath at ~90°. Add 1 ml of sodium chromate solution. Digest with occasional stirring for 10–15 min. Cool. Centrifuge.	Separation of Ba from Sr.
10. Decant the supernate into a polyethylene bottle. Add 2–3 drops of HCl and 1 ml of yttrium carrier solution. Allow solution to stand for 2 weeks.	Equilibration of ^{90}Sr and ^{90}Y.
11. Dissolve the precipitate from step 9 with 5 ml of 0·5*N* HCl. Transfer to a polyethylene bottle and add 1 ml of lanthanum carrier. Store for 10 days and reserve for step 1, Section 2B.	Equilibration of ^{140}Ba and ^{140}La.
12. Transfer the equilibrated solution from step 10 to a 40-ml centrifuge tube. Heat in a water bath. Adjust to pH 8 with NH_4OH and add 6 drops of 30% H_2O_2. Heat with occasional stirring for 15 min. Cool. Centrifuge. Record hour and date.	Second milking of ^{90}Y.
13. Transfer the supernate to a 100-ml beaker, and reserve for step 16. Dissolve the precipitate with 3 drops of HCl and dilute to 20 ml with water.	
14. Heat in a water bath. Adjust to pH 8 with NH_4OH. Cool. Centrifuge. Combine supernate with that from step 13 and reserve for step 16.	Purification of Y.
15. Dissolve the precipitate with 3 drops of concentrated HCl. Add 20 ml of distilled water. Heat in a water bath and add 1 ml of saturated oxalic acid. Digest with occasional stirring for 5 min. Cool, filter, dry, and mount. Discard filtrate.	Final precipitation of ^{90}Y as the oxalate.
16. Heat the combined supernates from step 14 to just below the boiling point. Add 10 ml of a saturated solution of sodium carbonate with stirring. Cool and filter over a weighed filter. Wash precipitate with Na_2CO_3 wash solution. Dry, weigh, mount, and count.	Final precipitation of Sr as the carbonate.
Section 2B—*Barium*	
1. Transfer the solution from step 11, Section 2A to a 40-ml centrifuge tube. Dilute to 20 ml. Heat and add 3 drops	Dissolved $BaCrO_4$ precipitate.

Procedure	*Remarks*
of H_2SO_4, allow to stand for 1 hr. Centrifuge. Record hour and date.	Separation of Ba and La.
2. Transfer the supernate to a centrifuge tube. Adjust to pH 10 with NH_4OH. Add 6 drops of 30% H_2O_2. Digest in water bath for 20 min. Cool. Centrifuge, discard supernate. Wash precipitate with H_2O. Discard wash.	Collection of La as the hydroxide.
3. Dissolve the precipitate with 3 drops of HCl. Dilute to 20 ml. Heat. Add 1 ml of saturated $H_2C_2O_4$. Digest for 15 min with stirring.	Final precipitation of La as the oxalate.
4. Cool. Filter through glass-fibre filter paper. Dry, mount, and count.	
5. Slurry the precipitate from step 1 with 0·5*N* HCl. Filter through a weighed glass-fibre filter paper washing with H_2O. Dry and weigh.	Gravimetric determination of Ba as the sulphate.

Section 3A—*Tungsten*

Procedure	*Remarks*
1. Acidify the solution from step 6, Section 1A, with HCl and add a 100-ml excess. Evaporate to dryness. Add 100-ml of HCl, evaporate to dryness and bake.	Dehydration of silica.
2. Slurry with 500 ml of hot water and heat to just below boiling on a sand bath. Add 20 ml of HCl, 10 ml of HNO_3 and 10 ml of cinchonine solution.	Precipitation of W as the acid.
3. Add 10 ml of wet paper pulp. Digest with occasional stirring for 1 hr.	Coagulation of H_2WO_4.
4. Allow solution to cool to room temperature. Filter over No. 42 Whatman filter paper. Wash the precipitate with hot cinchonine wash solution. Collect the filtrate in a 600-ml beaker and reserve for step 1, Section 3B.	Reserve for Cs analysis.
5. Transfer the filter and precipitate to a platinum crucible. Dry at 110° and ignite at 500°.	Destruction of filter paper.
6. Add 5 ml of HNO_3 and 20 ml of HF to crucible. Evaporate to dryness. Cool.	Volatilisation of silica.
7. Add 1 ml of 6*M* NaOH. Heat and transfer to a 40-ml centrifuge tube using distilled water.	Dissolution of H_2WO_4.
8. Adjust the volume to 20 ml with distilled water and add 10 ml of HNO_3.	
9. Digest for 1 hr in a water bath at 95°. Cool and centrifuge. Decant and discard the supernate.	Re-precipitation of W as the acid.
10. Add to the precipitate 1 ml of 6*M* NaOH. Heat in a water bath at 95° to effect solution. Add 3 ml of saturated tartaric acid solution and adjust the volume to ~15 ml with 1*N* HCl.	Complexing of W for anion-exchange purification.
11. Pass the solution through a prepared Dowex 1 X-4 column* at a flow-rate of 0·5 ml per min. Wash the resin bed with 100 ml of 1*N* HCl. Discard waste and wash solutions.	Exchange of W-tartrate complex.
12. Transfer the resin to a platinum crucible. Dry at 110°. Ignite at 500°.	Destruction of resin and tartrate radical.
13. Add 2–3 ml of NH_4OH dropwise, and 5 ml of water. Digest.	
14. Transfer the solution to a 100-ml beaker with water and dilute to ~50 ml.	

---

* See preparation of tungsten column under *Special Apparatus*.

Procedure	*Remarks*
15. Add 1 ml of 6*M* acetic acid solution and 2 ml of 6*M* ammonium acetate solution, adjusting to pH 5·5, if necessary, with HCl.	
16. Heat at 90° on a sand bath and add 2 drops of 0·1% Aerosol solution. Add 3 ml of 8-hydroxyquinoline solution. Stir the solution for 2 min. Cool.	Final precipitation of W as the hydroxyquinolate.
17. Filter over a weighed filter paper. Wash with 8-hydroxyquinoline wash solution. Dry at 110°. Weigh, mount and count.	

Section 3B—*Caesium*

1. To the filtrate from step 4, Section 3A, add 50 ml of HCl. Evaporate the solution carefully to dryness, and char organic material. Ignite at 500°	Filtrate from precipitation of H_2WO_4.
2. Dissolve the salts in 200 ml of distilled water. Add 50 ml of HCl. Evaporate to dryness.	Dehydration of silica.
3. Dissolve in 100 ml of distilled water. Filter over No. 42 Whatman paper. Wash the residue with hot 5% HCl. Discard the residue.	
4. Add 4 ml of chloroplatinic acid solution. Stir for 1 hr. Allow to stand overnight in a refrigerator. Filter over a weighed filter. Weigh, mount, and count.	Final precipitation of Cs as the chloroplatinate.

Section 4A—*Zirconium*

1. Evaporate the solution from step 3, Section 2A, to less than 20 ml and transfer to a 40-ml centrifuge tube. Adjust to pH 10 with NH_4OH. Digest, cool, and centrifuge. Discard supernate.	Filtrate from nitric acid collection step. Collection of hydroxides.
2. Wash the precipitate twice with 20-ml portions of H_2O. Discard the wash solutions. Dissolve the precipitate with 10 ml of HCl.	Complexing of Zr-Nb for anion-exchange separation.
3. Pass the solution through a prepared Dowex 1 X-2 column.* Wash with 100 ml of HCl. Collect the effluent and wash solution in a 250-ml beaker and reserve for step 1, Section 5B.	Separation of Y from Zr-Nb. Reserve for Y determination.
4. Pass the solution from step 5, Section 1B, through the same resin column used in step 3. Wash with 100 ml of HCl. Collect the effluent and wash solution in a 250-ml beaker and reserve for step 1, Section 5A.	Separation of Ce from Zr-Nb. Reserve for Ce determination.
5. Pass through the column 100 ml 6·5*N* HCl. Reserve the column for step 1, Section 4B. Collect the effluent in a 250-ml beaker and evaporate to 10–20 ml.	Elution of Zr. Reserve column for Nb determination.
6. Transfer to a 40-ml centrifuge tube and adjust to pH 10 with NH_4OH. Digest, cool and centrifuge. Discard the supernate. Dissolve the precipitate with 3 ml of HCl. Add 25 ml of H_2O and 4 ml of 16% mandelic acid.	Final precipitation of Zr as the mandelate.
7. Heat at 95° for 45 min with occasional stirring. Cool and filter over weighed glass-fibre filter paper. Wash the precipitate with mandelic acid wash solution. Dry at 110°, weigh, mount, and count.	

Section 4B—*Niobium*

1. Pass through the resin column from step 5, Section 4A, 100 ml of 4·5*N* HCl–0·06*N* HF. Collect in a 250-ml beaker.	Elution of Nb from resin column. Collection of Nb as the hydroxide.

---

* See preparation of zirconium column under *Special Apparatus*.

Procedure	*Remarks*
Adjust to pH 10 with NH_4OH. Heat for 5 min on hot plate.	
2. Filter over Whatman No. 40 filter paper. Discard the filtrate. Dry and ignite the precipitate at 500°. Transfer the material to a 5-ml glass vial, and count.	Preparation of Nb for γ-counting.
Section 5A—*Cerium*	
1. Evaporate the solution from step 4, Section 4A, to approximately 20 ml and transfer to a 40-ml centrifuge tube. Adjust to pH 9 with NH_4OH. Digest, cool and centrifuge. Discard the supernate.	Effluent and wash solutions from Zr and Nb adsorption. Collection of Ce and rare earths as hydroxides.
2. Dissolve the precipitate with 10 ml of HNO_3, add 0·3 ml of 30% H_2O_2 and allow 5 min for reaction time.	Dissolved hydroxides from column effluent. Reduction of Ce^{IV} to Ce^{III}.
3. Add 20 ml HIO_3, cool and centrifuge. Decant the supernate into a 40-ml Lusteroid centrifuge tube and discard the precipitate.	Scavenging step to remove traces of Zr, Th, or Po.
4. To the supernate, add 5 ml of HF with stirring. Centrifuge and discard the supernate.	Collection of Ce and rare earths as fluorides.
5. Slurry the precipitate with 1 ml of saturated boric acid, add 5 ml of HNO_3 and transfer to a 40-ml centrifuge tube. Dissolve the precipitate by heating and adjust to pH 9 with NH_4OH. Cool and centrifuge. Discard the supernate.	Collection of Ce and rare earths as hydroxides.
6. Dissolve the precipitate in 10 ml of HNO_3. Add 20 ml of HIO_3 and immerse in an ice bath. Add 1 ml of $NaBrO_3$ solution, allow to digest for 10 min. Centrifuge. Discard the supernate.	Oxidation of Ce^{III} and precipitation of cerium as the iodate.
7. Dissolve the precipitate with 10 ml of HNO_3, 3 drops of HCl, and 3 drops of H_2O_2. Boil off the peroxide and cool in ice bath. Add 20 ml of HIO_3 and 1 ml of $NaBrO_3$.	Re-precipitation of $Ce(IO_3)_4$.
8. Cool. Filter over weighed glass-fibre filter paper. Weigh, mount, and count.	
Section 5B—*Yttrium*	
1. Evaporate the solution from step 3, Section 4A, to 20 ml and transfer to a 40-ml Lusterloid centrifuge tube. Adjust to pH 8 with NH_4OH. Digest, cool, and centrifuge. Discard the supernate.	Collection of Y and rare earths as the hydroxides.
2. Dissolve the precipitate in 10 ml of HNO_3 and dilute with water to about 30 ml. Add 5 ml of HF. Stir and digest for 15 min at room temperature. Centrifuge, decant, and discard the supernate.	Collection of Y and rare earths as the fluorides.
3. Slurry the precipitate with 1 ml of saturated boric acid, add 5 ml of HNO_3 and transfer to a 40-ml centrifuge tube. Dissolve the precipitate by heating and adjust to pH 9 with NH_4OH. Cool and centrifuge. Discard the supernate.	Collection of Y and rare earths as hydroxides.
4. Dissolve the precipitate with 3 drops of HCl. Add 3 ml of 4·25% lactic acid (pH 3·5).	
5. Pass the solution through a prepared* Dowex 50 X-8 column. Wash the centrifuge tube with two 5-ml portions of hot water, passing each through the column. Discard waste and wash solutions. Pass 100 ml of the lactic acid solution (pH 3·5) through the column.	Separation of Y from rare earths.

* See preparation of yttrium column under *Special Apparatus*.

Procedure	*Remarks*
6. Collect eluant in a 150-ml beaker to which 1 ml of saturated oxalic acid has been added. Reserve the column for step 1, Section 6.	
7. Digest with occasional stirring for 10 min. Cool and filter over weighed glass-fibre filter paper. Wash the precipitate with distilled water. Dry, weigh, mount, and count.	Final precipitation of Y as oxalate.

Section 6—Rare earths

1. Pass through the column from step 5, Section 5B, 100 ml of 4·25% lactic acid, pH 3·7. Collect the eluant in a 150-ml beaker to which 1 ml of lanthanum carrier has been added.	Elution of rare earths.
2. Digest for 10 min. Add 1 ml of saturated oxalic acid. Cool, filter, mount, and count.	Final precipitation of rare earths using La as carrier.

DISCUSSION

Yields of the various elements from experimental samples are listed in Table I. The matrices were composed of 1- and 2-gram aliquots of representative United States soils with known quantities of activities and carriers added. In all cases the results of gravimetric and radiometric recovery measurements agree within the probable error of their determination, indicating that equilibration takes place before chemical losses occur. Results of tracer studies indicate that ^{95}Nb generally follows zirconium carrier and that its recovery is more reproducible when niobium carrier is not used until the final stages of the procedure.

TABLE 1. RESULTS OF GRAVIMETRIC AND RADIOMETRIC ANALYSES

Element	Number of analyses performed	Average % recovery	
		Gravimetric	Radiometric
Sr	36	83	77
Cs	24	79	77
Ce	20	83	80
Y	10	86	82
Zr	24	88	80
W	72	72	76
Nb	24	—	90

Cross contamination analyses were conducted on most of the recovery samples using β-absorption[21] and decay study[22] techniques. In no case was more than 0·001% of any added alien activity detected in a finally precipitated elemental fraction.

The method has also been used satisfactorily for the comprehensive analysis of more than 200 actual fallout samples collected in New York City.[23] Since bulk quantities of iron, silica and calcium were handled without interference, many other biospheric sample types are within the scope of the procedure. In addition, with some alterations, the analyses of other individual rare earths, ruthenium, iodine and molybdenum are possible.

Zusammenfassung—Eine Methode wird beschrieben zur Bestimmung der wichtigsten Radionucleide von Sr, Ba, Ce, Cs, Y, Zr, Nb und W in einer einzigen "Fallout"-Probe, die als Hauptmestandteile

Si, Fe und Ca enhält. Die Probe wird nach Zusatz von Trägermaterial mit Natriumcarbonat geschmolzen und der Schmelzkuchen erst mit Wasser und dann mit Salzsäure ausgezogen. W und Cs werden aus dem wässrigen Auszug gewonnen. Sr, Ba, Y und die schwereren seltenen Erden scheinen im salzsauren Auszug auf. Ce wird im Auszugsrückstand gefunden, während Zr und Nb sowohl im Rückstand als auch im Säureextrakt vorhanden sind. Zr und Nb aus dem Ruckstand werden von Ce durch Adsorption an einem Anionenaustauscher aus salzsaurer Lösung getrennt. Das im sauren Extrakt enthaltene Zr und Nb wird von Sr und Ba durch Fällung der letzteren als Nitrate getrennt und dann vom Y und den schwereren seltenen Erden durch Anionenaustauscher separiert. Die kombinierten Zr-Fraktionen werden mit verdünnter Salzsäure und das Nb mit Salzsäure-Flussäure eluiert.

Résumé—Les auteurs présentent une méthode de dosage des principaux radioéléments de Sr, Ba, Ce, Cs, Y, Zr, Nb et W dans des échantillons contenant de grandes quantités de Si, Fe et Ca. L'échantillon et les supports ajoutés sont dissous par fusion avec du carbonate de sodium. La masse fondue est lavée d'abord avec de l'eau bouillante, puis avec de l'acide chlorhydrique. W et Cs sont récupérés à partir de l'eau de lavage. Sr, Ba, Y et les terres rares plus lourdes apparaissent dans l'acide chlorhydrique de lavage. Ce est trouvé dans le résidu de lavage et Zr et Nb à la fois dans le résidu et dans l'acide chlorhydrique de lavage. Zr et Nb dans le résidu sont séparés de Ce par absorption sur un échangeur d'anions à partir d'acide chlorhydrique.

Zr et Nb dans l'acide chlorhydrique de lavage sont séparés de Sr et Ba par précipitation de Sr et Ba à l'état de nitrates, et ensuite séparés de Y et des terres rares plus lourdes par absorption sur un échangeur d'anions. Les fractions de Zr combinées sont éluées avec de l'acide chlorhydrique dilué et Nb avec un mélange acide chlorhydrique-acide fluorhydrique.

REFERENCES

[1] M. Eisenbud and J. Harley, *Science*, 1956, **124**, 251; 1958, **128**, 399.

[2] C. Coryell and N. Sugarman, *Radiochemical Studies: The Fission Products.* McGraw-Hill, New York, 1951.

[3] J. Kleinberg, *Los Alamos Scientific Laboratory Report* No. LA-1721, 1954.

[4] *Manual of Standard Procedures,* USAEC Report No. NYO-4700, March 1957.

[5] E. Crouch and G. Cook, *J. Inorg. Nuclear Chem.*, 1956 **2**, 223.

[6] L. Salter, *Procedures for Radiochemical Analysis of Low Level* Sr^{89}, Sr^{90}, Zr^{95}, Cs^{137}, Ba^{140}, *and* Ce^{144} *in Solutions of Air Filter Samples,* Nuclear Science and Engineering Corporation, Pittsburg, Pa., 1957.

[7] R. Osmond, A. Pratchett, and J. Warricker, *The Determination of Long-Lived Fallout in Rainwater,* Atomic Energy Research Establishment, G.B., Publ. No. AERE C/R 2165, August 1957.

[8] W. Merritt, *Canad. J. Chem.*, 1958, **36**, 425.

[9] E. Martell, *Science*, 1959, **129**, 1197.

[10] G. Welford and J. Harley, *A New Method for the Collection of Fallout Material from Nuclear Detonations,* USAEC Report No. HASL-42 Part IV, October 1958.

[11] J. Holland, USAEC Report No. WASH-1016, January 1959.

[12] W. Scott, *Standard Methods of Chemical Analysis.* D. Van Nostrand, New York, 1944.

[13] *A.S.T.M. Methods for Chemical Analysis of Metals.* American Society for Testing Materials, Philadelphia, Pa., 1950.

[14] A. Noyes and W. Bray, *A System of Qualitative Analysis for the Rare Elements.* Macmillan, London, 1948.

[15] G. Lundell and J. Hoffman, *Outline of Methods of Chemical Analysis.* John Wiley, New York, 1954.

[16] J. Fresco, E. Hardy, and G. Welford, USAEC Report No. NYO-4617, December 1954.

[17] K. Kraus and G. Moore, *J. Amer. Chem. Soc.*, 1951, **73**, 9.

[18] J. Cuninghame, M. Sizeland, H. Willis, J. Eakins, and E. Mercer, *J. Inorg. Nuclear Chem.*, 1955, **1**, 163.

[19] W. Collins and G. Welford, USAEC Health and Safety Laboratory Lab Report No. 58-3, June 1958.

[20] R. Ewing, USAEC Report No. HW-18146, June 1950.

[21] J. Harley and N. Hallden, *Nucleonics*, 1955, **13**, 32.

[22] G. Friedlander and J. Kennedy, *Nuclear and Radiochemistry.* John Wiley, New York, 1955.

[23] G. Welford and W. Collins, *Science*, 1960, **131**, 1711; 1791.

Talanta, 1960, Vol. 5, pp. 179 to 188. Pergamon Press Ltd. Printed in Northern Ireland

CHLORITE AS AN OXIDISING AGENT IN TITRIMETRIC ANALYSIS

JERZY MINCZEWSKI
Technical University, Department of Analytical Chemistry, Warsaw, Poland
and
URSZULA GLABISZ
Technical University, Department of Inorganic Chemical Technology
Szczecin, Poland

(*Received* 23 *April* 1960)

Summary—The possibilities of using a solution of sodium chlorite as an oxidising agent in titrimetric analysis have been investigated. Such a solution, in the absence of light, is chronometrically stable and convenient for the direct titration of sulphite (in applying the titre to a known solution of sulphite); iron, by its reduction to iron^{II} with tin^{II} chloride (the result to be read from the difference between the potential-jump corresponding to iron^{II} × tin^{II} and the first jump corresponding to tin^{II}); arsenite; iodide. The titration is generally carried out in an acidic medium, with the occasional application of catalysts such as potassium iodate.

INTRODUCTION

THE possibility of using sodium chlorite in chemical analysis has been known for some time. Yet there are in the literature very few references to using that substance as a titrimetric reagent. A priority for applying chlorites in titrimetric analysis has been claimed by Levi.[1] The latter was also the first author to deal with the problem of the stability of chlorite solutions.[2]

Levi and his co-workers also occupied themselves with obtaining the chlorites of the alkali and the alkaline earth metals.[3,4] They described, too, both the reductimetric and oxidimetric use of chlorite in chemical analysis.[5] On the one hand they used chlorite as a reducing agent for the quantitative determination of permanganate.[6] On the other hand, however, they state that chlorite quantitatively oxidises arsenite, stannite and antimonite in an alkaline medium,[7] as well as sulphite. The question of oxidising thiosulphate[7] with chlorite is discussed. Jackson and Parsons[8,9] proposed a method of determining sulphite with chlorite. Yntema and Fleming[10] discussed the quantitative oxidation of iodide to iodate with chlorite; and Brown[11] reported on the application of chlorite to the titrimetric determination of arsenite.

An indirect analysis with application of chlorite is proposed by Paul and Singh.[12] These authors consider that a series of reducing substances might be quantitatively determined by means of their pre-oxidation with iodine monochloride, the liberated iodine being subsequently oxidised by a standard solution of chlorite to IBr_2^-, in the presence of potassium bromide. However, they give no further details or results.

In a general way it may be stated that the literature pertaining to the use of chlorite in titrimetric analysis is scarce and, moreover, it often suggests some doubts.

The oxidation potential of chlorite has been studied by Holst,[13] then by Flis[14] over a wide range of pH. The data given by them are concordant. Comparing the potential values given by Holst and Flis with that of the redox potential in the systems discussed by the authors mentioned before, it seems, in some cases, improbable to admit the possibility of a quantitative oxidation, especially in such a medium as described. It would, therefore, be of much interest on the one hand to re-examine the redox systems already described and on the other hand to establish the possibility of quantitative oxidation with chlorite of a series of other reducing substances.

EXPERIMENTAL

Reagents

Titrant: Technical sodium chlorite solutions were employed ($NaClO_2$ content about 80%, with impurities of $NaClO_3$, NaCl, NaOH).

After storing 0·1*N* chlorite solution for a long time, both out of light and exposed to light, it has been found that with light excluded the solution remains perfectly stable for a period of not less than 3 months (see Table 1).

TABLE I.—STABILITY TEST OF 0·1*N* SODIUM CHLORITE SOLUTION

Time, *days*	Normality of $NaClO_2$ solution protected against light	Normality of $NaClO_2$ solution exposed to light action
0	0·9905	0·9905
1	0·9905	0·9905
2	0·9905	0·9802
3	0·9905	0·9200
5	0·9905	0·9103
8	0·9905	0·9056
10	0·9904	0·8925
15	0·9904	0·8632
30	0·9904	0·8332
60	0·9904	0·8245
90	0·9904	0·8115

Standardisation of sodium chlorite solution

The equivalent weight of chlorite is 1/4 of its molecular weight according to the equation:

$$ClO_2^- + 4H^+ + 4e \rightarrow Cl^- + 2H_2O$$

The standardisation of chlorite solution was carried out by the method due to Bray.[15] A measured quantity of chlorite solution (10 ml) was treated with 15 ml of 10% potassium iodide solution and 10 ml of 2*N* sulphuric acid, diluted with 65 ml of water, and the liberated iodine immediately titrated with 0·1*N* sodium thiosulphate solution. For titration purposes in an acidic medium, the standardisation of chlorite solution was carried out in a solution of the same acid concentration as used in the experiments. The thiosulphate solution was standardised by means of dichromate.

Apparatus

Quantitative titration of reducing substances with sodium chlorite was carried out by potentiometric titration with the electrode system: platinum-saturated calomel. The electromotive force of the system was measured with a direct-reading pH-meter ("Orion," Hungarian made), or, more accurately, with a compensating method using a pH-meter with an electronic amplifier ("Ridan," Polish made). The latter method ensured a titration accuracy within a limit of 1 mV. The results were computed after the method of Hahn.[16] The characteristic graphs of the titration are shown in Fig. 1.

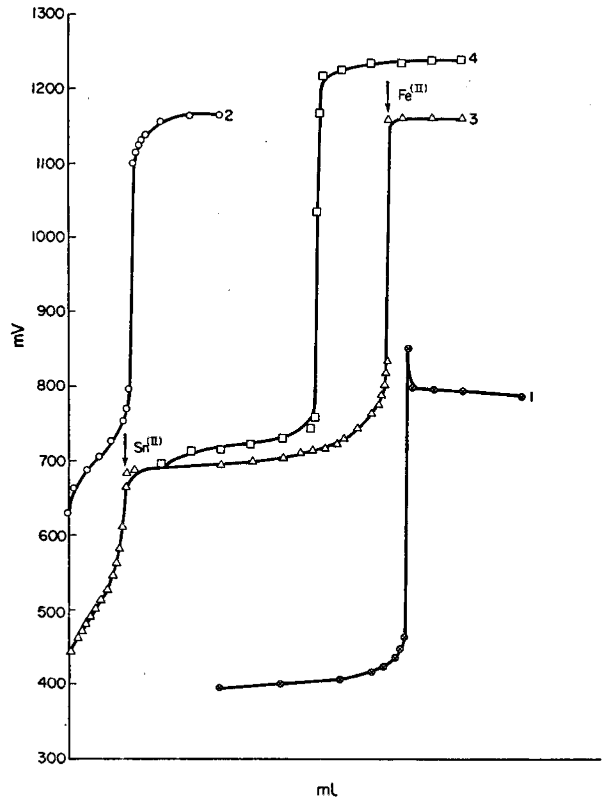


Fig. 1.—Some titration curves obtained with sodium chlorite solution.

1. Titration of sulphite (pH 4·08)
2. Titration of iodide (2*N* H_2SO_4)
3. Titration of Fe^{II} with Sn^{II} present in excess (2*N* HCl + 2*N* H_2SO_4 + KI)
4. Titration of arsenite (2*N* HCl + KIO_3).

RESULTS AND DISCUSSION

Oxidation of sulphite

The study of the possibility of titration of sulphite with chlorite was initiated by checking the method proposed by Jackson and Parsons.[9] These authors considered the reaction:

$$ClO_2^- + 2SO_3^{2-} \rightarrow Cl^- + 2SO_4^{2-}$$

to be too slow for analytical purposes; they stated that a small addition of potassium iodide results in a considerable acceleration. Supposing that oxidation of sulphite with chlorite occurs indirectly through the following reactions:

$$ClO_2^- + 4I^- + 4H^+ \rightarrow Cl^- + 2I_2 + 2H_2O$$

$$2H_2O + 2I_2 + 2SO_3^{2-} \rightarrow 2SO_4^{2-} + 4I^- + 4H^+$$

then they are applying the classical titration of sulphite in an acetic acid medium using the chlorite solution with starch as indicator.

The determination of sulphite, performed according to the above method, yielded results which were too low compared with those by the iodometric method which was

TABLE II.—DETERMINATION OF SULPHITE

Concentration of sulphite determined iodometrically (100%)	Concentration of sulphite determined with $NaClO_2$ (by the present method)															
	Medium															
	0·1*N* H_2SO_4		pH 1·98		pH 2·87		pH 4·07		pH 4·56		pH 5·1		pH 6·09		pH 7·02	
mol/l.	*mol/l.*	%	*mol/l.*	%	*mol/l.*	%	*mol/l.*	%	*mol/l.*	%	*mol/l.*	%	*mol/l.*	%	*mol/l.*	%
0·0327	0·0225	68·81	0·02475	75·69	0·02975	90·89	0·03075	94·04	0·03080	94·19	0·02625	80·27	0·0240	73·39	0·02180	66·27
0·0421	0·0293	69·50	0·03199	76·00	0·03789	90·00	0·03957	94·00	0·03968	94·25	0·03347	79·50	0·03069	72·90	0·02779	66·00
0·0500	0·0338	67·50	0·03745	74·90	0·04550	91·00	0·04705	94·10	0·04707	94·15	0·04025	80·50	0·03690	73·80	0·03260	65·20

taken as a standard method. The error in the above-described method amounted to about 17%. It seems evident that acidifying a sulphite solution with even a weak acid, such as acetic acid, causes its decomposition with loss of gaseous sulphur dioxide. In order to eliminate this source of error, the possibilities of quantitative oxidation of sulphite with chlorite within the pH range of 1 to 7 were examined. The concentration of sulphite solution was determined by the iodometric method.

Buffer solutions used in the analysis in order to keep the desired pH of the titrated solution were prepared according to Britton and Robinson and their pH was determined by the compensation method.

The results shown in Table II confirm the preceding observations. In a medium with a pH of below 4, decomposition of sulphite takes place with loss of sulphur dioxide, and this is increased in proportion as the pH of the titrated solution is lowered. In a medium of pH above 5 sulphite oxidation is very slow and the results obtained are likewise too low.

The optimal pH range for the titration proved to be from 4 to 4·6. Within these pH limits the reaction occurs with a rate sufficient for analytical purposes, whereupon the results obtained are so reproducible that in standardising the chlorite solution with a sulphite solution of a known concentration, it is possible to put this method into practice.

Oxidation of iodide

In starting tests of titrating iodide with chlorite it was assumed that the reaction would be:

$$4KI + NaClO_2 + 2H_2SO_4 \rightarrow 2I_2 + NaCl + 2K_2SO_4 + 2H_2O$$

The potential of the redox system

$$I_2 + 2e \rightleftharpoons 2I^-$$

amounts to 0·535 V.

From that background, tests have been made of the titration of iodide with chlorite in an acidic medium. Diluted (about 0·02*N*) iodide solutions were prepared with a view to preventing a volatisation of the liberated iodine. The concentration of the iodide solution was determined by titration with iodate using Andrews' method. For the titration, 0·1*N* and 0·02*N* solutions of sodium chlorite were used. Oxidation of iodide was carried out in a sulphuric acid medium (0·01*N*, 0·2*N*, 1*N*, 2*N* and 4*N*H_2SO_4).

TABLE III.—DETERMINATION OF IODIDE

Concentration of iodide determined by titration with iodate	Concentration of iodide determined with $NaClO_2$ (by the present method)							
	0·1*N* solution of $NaClO_2$					0·02*N* $NaClO_2$ solution		
	Medium							
	4*N* H_2SO_4	2*N* H_2SO_4	1*N* H_2SO_4	0·2*N* H_2SO_4	0·01*N* H_2SO_4	2*N* H_2SO_4	1*N* H_2SO_4	0·2*N* H_2SO_4
mol/l.	*mol/l.*	*mol/l.*	*mol/l.*	*mol/l.*	*mol/l.*	*mol/l.*	*mol/l.*	*mol/l.*
0·02067 0·02058 0·02058 0·02058 0·02058	0·02061	0·02075 0·02061 0·02068 0·02061 0·02061	0·02062 0·02061 0·02061 0·02062	0·02061 0·02062 0·02061 0·02061 0·02062	0·0224 0·0231	0·02075 0·02076 0·02065	0·02076 0·02069 0·02070	0·0224 0·0224 0·0213 0·0210 0·0216

As seen from Table III, the titration of iodide with chlorite gave entirely satisfactory results. Chlorite, in an acidic medium, oxidises iodide to iodine. Nevertheless, stress must be placed on the necessity of keeping a sufficiently high acidity in the medium. For, when using $0{\cdot}1N$ sodium chlorite for oxidising purposes in $0{\cdot}01N$ sulphuric acid solution, a slow stabilisation of potential of the titrated system will take place, as well as retardation of the potential-jump. Reproducible results are then no longer obtainable. The same effect is to be observed when using $0{\cdot}02N$ sodium chlorite in a $0{\cdot}2N$ sulphuric acid medium. At a higher degree of acidity the potential of the titrated system is instantaneously stabilised, and the potential-jump (260–300 mV) takes place at the correct point.

In the second part of this experimental series, tests were made of oxidising iodide to iodate with chlorite according to the work of Yntema and Fleming.[10] These authors consider that the difference of the potentials of the systems ClO_2^-/Cl^-(1·56 V) and IO_3^-/I^-(1·085 V) is sufficient for carrying out a titration. However, they do not take into consideration that such a high oxidising power as that of the system ClO_2^-/Cl^- is only obtainable in a strongly acidic medium. On the contrary, in a medium of pH 5–6 like that of their experiments, the potential is considerably lower.

Iodide was titrated in an acidic medium as well as in solutions with a higher pH (5, 5·5 and 6) following the Yntema–Fleming method. A series of tests was also made of titrating chlorite with iodide. In none of these cases were reproducible results obtained. According to our experiences, it has been found that:

1. During the titration in an acidic medium, the iodine separated in the first phase (the first potential-jump) became oxidised proportionally following the addition of consecutive portions of the reagent to the I^+ ion (the colour of the solution was changing from reddish-brown to pink-red and the liquid gave no blue tint with starch). Then, the coloration of the solution disappeared with a simultaneous appearance of an odour of chlorine dioxide. At that moment a second potential-jump took place. Following the addition of further portions of the reagent, the potential fell abruptly (Fig. 2).

2. During the titration within the pH limits of 5–6, there was no liberation of iodine. The potential rose regularly, with no appearance of a potential-jump corresponding to the oxidation of iodide to iodine. Following the addition of further portions of reagent, just prior to the end-point a slight yellow-brown coloration appeared (this was caused by the liberation of iodine, which was proved by the addition of starch), afterwards changing to pink I^+, whereupon the coloration disappeared and simultaneously a potential-jump occurred with the manifestation of a chlorine dioxide odour.

3. During the titration in an acidic medium as well as at a pH of 5–8, it was observed that the position of the end-point depends on the rate at which the titration has been carried out. The slower the reagent was added, the smaller the quantity used up to the moment of the potential-jump, and *vice versa.* The reaction rate may be estimated at pH 5·5 from the result of an experiment where a measured quantity of iodide solution was treated with chlorite in excess; the liquid was mixed and its potential measured every few min. The potential-jump occurred only after 30 min, with the simultaneous manifestation of a chlorine dioxide odour.

From the above observations it was concluded that a potential-jump takes place in the titration system at the moment when chlorine dioxide appeared in the solution, following decomposition of chlorite, rather than at the moment of complete oxidation of iodide to iodate. Indeed, according to Flis,[14] the reaction

$$ClO_2^- \rightarrow ClO_2 + e$$

already occurs within a medium of pH < 6·5 and the potential of such a system, within the limits of pH of 4–8, is 0·934 V. Accordingly, the possibility of quantitatively oxidising iodide to iodate by chlorite seems to be problematical.

Oxidation of iron^{II}

The redox potential of the system

$$Fe^{3+} + e \rightleftharpoons Fe^{2+}$$

is high and amounts to 0·77 V. It could, therefore, be reasoned that the oxidation of iron^{II} to iron^{III} with chlorite would find its only chance of realisation in a strongly acidic medium. The concentration of the iron^{II} solution was determined by a manganometric method. The iron^{III} compounds were reduced with tin^{II} chloride. Therefore, at the outset, the conditions were settled for the quantitative oxidation of tin^{II} with chlorite. It has been stated that the potential of the titrated system become stabilised in the quickest possible way in a 2*N* solution of sulphuric acid. The potential-jump was very distinct and covered about 600 mV (450 → 1100 mV)

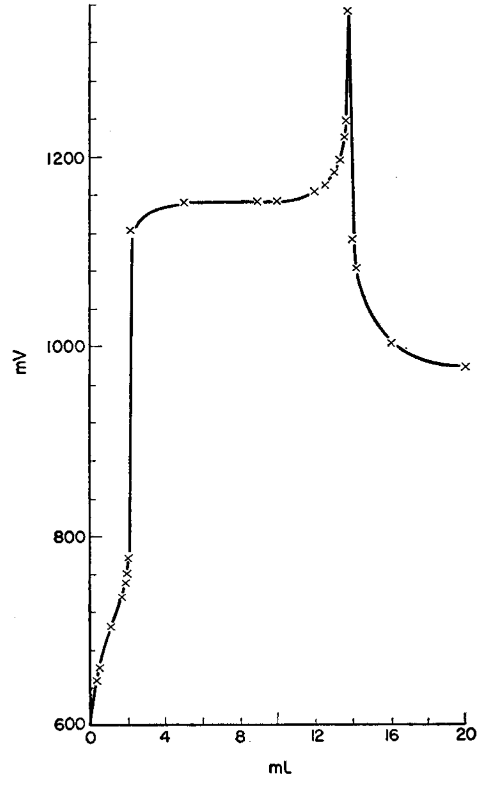


FIG. 2.—Oxidation curve of iodide to iodate with 0·1*N* solution of sodium chlorite (1*N* H_2SO_4)

A very small addition of potassium iodide as a catalyst improved the titration conditions and the results of the determination. The tests of titrating an iron^{II} salt solution with chlorite were carried out in a hydrochloric acid medium (5·5*N*, 2*N* and 1*N*) and in a sulphuric acid medium (2*N* and 1*N*). The results of the experiments are given in Table IV. During the titration two potential-jumps were obtained, the first one for tin^{II}, the second for iron^{II}. The titration in sulphuric acid medium gives a retarded potential-jump and thereby too high results are obtained. The potential of the system, after the first jump, stabilises slowly; the reaction rate for oxidising iron with chlorite in this medium is too small for analytical purposes.

TABLE IV.—DETERMINATION OF IRON

Concentration of iron determined by manganometric method	Concentration of iron determined with $NaClO_2$ (by the present method)						
	Medium						
	5·5*N* HCl	2*N* HCl	1*N* HCl	2*N* H_2SO_4	1*N* H_2SO_4	2*N* HCl + 2*N* H_2SO_4	
						without a catalyst	with KI present as catalyst
equiv./l.	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*
0·0762				0·0917	0·0912		
0·0781	0·0735	0·0793				0·0793	0·0783
0·0781	0·0735					0·0798	0·0780
0·1694	0·1560	0·1680	0·1690			0·1750	0·1698
0·1694	0·1560	0·1710	0·1700			0·1740	0·1692
0·1694	0·1554	0·1708				0·1732	0·1696
0·1694	0·1574					0·1740	0·1694

The tests of the titration in the presence of hydrochloric acid confirmed the observations made in studying the system Sn^{II}/ClO_2^-. The potential of the system, up to the first jump corresponding to tin^{II}, stabilised slowly, whereas in the second phase of titration this occurred instantaneously. In the tests in which 5·5*N* hydrochloric acid was used, the potential-jump, corresponding to the oxidation of iron^{II}, took place too early. It seems probable that with such a high acidity the decomposition rate of chlorite to form chlorine dioxide is higher than the rate of oxidation of iron^{II}. Thus the observed potential-jump corresponds rather to the first reaction. During the titration of iron^{II} in a medium of 2*N* and 1*N* hydrochloric acid the potential-jump took place at the correct point.

Because of these observations there was applied, in a further series of tests, a mixed medium of the two acids (sulphuric and the hydrochloric acids), with the particular provision that the reduction of iron^{III} with tin^{II} chloride was carried out in a 2*N* solution of hydrochloric acid, 2*N* sulphuric acid being added just before the titration. Within this titration series, the potential of the system, during the whole titration time stabilised very quickly but the results of the determination were too high. Therefore, according to the observations derived from the tests for the quantitative oxidation of tin^{II} an addition of potassium iodide as catalyst was applied, and satisfactory results obtained. The potential of the system, during the entire titration time, stabilised quickly, and the precision of the determination, as seen from Table IV, was fully sufficient. It was also observed in a complete series of tests that a chlorine dioxide odour, which is perceivable even in very small concentrations, showed itself only after the end-point of the titration was attained. It is a proof that the oxidation reaction of iron^{II} with chlorite is completed quantitatively.

Oxidation of arsenite

Brown,[11] like many other authors,[15,17,18,19,20] found that the reaction:

$$\mathrm{NaClO_2 + 2HAsO_2 + 2H_2O \rightarrow NaCl + 2H_3AsO_4}$$

is very slow; however, in the presence of a catalyst—osmium tetroxide—the reaction develops a rate sufficient for analytical purposes. Brown titrated chlorite with a solution of sodium arsenite at pH 8·2 in the presence of osmium tetroxide. He defined the cited pH as an optimum, since with a lower pH a decomposition of chlorite takes place with liberation of chlorine dioxide, and with a higher pH the reaction is too slow. Further, he stated that at pH 8·2 an reverse titration, when applying potentiometric analysis, gives no result, as proportionally with addition of the reagent, a gradual rise of the potential of the system takes place, without any jump of potential.

The series of experiments with quantitative oxidation of arsenite was started by checking Brown's method, whereupon a confirmation of his results was obtained. Next, the possibility of determining arsenite with chlorite in the absence of a catalyst was examined. The redox-potential of the system

$$\mathrm{H_3AsO_4 + 2H^+ + 2e \rightarrow HAsO_2 + 2H_2O}$$

amounts to 0·559 V. The oxidation of arsenite with chlorite was carried out in an acidic medium. The concentration of sodium arsenite solution (about 0·1*N*) was determined iodometrically. The oxidation of arsenite was carried out in a hydrochloric acid (5·5*N*, 2*N* and 1*N*) and in a sulphuric acid (2*N*) medium. 0·1*N* sodium chlorite solution was employed as titrant. The results are given in Table V.

TABLE V.—DETERMINATION OF ARSENITE

Concentration of arsenite determined iodometrically	Concentration of arsenite determined with $NaClO_2$ (by the present method)								
	Medium								
	5·5*N* HCl				2*N* HCl				1*N* HCl
	without a catalyst	with KIO_3	with ICI	with KI	without a catalyst	with KIO_3	with ICI	with KI	without a catalyst
equiv./l.	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*	*equiv./l.*
0·0518	0·0528	0·0518	0·0528	0·0528	0·0529	0·0518			0·0568
0·0518	0·0519	0·0515	0·0528	0·0530	0·0538	0·0515			0·0560
0·0518	0·0519	0·0516	0·0523		0·0538	0·0517			
0·0518	0·0528				0·0553				
0·0518	0·0523								
0·0504	0·0506	0·0501							
0·0504	0·0506	0·0503							
0·0504	0·0506								
0·0610	0·0610	0·0608	0·0610	0·0613			0·0625	0·0623	
0·0610	0·0610	0·0608	0·0610	0·0613			0·0620		

During the titration in a hydrochloric acid medium, the stabilisation speed of the potential of the titrated system was dependent on the acidity of the medium. The use of 5·5*N* and 2*N* hydrochloric acid was found to be most favourable. With these two concentrations of hydrochloric acid, the rate of stabilisation of the potential was equal to the speed of this process with the iodometric method. The potential-jump, in all cases, was very distinct and amounted to about 250–300 mV. Nevertheless, this jump occurred at the correct point only with a titration in a 5·5*N* solution of hydrochloric acid. With lower concentrations of acid, the jump was retarded. Further, it was found that the addition of a small amount of potassium iodate has a catalysing action on the oxidation reaction of arsenite in a hydrochloric acid medium. This observation allowed the quantitative determination of arsenite to be made in a 2*N* solution of hydrochloric acid. The addition of potassium iodide or iodine monochloride did not influence the process. Attempts to titrate arsenite in a sulphuric acid solution gave no results. Indeed, the potential of the titrated solution rose regularly and revealed no jump.

It may be concluded from the experiments performed that, in a medium of 5·5*N* or 2*N* hydrochloric acid, with the addition of potassium iodate as a catalyst, a quantitative determination of arsenite with chlorite can be carried out with sufficient precision.

Further experiments in the application of chlorite as an oxidising agent as well as the use of redox indicators in these titrations are being made.

Zusammenfassung—Möglichkeiten Natriumchloritlösungen als oxydierendes Agens in der Massanalyse zu verwenden wurden untersucht. Es wird angegeben, dass solche Lösungen unter Ausschluss von Licht für einige Zeit stabil sind. Sie sind geeignet zur direkten potentiometrischen Titration von Sulfite, Eisen(III) (nach Reduktion zu Eisen(II) mit $SnCl_2$), Arsen(III) und Jodid. Die Titrationen werden im allgemeinen in säurem Medium durchgeführt wobei manchmal Katalysatoren, wie z.B. KJO_3 verwendet werden.

Résumé—Les auteurs ont étudié la possibilité d'utiliser des solutions de chlorite de sodium comme agent oxydant dans l'analyse titrimétrique. De telles solutions en l'absence de lumière sont stables pendant un certain temps, et conviennent pour le titrage potentiométrique direct du sulfite, du fer (III) (après réduction en fer (II) par $SnCl_2$), de l'arsenic (III) et de l'iodure. Le titrage est effectué généralement en milieu acide, quelquefois en utilisant des catalyseurs tels que KIO_3.

REFERENCES

[1] G. R. Levi, *Gazetta*, 1922, **52**, 58; *Chem. Zentr.*, 1938, **II**, 560.
[2] G. R. Levi and G. Natta, *Gazetta*, 1923, **53**, 532; *Chem. Abs.*, 1924, **18**, 348.
[3] G. R. Levi, *Gazetta*, 1922, **52**, 417.
[4] G. Bruni and G. R. Levi, *Atti Ist. Veneto Sci. Let. Arti*, 1910, **74**, II, 1711; *Chem. Abs.*, 1916, **10**, 570.
[5] G. R. Levi, *Atti Acad. naz. Lincei*, 1922, **31**, I, 370; *Chem. Abs.*, 1922, **16**, 3789.
[6] G. R. Levi and L. Ghiron, *Atti Accad. naz. Lincei*, 1930, **11**, 1005; *Chem. Abs.*, 1931, **25**, 654.
[7] G. R. Levi and C. C. Bisi, *Gazetta*, 1957, **87**, 366.
[8] J. L. Parsons, *Ind. Eng. Chem. Anal.*, 1937, **9**, 250.
[9] D. T. Jackson and J. L. Parsons, *ibid.*, 1937, **15**, 14.
[10] L. F. Yntema and T. Fleming, *ibid.*, 1939, **11**, 375.
[11] E. G. Brown, *Analyt. Chim. Acta*, 1952, **7**, 494.
[12] Ram Chand Paul and Apar Singh, *J. Indian Chem. Soc.*, 1958, **35**, 294.
[13] G. Holst, *Svensk Papperstidn.*, 1945, **48**, No. 2, 23.
[14] J. E. Flis and P. M. Wasiliew, *Zhur. obshchei Khim.*, 1956, **26**, 1272; J. E. Flis, *Zhur. fiz. Khim.*, 1958, **32**, 573.
[15] W. Bray, *Z. phys. Chem.*, 1905, **54**, 576.
[16] F. L. Hahn and G. Weiler, *Z. analyt. Chem.*, 1926, **69**, 417, after *Metrohm Bulletin* (Switzerland) 1950, **1**, No. 2, 20.
[17] I. M. Kolthoff, *Rec. Trav. chim.*, 1922, **41**, 742.
[18] E. Schulek and P. Endroï, *Analyt. Chim. Acta*, 1951, **5**, 368.
[19] F. Foerster and P. Dolch, *Z. Elektrochem.*, 1917, **23**, 138.
[20] J. F. White, *Amer. Dyestuff Reporter*, 1947, **31**, 481.

Talanta, 1960, Vol. 5, pp. 189 to 192. Pergamon Press Ltd. Printed in Northern Ireland

THE RAPID DETERMINATION OF WATER OF HYDRATION IN MAGNESIUM PERCHLORATE DESICCANT

G. FREDERICK SMITH
Noyes Chemical Laboratories, University of Illinois, Urbana, Illinois, U.S.A.

(*Received* 26 *July* 1960)

Summary—The efficiency of "anhydrous" magnesium perchlorate as a desiccant, and its capacity in absorption of water vapour, ammonia gas, alcohol vapour, and other highly volatile organic vapours, is dependent upon the extent to which its water of hydration is removed in preparation for commercial distribution. American Chemical Society "Reagent Chemicals" specifications call for not more than 10% water as a maximum tolerance. The product is, by intent, not ordinarily manufactured for distribution in the completely dehydrated form and regularly contains approximately 5% unremoved water of hydration. This is the regular practice to insure a less friable granular structure than would result from complete dehydration. The method here described for the determination of its water content is rapid in application, sufficiently accurate for all practical demand, and requires very simple apparatus and manipulative details.

INTRODUCTION

MAGNESIUM perchlorate is obtained as the hexahydrate upon crystallisation from boiling saturated solution in water. By proper treatment in this process, its crystal aggregate is readily controlled in particle size for subsequent dehydration to give the ideal condition for its many analytical applications. In the successful elimination of combined water, vacuum drying is the most practical technique. This dehydration results in the following stepwise elimination of water:

$$\begin{aligned} &\mathrm{Mg(ClO_4)_2{\cdot}6H_2O} \rightarrow \mathrm{Mg(ClO_4)_2{\cdot}4H_2O} \\ &\qquad \rightarrow \mathrm{Mg(ClO_4)_2{\cdot}2H_2O} \rightarrow \mathrm{Mg(ClO_4)_2}\ \text{anhydrous} \end{aligned}$$

For the purpose of providing high porosity without alteration in chosen particle size, these dehydrations must be carried out without the various hydrates fusing in their own water of hydration. This demands stepwise dehydration and the final stage must be done in a good vacuum and at temperatures between 200 and 250°. Anhydrous granular magnesium perchlorate owes its dehydration efficiency to two distinct properties, the one based upon its high degree of porosity, and the other upon its re-hydration accompanied by high heat exchange in the latter process. The anhydrous material absorbs ammonia with greater heat interchange than occurs with water absorption. As in the absorption of water, ammonia forms the analogous di-, tetra- and hexa-ammoniates. The diammoniate is not dissociated with heat below approximately 200°, at which temperature it gives no odour of ammonia.

Magnesium perchlorate as a desiccant has been made commercially available for a period of almost 40 years.[1] Its many analytical and industrial applications are well known.[2] The dew-point of a gas with which its dehydration is at equilibrium is less than liquid air temperature. Magnesium perchlorate dihydrate cannot be further dehydrated in contact with phosphorus pentoxide[3] at any temperature at which the phosphorus desiccant is applicable and at temperatures under 150°. Since dry ammonia gas displaces the water of hydration from magnesium perchlorate, the ammoniates have greater stability than the hydrates.

Magnesium perchlorate is highly soluble in water and almost all organic solvents.

EXPERIMENTAL

Apparatus

Silvered Dewar Flask, 62·5 mm wide inside and 110 mm deep, capacity 300 ml.

Centigrade thermometer 0–100°.

Paraffined cork stopper, one hole for thermometer insertion, to fit top of Dewar.

A cylinder of filter paper 44 mm in diameter and 75 mm tall open at top. These are made from a rectangular piece cut from an 18·5-cm circular filter (a 100 × 150-mm section). Roll the paper on a template and fold around the bottom for closure. Use a small piece of masking tape for holding the side section and bottom in position. These containers are used to contain samples for test, weight 1·4 g.

A reasonably sensitive small platform balance. An Ohaus 700-g capacity balance was adequate for making weighings to the nearest 100 mg. A 100-ml graduated cylinder was used for water measurement.

Reagents

Water and the sample to be tested are the only reagents involved.

Analytical procedure

To the Dewar flask add 75 ml of water, put the thermometer and paraffined cork in place, and at equilibrium read the temperature. Place a 20·0-g sample of the magnesium perchlorate to be tested in the cylindrical paper container, and fold in the top. Drop the sample into the Dewar, insert the thermometer and cork cover, and at equilibrium measure the temperature rise in the Dewar flask. Stir by a gentle circular motion of the Dewar to ensure complete solution of sample.

From a calibration curve provided by the procedure to be described below determine the % of water left in the perchlorate drier. The dihydrate of magnesium perchlorate contains 13·9 % water of hydration. The temperature rise for 20 g of the exact dihydrate under the conditions described is 17·6°. For 20 g of anhydrous magnesium perchlorate it is 37·5°. The slope of the calibration curve is approximately 45°. The temperature increase for each removal of 1 % of water of hydration is approximately 2·7°. The accuracy is approximately ±0·2 % in water content determined. Duplicate determinations of temperature measurement are quite easily attained. Greater precision is not necessary.

Preparation of calibration data

Dry carefully 125–150-g batches of magnesium perchlorate hexahydrate in an electrically heated tube heater under vacuum of 0·25 mm and at stepwise increase in temperature starting at 125°. At 165°–170° the dehydration is complete to the formation of the dihydrate. For removal of the last two molecules of water, a temperature of 200°–225° is required and time intervals of 16–24 hr under continuous evacuation of less than 1 mm pressure. Pass the samples thus prepared at various time intervals several times through a 4-mesh sieve and allow to cool in a 500-ml plastic cap bottle in a desiccator charged with the same desiccant.

Weigh samples of 4–6 g into porcelain boats (16 × 1000 mm), using a ground-glass stoppered weighing pig. Determine their water content by complete dehydration at 225°–250° in vacuo. Determine the weight of the boat contents again, thus defining the residual water of hydration. When analyses of the reference standards were made in duplicate, the results shown graphically in Fig. 1, were obtained.

As would be predicted, the increase in temperature of solution in water for the range 13·9–0·0 % of water is a straight line function within the range covered by the transformation $Mg(ClO_4)_2 \cdot 2H_2O$ to anhydrous desiccant.

The variation in temperature rise with each increase in % water found is indicated for the analytical purpose intended in Table I.

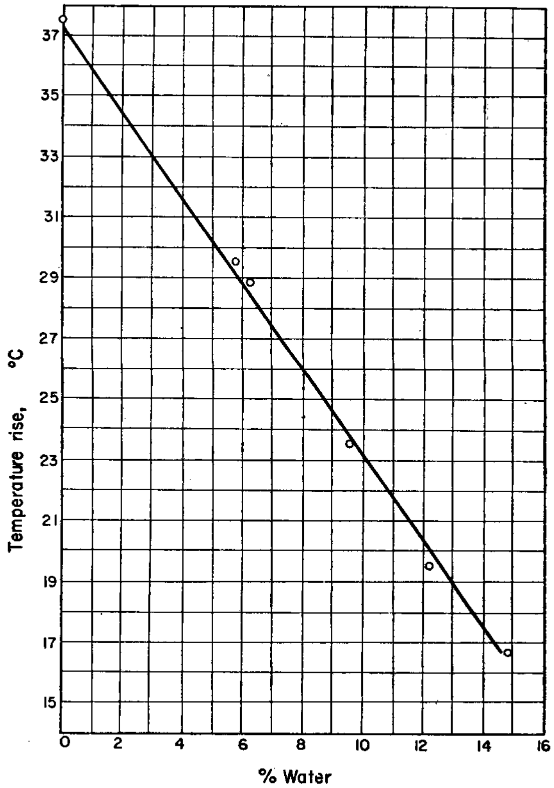


Fig. 1.

Table I.—Tabulation of the data shown in the graph of figure 1. Temperature vs. water content

Water found, %	Temp. rise, °*C*	Water found, %	Temp. rise °*C*	Water found, %	Temp. rise °*C*
0·0	37·5	6·0	28·9	11·0	21·7
1·0	35·9	7·0	27·4	12·0	20·3
2·0	34·5	8·0	26·0	13·0	19·0
3·0	33·1	9·0	24·6	13·9	17·7
4·0	31·6	10·0	23·2		
5·0	30·2				

DISCUSSION

The purpose of the filter paper sample-container is to bring about retarded solution of the sample in water. Failure to use such a procedure, particularly for water contents of 1–5%, causes loss of heat through transformation of some of the water content of the Dewar flask to steam. The thermometer often shows a temperature rise much in excess of the equilibrium value due to local heating. A steady reading, with complete solution of the sample, is ordinarily obtained after 20–25 sec. The contents of a reagent bottle of desiccant before analysis for its water content should be passed through a coarse sieve several times before sampling to insure uniformity. A sample bottle with even a tight-fitting screw top and paper or other type liner will be found in extended periods of shelf-life to admit sufficient water to the desiccant to alter the true water content of the original product on its top layer.

The regeneration of spent magnesium perchlorate by heating and evacuation, if porosity and granulation are to be maintained, is not a simple operation. Contamination of spent reagent with organic impurities, especially if acidic in reaction, may give rise to material decomposition. Unless such contamination is known to be absent such regeneration is ill advised.

REFERENCES

[1] H. H. Willard and G. Frederick Smith, *J. Amer. Chem. Soc.*, 1922, **45**, 2816.
[2] G. Frederick Smith, *Chem. and Ind.* 1934, 357.
[3] G. Frederick Smith, O. W. Rees and V. R. Hardy, *J. Amer. Chem. Soc.* 1932, **54**, 3513.

Talanta, 1960, Vol. 5, pp. 193 to 198. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF LEAD, CADMIUM AND ZINC IONS IN LARGE EXCESS OF INDIUM ION USING THE ALTERNATING CURRENT POLAROGRAPH

TAKEO TAKAHASHI and HIDEKO SHIRAI
Institute of Industrial Science, University of Tokyo, Tokyo, Japan

(*Received* 10 *February* 1960)

Summary—Lead, cadmium or zinc ions in the presence of a large excess of indium ion can be determined, without removal of excess indium and dissolved oxygen, by means of the alternating current polarograph in supporting electrolytes such as nitric acid or phosphoric acid.

INTRODUCTION

SINCE the half-wave potentials of indium and cadmium ions are very close to each other, their separation being about 0·1 ~ 0·2 V in KBr or KCl electrolyte solution, their polarographic determination is regarded as being comparatively difficult using the conventional d.c. polarograph. But a.c. polarograms of these metallic ions show well-separated reduction waves in the same supporting electrolyte solutions, when the concentrations of the elements are almost equal.

However, when the concentration ratio of indium ion to cadmium ion becomes large, the reduction wave of cadmium ion is not so easily separated from that of indium ion, even by the a.c. polarographic method. Although it is possible to apply the suppression method to the indium ion using dissolved oxygen, this method is not very effective for separating the cadmium wave from the indium wave when indium is present in large excess (over 0·2 *mM*). It is therefore necessary to find another suitable electrolyte solution for the separation of cadmium and indium ion, such that in it either the potential of indium ion moves towards a more negative potential than that of cadmium ion, or the indium ion is reduced irreversibly so that its peak height is decreased as much as possible. In the present study, phosphoric acid was found to be a suitable electrolyte for the separation of the reduction waves of the ions, and it permits determination of cadmium, lead and zinc ions in the presence of a large excess of indium ion by means of a.c. polarography.

EXPERIMENTAL

Reagent and apparatus

Indium nitrate is prepared by dissolution of indium metal (99·9%) in nitric acid (specially pure), evaporation on the water-bath to dryness and dissolution in the appropriate amount of distilled water to give 1*M* $In(NO_3)_3$ solution. Lead nitrate, thallium nitrate, cadmium sulphate and lead nitrate used as the metallic ions to be determined are specially purified grade. Phosphoric acid, nitric acid or ammonium nitrate used for the supporting electrolyte are also specially purified grade.

The d.c. and a.c. polarographs employed in the present experiment have already been described.[1] In the a.c. polarograph R_s and C_s are respectively 0·5 KΩ and 0·2 μF. The reference electrode (1*N* calomel electrode) is connected through agar–agar with the polarographic solution; the mercury flow from the capillary is 2·79 mg/sec; the drop time in 0·5*N* nitric acid at −1·0 V is 4·3 sec/drop.

1. *A.c. polarograms in various electrolytes*

(a) *Ammonium nitrate electrolyte:* From the d.c. polarogram of indium in 0·5*M* ammonium nitrate solution (pH 2), it is found that the reduction wave appears at about −0·53 V and its electrode

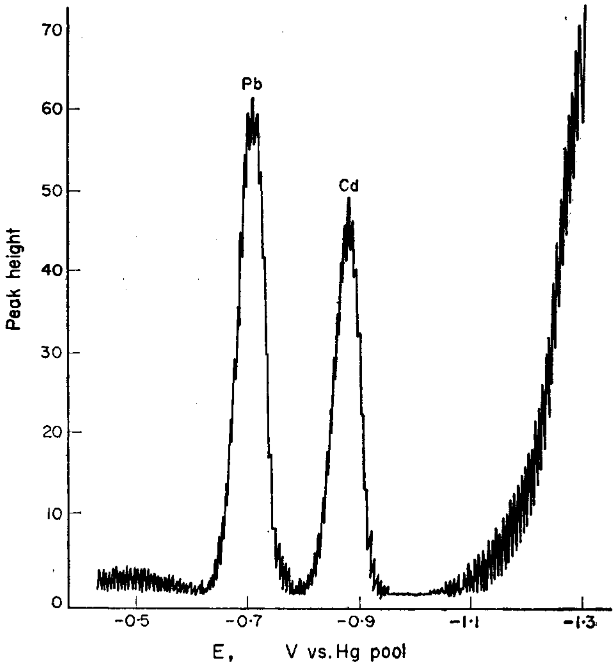


FIG. 1.—A.c. polarograms of lead, cadmium and zinc ions in the presence of large excess of indium ion (in 0·5M NH_4NO_3). (0·25 mM Cd and Pb; 0·5 mM Zn; 10 mM In, 25°).

reaction proceeds irreversibly as shown by the slope of the reduction waves. In agreement with this, the a.c. polarogram of indium has a very low peak height, as shown in Fig. 1, in comparison with those shown by 0·25 mM lead or cadmium ions. However, it is evident that the peak height of cadmium is affected by that of indium, although the peak height of lead is not so affected. This appears from the calibration curves for lead and cadmium, shown in Fig. 2, in which the lead curve is a straight line passing through the origin, but the cadmium curve, although a straight line, does not pass through

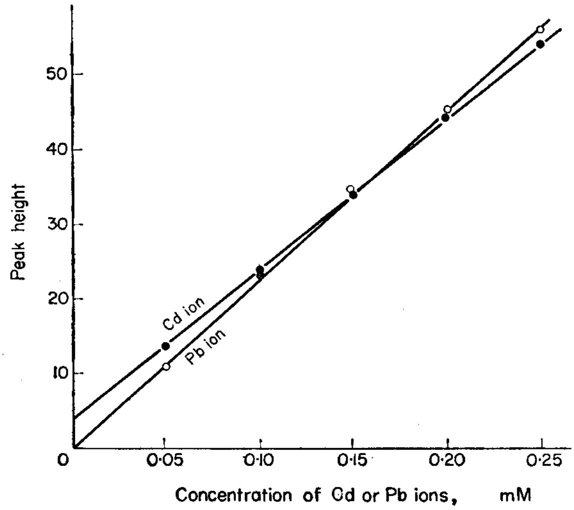


FIG. 2.—Calibration curves for cadmium and lead ions in the presence of large excess of indium (10 mM) in 0·5 M NH_4NO_3 solution (25°) (● Cd ion; ○ Pb ion).

the origin. The peak heights are expressed by measuring the distance of the top of the peak from the curve for supporting electrolyte alone in the a.c. polarogram of the metallic ion. The reduction wave of zinc overlaps the hydrogen discharge wave, so that it is impossible to determine zinc together with lead and cadmium in ammonium nitrate electrolyte solution.

(b) *Nitric acid electrolyte:* Since the a.c. polarogram for indium shows a reversible wave in 0·5*N* nitric acid solution, its peak appearing at about −0·8 V vs. N.C.E., the presence of indium does not affect the reduction waves of cadmium and lead, as shown in Fig. 3. The reduction wave for zinc is obscured owing to the hydrogen discharge wave, making the polarographic determination of zinc impossible.

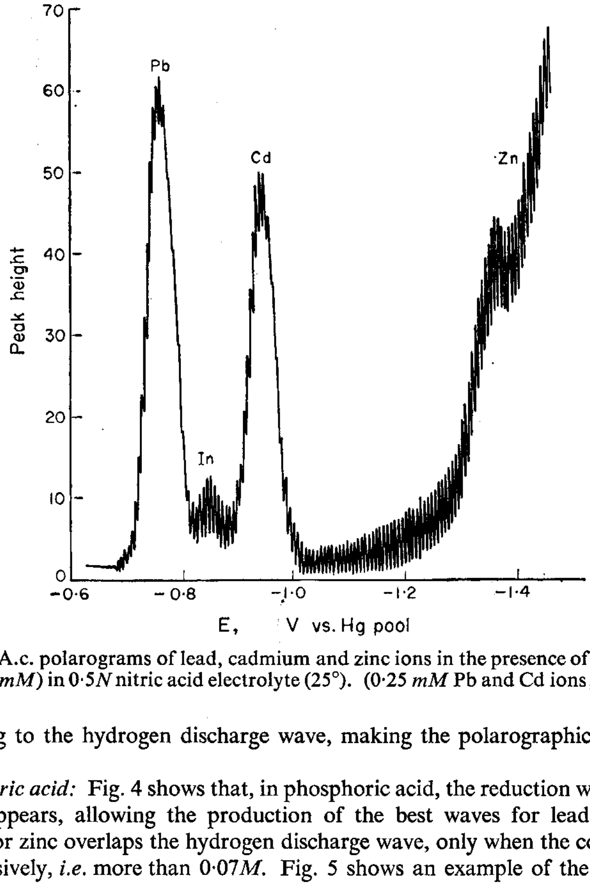


FIG. 3.—A.c. polarograms of lead, cadmium and zinc ions in the presence of large excess of indium (10 *mM*) in 0·5*N* nitric acid electrolyte (25°). (0·25 *mM* Pb and Cd ions; 0·5 *mM* Zn ion).

(c) *Phosphoric acid:* Fig. 4 shows that, in phosphoric acid, the reduction wave for indium [0·07*M*, $In(NO_3)_3$] disappears, allowing the production of the best waves for lead, cadmium and zinc.

The wave for zinc overlaps the hydrogen discharge wave, only when the concentration of indium increases excessively, *i.e.* more than 0·07*M*. Fig. 5 shows an example of the a.c. polarogram when the concentration of indium is 0·33*M*. In such a case there is no effect on the waves for lead and cadmium.

Fig. 6 gives the calibration curves for lead, cadmium and zinc in the presence of 20 *mM* indium nitrate in 1*M* phosphoric acid and indicates the good linear relationship between the metal ions and peak heights, provided that their concentrations are in the range 0·25 ∼ 0·05 *mM*.

2. *Effect of the presence of other ions*

(a) *Effect of thallium on the waves of lead and cadmium:* The wave for thallium lies between those of lead and cadmium. Therefore the waves for lead and cadmium are both influenced by the thallium wave, becoming higher than in individual solutions of each ion. Fig. 7 shows this situation in phosphoric acid electrolyte and indicates that the influence is more pronounced in the lead wave than in that of cadmium. The increase in peak height almost equals the overlap of the thallium wave with those of lead or cadmium. Such overlapping is probably due to the fact that the peak potential of thallium is closer to that of lead than to that of cadmium. This influence was found with nitric acid or ammonium nitrate, as well as with phosphoric acid as supporting electrolyte.

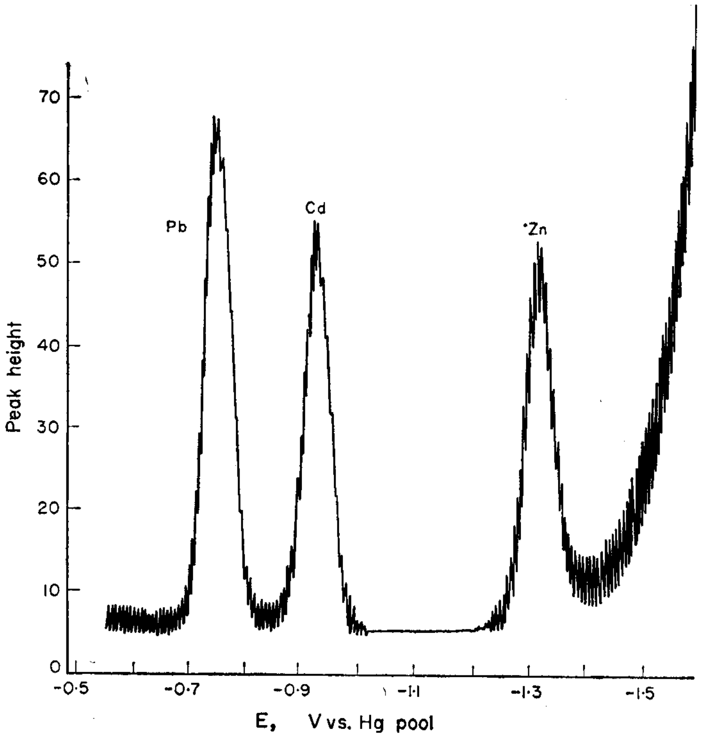


FIG. 4.—A.c. polarograms of lead, cadmium and zinc ions in 1*M* phosphoric acid electrolyte (25°). (0·25 *mM* Cd and Pb; 0·5 *mM* Zn; 0·07*M* In).

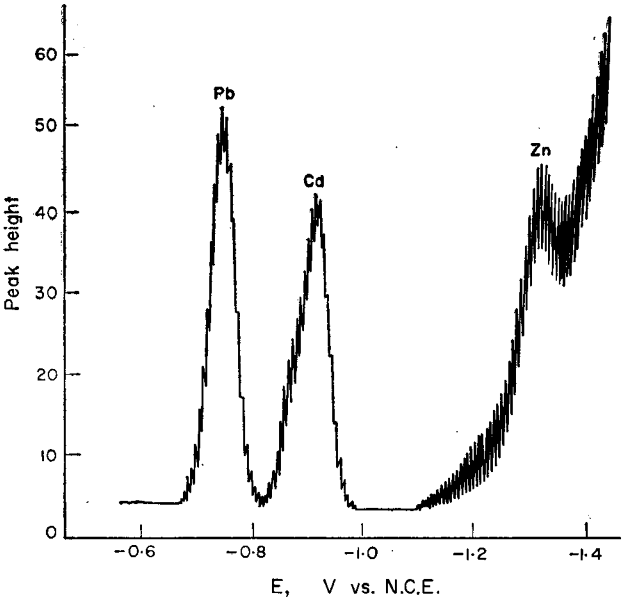


FIG. 5.—A.c. polarograms of lead, cadmium and zinc ions in 1*M* phosphoric acid (25°). (0·2 *mM* Pb and Cd; 0·4 *mM* Zn; 0·33*M* In).

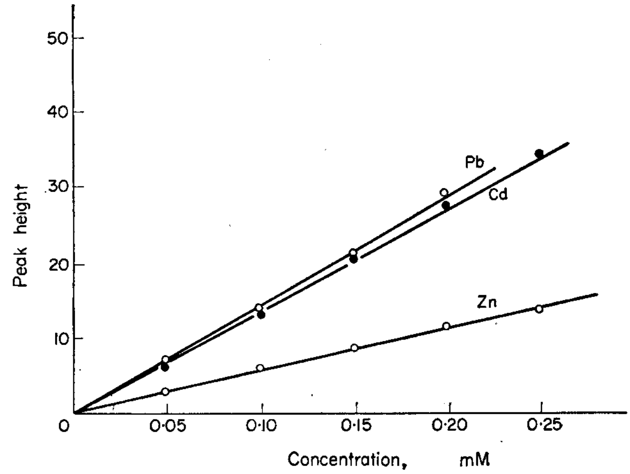


FIG. 6.—Calibration curves for lead, cadmium and zinc ions in the presence of 20 *mM* indium nitrate in 1*M* phosphoric acid (20°). (10 scale units of peak height equal 0·2 mV).

(b) *Effect of halide ion on the peak height of indium:* If halide is present in a supporting electrolyte such as nitric acid, phosphoric acid or ammonium nitrate, the indium wave appears between the waves of lead and cadmium. Such a medium influences the waves of lead and cadmium if the concentration of indium ion is large. In Table I the effect of chloride and iodide on the indium wave (concentration 0·16 *mM*) is shown.

The influence of iodide ion is even more marked at very low concentration than that of chloride ion.

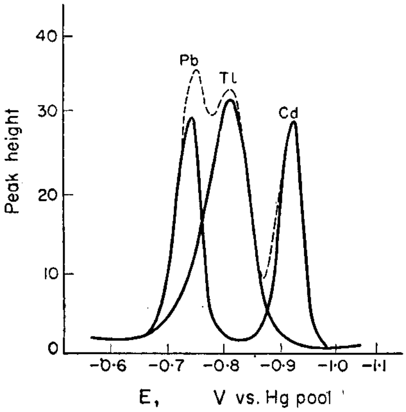


FIG. 7. A.c. polarograms of lead and cadmium ions with (– – –) and without (—) thallium ion in large excess of indium ion (10 *mM*). (0·2 *mM* Cd and Pb; 0·4 *mM* Tl. 20°).

DISCUSSION

In a supporting electrolyte of 1*M* phosphoric acid, it was found[2] that indium ion is present as a soluble complex ion with phosphoric acid such as $[In(HPO_4)]^{(3-2n)+}$ or $[In(H_2PO_4)_n]^{(3-n)+}$. This complexing of the indium ion is the cause of the disappearance of the indium wave at a more positive potential than the reduction potential of the hydrogen ion.

In a supporting electrolyte of nitric acid,[3] indium ion forms an aquo-complex such as $[In(H_2O)_6]^{3+}$. This complex also causes the disappearance of the indium wave.

TABLE I. EFFECT OF THE CONCENTRATION OF HALIDE ION UPON THE PEAK HEIGHT OF INDIUM ION

Conc. of halogen ion, M	Cl^- in			I^- in $0\cdot5M$ NH_4NO_3
	$1M$ NH_4NO_3	$0\cdot5M$ NH_4NO_3	$1M$ H_3PO_4	
$0\cdot5 \times 10^{-1}$	6·8	—	—	—
1×10^{-1}	9·5	14·5	7·5	—
2×10^{-1}	20·8	22·5	15·5	—
3×10^{-1}	24·0	30·0	21·5	—
4×10^{-1}	32·0	—	—	—
$0\cdot2 \times 10^{-4}$	—	—	—	1·5
$0\cdot5 \times 10^{-4}$	—	—	—	2·0
1×10^{-4}	—	—	—	3·5
$2\cdot5 \times 10^{-4}$	—	—	—	7·5
5×10^{-4}	—	—	—	10·5

But an irreversible reduction wave for indium appears at −0·6 V vs. N.C.E. in ammonium nitrate electrolyte (pH 2) and disappears when the electrolyte solution is acidified by nitric acid to the extent of 0·1*N*. The irreversible reduction wave is therefore thought to be due to the formation of a basic aquo-complex such as $[In(H_2O)_5(OH)]^{2+}$, which is implied by the study of Cozzi and Vivorelli.[3]

This basic complex is reduced at a more positive potential than the aquo-complex and when the electrolyte solution is acidified, it releases the co-ordinated OH group, resulting in the formation of the aquo-complex, which is reduced at a more negative potential than the former basic aquo-complex. Indium ion tends to form a halogeno-complex with halide ion, which complex is reduced at a more positive potential than the aquo-complex, resulting in the appearance of a reversible wave with a distinctly higher peak in the a.c. polarogram.

If the aquo-, basic aquo- or phosphoric complexes of indium ion described above exist in the presence of halide ion, indium ion forms more stable complexes than these and shows a higher peak with increase in the concentration of halide ion.

The effect of halide ion on the reduction wave of indium ion varies in accordance with the difference between the stabilities of the complexes and their halogeno-complexes. Also the effect of iodide ion is more pronounced than that of chloride ion.

Zusammenfassung—Blei, Cadmium und Zink können in Gegenwart eines grossen Überschusses von Indium ohne Entfernung von gelöstem Sauerstoff bestimmt werden, wenn man mit Wechselstrom-polarographie in einer Grundlösung aus Sälpeter- oder Phosphorsäure arbeitet.

Résumé—Les ions du plomb, du calcium ou du zinc peuvent être dosés en présence d'un grand excès d'ion de l'indium sans élimination de l'excès d'indium ou de l'oxygène dissous si le dosage est réalisé à l'aide d'un polarographe à courant alternatif dans un électrolyte support tel que l'acide nitrique ou l'acide phosphorique.

REFERENCES

[1] T. Takahashi, H. Shirai and E. Niki, *Report of the Institute of Industrial Science*, University of Tokyo, 1959, **8**, 153; T. Takahashi and E. Niki, *Talanta*, 1959, **1**, 245.
[2] A. Holroyd and J. E. Salmon, *J. Chem. Soc.*, 1956, 269.
[3] D. Cozzi and S. Vivorelli, *Z. Electrochem.*, 1953, **57**, 408.

Talanta, 1960, Vol. 5, pp. 199 to 204. Pergamon Press Ltd. Printed in Northern Ireland

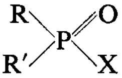
DETECTION OF MONOBASIC PHOSPHORUS ACID ESTERS BY CONVERSION TO CHOLINESTERASE INHIBITORS

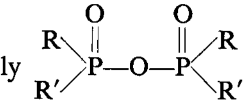
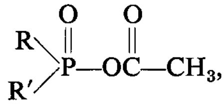
HARVEY W. YUROW*, DAVID H. ROSENBLATT and JOSEPH EPSTEIN†
Biochemical Research Division, U.S. Army Chemical Warfare Laboratories, Army Chemical Center, Maryland, U.S.A.

(*Received* 11 *May* 1960)

Summary—Many monobasic acids of quinquevalent phosphorus form cholinesterase inhibitors when exposed to ketene. Based upon this finding, a sensitive test to detect the presence of these compounds on filter paper has been developed. Seventeen out of nineteen of these acids tested gave positive results. Negative results obtained with the remaining two are attributable to steric factors or to the high hydrolysis rate of the acetylated product. Only one of eighteen phosphorus compounds other than the monobasic acids examined, namely *n*-butylphosphonic acid, gave a positive test; an explanation is offered to account for this exception.

WITH the demonstration by Cook[1] that very sensitive cholinesterase inhibition tests could be applied directly to paper chromatograms, a new approach to the detection of enzymatically inactive compounds, by the *in situ* conversion to active cholinesterase inhibitors, became attractive.

Compounds of the type  $\mathrm{RR'P(=O)X}$ (R and R′ are alkyl or alkoxy) are generally active cholinesterase inhibitors[2] if the hydrolysis product HX has a pK_a less than 7. Thus, conversion of a monobasic acid of quinquevalent phosphorus to a derivative satisfying this requirement should permit use of an enzymatic method.

Procedures for converting the acids to two classes of derivatives of the required type, namely  $\mathrm{RR'P(=O){-}O{-}P(=O)RR'}$ I and  $\mathrm{RR'P(=O){-}OC(=O){-}CH_3}$ II, were selected for study because the reactions were well known[3,4] and because compounds of these classes are good cholinesterase inhibitors (*e.g.* tetra-ethylpyrophosphate and diethylacetylphosphate). Lack of sufficient information precluded selection of either class over the other on the basis of relatively superior inhibitory power. The preparation of I can be accomplished by reaction of the appropriate monobasic acid with N:N′-disubstituted carbodi-imide,[3] while II can be made with the acid and ketene; of the two reagents, only the latter can be removed, if in excess, by volatilisation at a relatively low temperature. Moreover, the ketene method may be expected to yield twice as many moles of enzyme inhibitor as the carbodi-imide method. Based on these considerations, as well as on a few comparison tests, ketene was made the reagent of choice.

The product of reaction of ketene with a monobasic acid of phosphorus, under the conditions used here, is believed to be II; if, in fact, it were I, then II would most

---

* Present address: Department of Chemistry, Rutgers University, New Brunswick, N.J., U.S.A.
† To whom requests for reprints should be addressed.

probably be an intermediate in its formation. Assuming that I can be formed from II by reaction with a second molecule of the monobasic phosphorus acid, the likelihood of this second step would be minimised where the concentration of acid was quite small and that of ketene relatively high. A determination of the initial pseudo-first order rate constants at pH 7, by Michel's enzyme inhibition technique,[5] for the hydrolysis of authentic samples of I and II (R = ethyl, R′ = ethoxy) showed about a four-fold difference in hydrolysis rates ($k_{obs} = 0{\cdot}0042$ and $0{\cdot}018$ min^{-1}, respectively). An extract of filter paper which had been impregnated with the corresponding acid and exposed to ketene gave an initial hydrolysis rate constant ($0{\cdot}019$ min^{-1}) well in agreement with the supposition that II is the principal product in the phosphorus acid-ketene reaction.

The results of tests on 36 organophosphorus compounds are shown in Table I. In each case, the paper was spotted with 1 μg per cm^2 of the compound in methanol. Positive tests were also obtained with the sodium salt of *iso*propylmethylphosphonic acid and the di*cyclo*hexylamine salt of di-*iso*propylphosphoric acid.

DISCUSSION

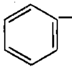
Cholinesterase hydrolyses acetylcholine to choline and acetic acid. In an unbuffered system, the latter product causes the indicator, bromothymol blue, to change from a blue to a yellow colour. The persistence of a blue colour indicates the presence of an enzyme inhibitor. In an atmosphere of high moisture content, or on over-exposure to ketene, the acid background is high (due, presumably, to the reaction between ketene and water to form acetic acid). In such cases, a larger quantity of enzyme spray solution will be required to give the overall blue colour specified in the procedure and will lead to decreased sensitivity of the test. Minimal quantities of spray reagent are required and maximum sensitivity is obtained if the paper is exposed to ketene, generated at a rate of from 10–40 mg/min, for 5 minutes. If too much acidic material is present at the phosphorus acid site, it may be necessary to neutralise the excess acidity before spotting or to use less of the phosphorus compound in order to achieve the desired overall blue colour.

Initially, the technique described by Cook,[1] in which four identical sized strips of filter paper, each containing a single reagent, are placed one on top of the other, was tried. Because of diffusion of the spots on the paper and attenuation of the spots among the four strips, the sensitivity was not good. The sensitivity of the test was improved significantly when enzyme, substrate, base and indicator were combined as a single spray reagent and one strip of paper was used.

Colorimetric and fluorescent acid-base indicators, other than bromothymol blue, were examined. None was more satisfactory.

Positive tests were given by 1 μg per cm^2 of all monobasic phosphorus acid esters after reaction with ketene, with the exception of dimethylphosphate and ethyl*iso*propylphosphonate. The failure of dimethylphosphate to behave like other monobasic phosphoric ester acids is possibly due to (*a*) the rapid hydrolysis rate of acetyldimethylphosphate or (*b*) the low rate of reaction of the acetylated compound with the esterases in horse serum. While there is no direct evidence on either of these possibilities, it is known that the hydrolysis constant of tetramethylpyrophosphate is 10 times that of TEPP[6] and its inhibitory power towards human plasma esterase 1/2500 that of TEPP.[7] The one monobasic phosphonate ester which gave a negative response

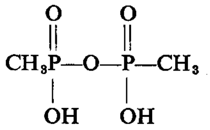
TABLE I. COMPOUNDS TESTED BY KETENE TEST

		Test result[a]	Sensitivity[d], *µg/cm*^{2}
Dibasic phosphate esters	$CH_3OPO(OH)_2$	—	
	$n C_3H_7OPO(OH)_2$	—	
	$i C_3H_7OPO(OH)_2$	—	
	$n C_4H_9OPO(OH)_2$	—	
Monobasic phosphate esters	$(CH_3O)_2PO(OH)$	—	
	$(C_2H_5O)_2PO(OH)$	±	1·0
	$(i C_3H_7O)_2PO(OH)^b$	+	0·2
	$(n C_4H_9O)_2PO(OH)$	+	0·5
Neutral phosphate ester	$(C_2H_5O)_3PO$	—	
Dibasic phosphonic acids	$CH_3PO(OH)_2$	—	
	$n C_4H_9PO(OH)_2$	+	0·5
	$n C_{16}H_{33}PO(OH)_2$	—	
	 $—PO(OH)_2$	—	
Monobasic phosphonate esters	$CH_3P(OCH_3)O(OH)$	+	0·5
	$CH_3P(OC_2H_5)O(OH)$	+	0·05
	$CH_3P(OC_3H_7 i)O(OH)^c$	+	0·05
	$CH_3P(OC_4H_9 n)O(OH)$	+	0·05
	$C_2H_5P(OCH_3)O(OH)$	+	0·2
	$C_2H_5P(OC_2H_5)O(OH)$	+	0·2
	$C_2H_5P(OC_2H_5)O(OH)$	+	0·2
	$C_2H_5P(OC_3H_7 i)O(OH)$	+	0·2
	$C_2H_5P(OC_4H_9 n)O(OH)$	+	0·05
	$i C_3H_7P(OC_2H_5)O(OH)^e$	—	
	$i C_3H_7P(OC_4H_9 n)O(OH)$	+	0·5
	$n C_4H_9P(OCH_3)O(OH)$	+	0·05
	$n C_4H_9P(OC_2H_5)O(OH)$	+	0·05
	$n C_4H_9P(OC_4H_9 n)O(OH)$	+	0·02
Neutral phosphonate esters	$CH_3(OC_3H_7 i)_2PO$	—	
	$C_2H_5(OC_2H_5)_2PO$	—	
	$n C_4H_9(OC_2H_5)_2PO$	—	
	$n C_4H_9(OC_4H_9 n)_2PO$	—	
Dialkyl phosphites	$(CH_3O)_2POH$	—	
	$(C_2H_5O)_2POH$	—	
Trialkyl phosphites	$(CH_3O)_3P$	—	
	$(C_2H_5O)_3P$	—	
	$(n C_4H_9O)_3P$	—	

to this test (as well as another which gave a relatively weak test) contains a bulky *iso*propyl group directly attached to the phosphorus atom; the sensitivity of enzymatic reactions to steric effects is well known.

All compounds which were not expected to form anticholinesterase compounds

TABLE 1 (*continued*)

		Test result[a]	Sensitivity[d], *µg/cm²*
Dibasic aryl phosphorus acid	$C_6H_5P(OH)_2$	—	
Phosphinic acids	$CH_3(C_2H_5)PO(OH)$	+	0·1
	$CH_3(nC_3H_7)PO(OH)$	+	0·1
Pyrophosphonic acid	 $CH_3\underset{OH}{\overset{O}{\overset{\|}{P}}}—O—\underset{OH}{\overset{O}{\overset{\|}{P}}}—CH_3$		

[a] — = negative ± = faintly positive; + = positive.

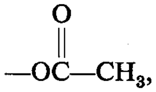
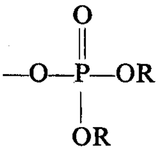
[b] The di*cyclo*hexylamine salt of this compound also gave a positive test.

[c] The sodium salt of this compound also gave a positive test.

[d] Smallest quantity necessary to give a faintly positive test.

[e] Gave a positive test with 2 *µg* per cm².

upon reaction with ketene, such as neutral phosphate and phosphonate esters, dibasic phosphate esters, dibasic phosponic acids, and phosphites gave negative tests with the exception of the dibasic *n*-butylphosphonic acid. It is to be expected that certain dibasic phosphonic and phosphoric acid esters will, after treatment with ketene, react with esterases (as was found with dibasic *n*-butylphosphonic acid). The basis for this statement is as follows: It has been shown that there is a relationship between the rate of the reaction of a given phosphorus ester or anhydride with the enzyme and hydrolysis rate of the compound,[8] the more easily hydrolysable compounds being the more rapid reactants with the enzyme. If, however, the hydrolysis rate is too high, the phosphate will have decomposed on the paper before it can react with the enzyme. One may expect, then, that a plot of the reactivity of a phosphorus compound with the enzyme in this test against the hydrolysis rate of the phosphorus ester will be bell-shaped in character, with both the extremely rapidly and the very slowly hydrolysing esters exhibiting low reactivity with the enzyme. All compounds capable of reacting with ketene to form anhydrides which will hydrolyse at intermediate rates (rates which would fall in the dome portion of the curve described above) will, in all probability, also exhibit some activity in the enzyme reaction.

The rate of hydrolysis of phosphorus esters will depend upon the nature of the groups attached to the phosphorus. For simple phosphate esters it has been shown that the rate of alkaline hydrolysis decreases as the size of the alkyl substituent increases, presumably due to the operation of steric factors.[9] The leaving group also affects the hydrolysis rate; the rate being higher as the acidity of the leaving group increases. For example, esters (or anhydrides) having leaving groups —F,  $—O\overset{O}{\overset{\|}{C}}—CH_3$,  $—O—\underset{OR}{\overset{O}{\overset{\|}{P}}}—OR$ etc. have high rates of hydrolysis; those in which the leaving group is

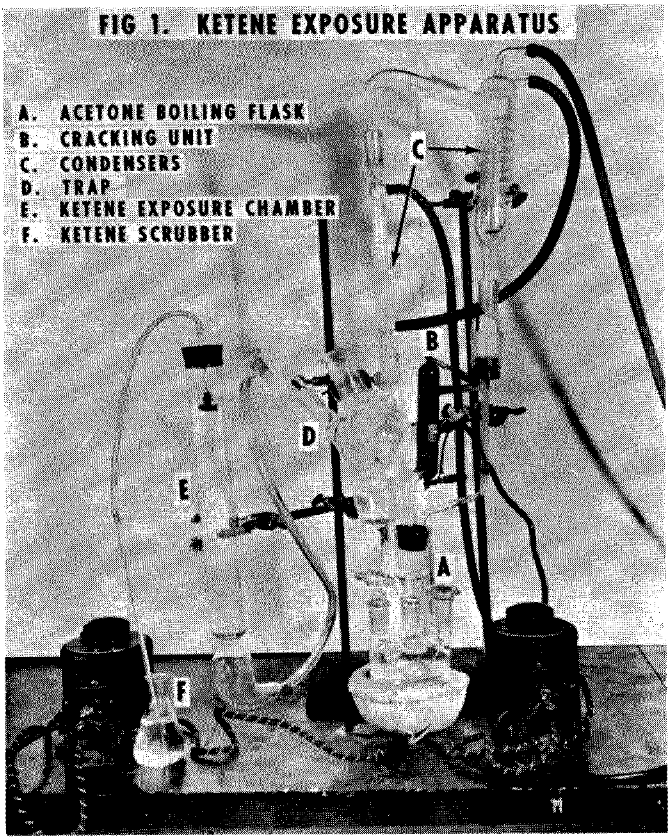
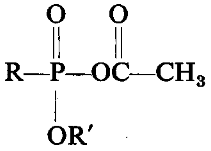
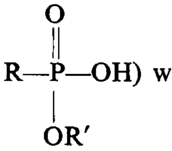
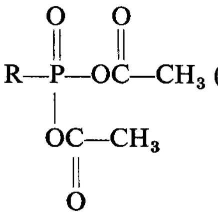


FIG 1. KETENE EXPOSURE APPARATUS

SR or OR have relatively low hydrolysis rates. If, now, two such highly acidic leaving groups are present in a single molecule, then the loss of one of these groups is very rapid. Thus, for example, the expulsion of one fluorine atom (as its ion) from methylphosphonodifluoridate is almost instantaneous; the hydrolysis of *iso*propylmethylphosphonofluoridate is rapid, but slow by comparison with the difluoro compound. In both cases, the hydrolytic products are no longer active anticholinesterases.

By analogy, it would be expected that  $R{-}\underset{\underset{OR'}{|}}{\overset{\overset{O}{\|}}{P}}{-}O\overset{\overset{O}{\|}}{C}{-}CH_3$ (the reaction product between ketene and  $R{-}\underset{\underset{OR'}{|}}{\overset{\overset{O}{\|}}{P}}{-}OH$) would hydrolyse rapidly but not instantaneously, and that the rate of hydrolysis would decrease as the alkyl group R (or R′) became larger. The compound  $R{-}\underset{\underset{\underset{\underset{O}{\|}}{OC-CH_3}}{|}}{\overset{\overset{O}{\|}}{P}}{-}O\overset{\overset{O}{\|}}{C}{-}CH_3$ (where R is the same alkyl group as in the monacetyl ester) would be expected to hydrolyse much more rapidly by comparison. If the alkyl groups in a diacetyl ester were of sufficient bulk, and the alkyl group in a monoacetyl ester sufficiently small, it would appear that there might be two compounds, one a diacetyl ester, the other a monoacetyl ester, of comparable rates of hydrolysis, both capable of exhibiting activity against the enzyme.

Sym-dimethylpyrophosphonate, which gave a negative test using the procedure described here, behaved as one would predict from the foregoing discussion. The product of reaction of dimethylpyrophosphonate with ketene, namely dimethyldiacetylpyrophosphonate, which contains two highly electronegative groups, would be expected to hydrolyse instantaneously to the inactive acid ester.

The choice of horse serum as the source of cholinesterase rested upon factors such as availability, cost and known sensitivity to a large group of pyro-esters (in the absence of information on the corresponding acetylesters). But it is well known that the reactivities of different organophosphorus compounds with esterases derived from various sources are not the same. For example, tetramethylpyrophosphate is more active against the cholinesterase in mouse brain than against the enzyme in human serum, while the reverse relationship holds for tetra-ethylpyrophosphate.[7] Hence, for the detection of special groups of acids of phosphorus, it may be advisable to use different enzyme sources.

EXPERIMENTAL

Apparatus and equipment

A diagram of the equipment is shown in Fig. 1. The ketene generator was constructed according to the directions of Wang and Schueler.[10] The apparatus was calibrated for ketene delivery by the method of Vogel.[11] The spray bottle was manufactured by Kontes Glass Co.

Reagents

Enzyme spray solution (freshly prepared) consists of 1 part by volume of horse serum (available from Pitman-Moore) plus 1 part by volume of 1·2% aqueous acetylcholine chloride plus 0·4 part by volume of 2·5% bromothymol blue in 0·1*N* NaOH.

Some of the organophosphorus compounds were kindly supplied *gratis* by Hooker Electrochemical Co. and the Victor Chemical Works. Other compounds were synthesised by Food Machinery Co., Fairfield Div. under contract to the U.S. Army Chemical Corps.

Procedure

The paper strip, spotted with a solution of the organophosphorus compound in absolute methanol, is placed in an oven for 5 min at 125° to remove the organic solvent completely. (Failure to eliminate the organic solvent results in the formation of products which strongly interfere in the test. While it was not the primary purpose of this research to investigate the use of the test in applications to particular chromatographic systems, it has been found that the condition described herein, *i.e.* oven heating for 5 min at 125°, is adequate for the following reagent grade solvents: methanol, ethanol, 2-propanol, 1-butanol, acetonitrile and water.) The strip is placed in the ketene exposure chamber for 5 min, with the apparatus set to deliver from 10 to 40 mg of ketene per min. *For operating directions and precautions to be observed in operation of the ketene generator, the reader is urged to consult the original article by Wang and Schueler.*[10] The paper is removed, heated in an oven for 1 min at 125° to remove excess ketene, sprayed with the enzyme spray solution to an overall blue colour and placed between two flat sheets of glass. The presence of an anticholinesterase is indicated by the persistence of a dark blue spot while the background is changing colour (usually from blue to yellow) during the course of about 30 min.

Zusammenfassung—Viele monobasische Säuren des fünfwertigen Phosphors bilden Cholinesterase-inhibitoren wenn sie Keten ausgesetzt werden. Diese Beobachtung wurde zur empfindlichen Nachweis dieser Verbindungen auf Tüpfelpapier ausgewertet. Siebzehn solcher Säuren (aus neunzehn untersuchten) gaben positive Reaktion. Die negativen Ergebnisse der verbleibende zwei werden auf sterische Faktoren oder zu hohe Hydrolysengeschwindigkeit der azetylierten Produkte zurückgeführt. Nur eine einzige der achtzehn nicht monobasischen Säuren gab einen positiven Test, nämlich n-Butylphosphonsäure. Eine Erklärung für dieses Verhalten wird gegeben.

Résumé—Beaucoup d'acides monobasiques du phosphore pentavalent forment des inhibiteurs cholinestérase quand ils sont exposés aux cétènes. Un test sensible, basé sur cette découverte, a été élaboré pour déceler la présence de ces composés sur papier filtre. Dix-sept parmi les dix-neuf acides testés donnaient des résultats positifs. Les résultats négatifs obtenus avec les deux autres acides sont attribués aux facteurs stériques ou à la grande vitesse d'hydrolyse du produit acétylé. Seul un des dix-huit acides du phosphore examinés, autres que les acides monobasiques, à savoir, l'acide n-butylphosphorique, donnait un test positif; une explication est proposée pour interpréter cette exception.

REFERENCES

[1] J. W. Cook, *J. Assoc. Offic. Agr. Chemists*, 1955, **38**, 150.
[2] R. L. Metcalf, *Organic Insecticides*. Interscience Publishers, Inc., New York, 1955, p. 289.
[3] H. G. Khorana and A. R. Todd, *J. Chem. Soc.*, 1953, 2257.
[4] R. Bentley, *J. Amer. Chem. Soc.*, 1948, **70**, 2183.
[5] H. O. Michel, *J. Lab. Clin. Med.*, 1949, **34**, 1564.
[6] R. L. Metcalf, *loc. cit.*, p. 287.
[7] R. W. Brauer, *J. Pharmacol. Exptl. Therap.*, 1948, **92**, 162.
[8] N. Aldridge and A. N. Davidson, *Biochem. J.* (*London*), 1952, **51**, 62.
[9] R. L. Metcalf, *Advances in Pest Control Research*. Interscience Publishers, Inc., New York, 1957. Vol. I, p. 167.
[10] S. C. Wang and F. W. Schueler, *J. Chem. Educ.*, 1949, **26**, 323.
[11] A. I. Vogel, *Practical Organic Chemistry*. Longmans, Green and Co., London, 1948, p. 369.

Talanta, 1960, Vol. 5, pp. 205 to 212. Pergamon Press Ltd. Printed in Northern Ireland

COULOMETRIC TITRATION OF IRON^{II} BY ELECTROLYTICALLY GENERATED BROMINE

TAKEO TAKAHASHI and HIROSHI SAKURAI
Institute of Industrial Science, University of Tokyo, Japan

(*Received* 17 *May* 1960)

Summary—Iron^{II} reacts with bromine more smoothly in acetic acid-sodium acetate medium than in sulphuric acid medium, producing a marked potential change at the end-point. The titration curves and the reaction velocities of the reaction have been studied with regard to various compositions of the electrolytic solution. It was found that iron^{II} from 0·01 meq to 0·1 meq could be titrated coulometrically with less than about 1% error, if the electrolytic solution contained 0·1*M* potassium bromate, 1*N* acetic acid and 0·2*N* sodium hydroxide.

INTRODUCTION

THE coulometric titration of iron^{II} is one of the earliest examples of this type of method in chemical analysis. As the titrating reagent, Furman, Cooke and Reilley[1] used cerium^{IV} generated electrolytically from cerium^{III}; and Tutundžić and Mladenović[2] used permanganate ion generated electrolytically from manganese sulphate in sulphuric acid. Those methods are not considered to be particularly useful for continuous coulometric titration, although theoretically they should be versatile. Furman's method is associated with troublesome recovery of the valuable cerium^{IV} from the effluent electrolytic solution; Tutundžić's method is faced with the difficult problem of adopting the best conditions for avoidance of the generation of manganese dioxide or manganese^{III} as well as permanganate ion and yet keep the electrolytic current efficiency at 100%. The electrolytic current must change continuously in conjunction with the concentration of the component to be determined in the sample stream. It is therefore very difficult, in continuous coulometric titration, to hold the electrolytic current efficiency at 100% over the wide range of the charge density on the surface of the generating electrode.

Electrolytically generated bromine is extensively employed as an oxidising agent in coulometric titration, but the reaction of bromine with iron^{II} is too slow to be useful, in comparison with conventional titration. The present authors discovered that bromine reacts more rapidly with iron^{II} in acetic acid-sodium acetate medium than in sulphuric acid medium and studied the titration curve of these reactions. In consequence a new coulometric titration of iron^{II} by electrolytically generated bromine, in a medium of a suitable composition, has been established.

APPARATUS AND REAGENTS

The apparatus used in the present work has already been described.[3] The constant-current source and the direct-reading potentiometer are both of the electronic type, constructed in our laboratory. The electrolytic time is measured by an integral-type stop-watch. The titration apparatus is shown in Fig. 1. The generating anode and cathode are both made of platinum, the former being 20 × 20 mm^2, and the latter a platinum spiral immersed in 15% ammonium sulphate solution, separated by a sintered-silica disc from the anode solution.

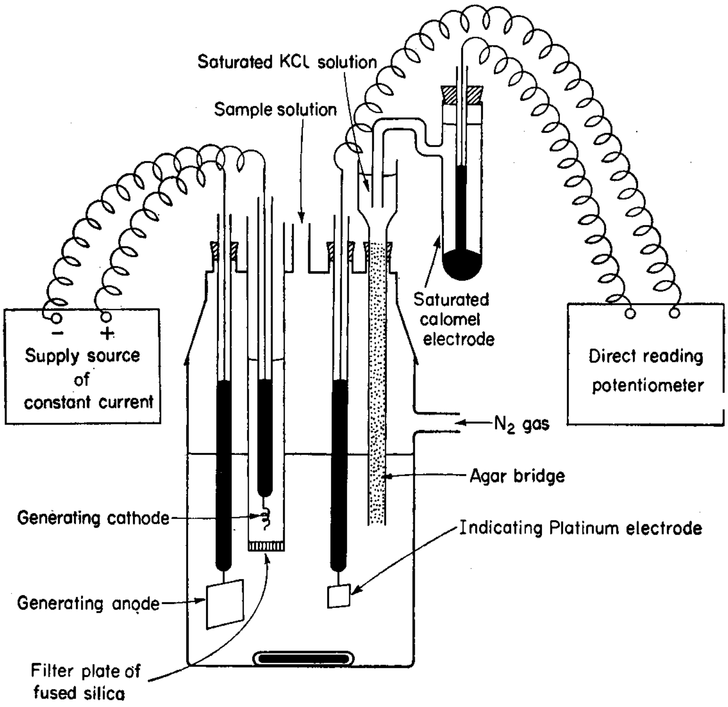


FIG. 1.—Apparatus for coulometric titration.

Fig. 2 shows the constant-current generator circuit. The electrolytic current flows through resistances R_2 and R_3, the iR drop across which is the input of a conventional voltage regulator circuit. By holding the iR drop across R_2 and R_3 constant, the voltage regulator circuit supplies a constant output to the cell. The electrolytic current is controlled to the desired value by adjusting R_3.

The indicating electrode is a platinum plate (15×15 mm^2) and the reference electrode a saturated calomel electrode, which is connected to the electrolytic solution through saturated potassium chloride solution and an agar bridge. The indicator circuit, as shown in Fig. 3, is constructed with a bridge, the

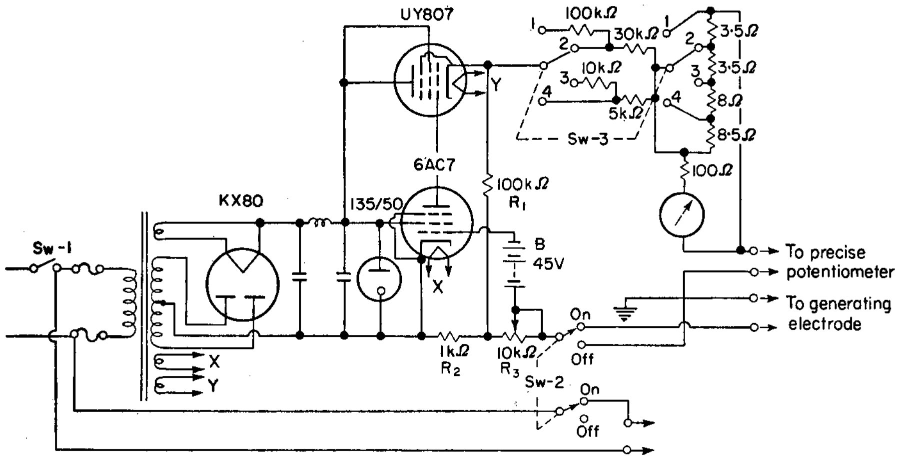


FIG. 2.—Constant-current generator circuit for coulometric titration.

components being two vacuum tubes (6SJ7) and two resistances (R_2 and R_3). This circuit is very stable towards fluctuations of the supplied voltage.

All the reagents used were of commercial special grade and water was purified by an ion-exchange resin. The electrolytic solution was prepared by dissolving 120 g of acetic acid and 8 g (or 16 g) of sodium hydroxide in 500 ml of purified water to which 24 g of potassium bromide was added, and making the solution up to 1 litre with purified water. The solution in the generating cathode chamber was prepared by dissolving 150 g of ammonium sulphate in 850 g of purified water. The sample solution (iron^{II} solution) is made from a stock solution prepared by dissolving 39·3 g of ferrous ammonium sulphate in 1N sulphuric acid, making up to 1 litre and standardising with potassium permanganate standard solution.

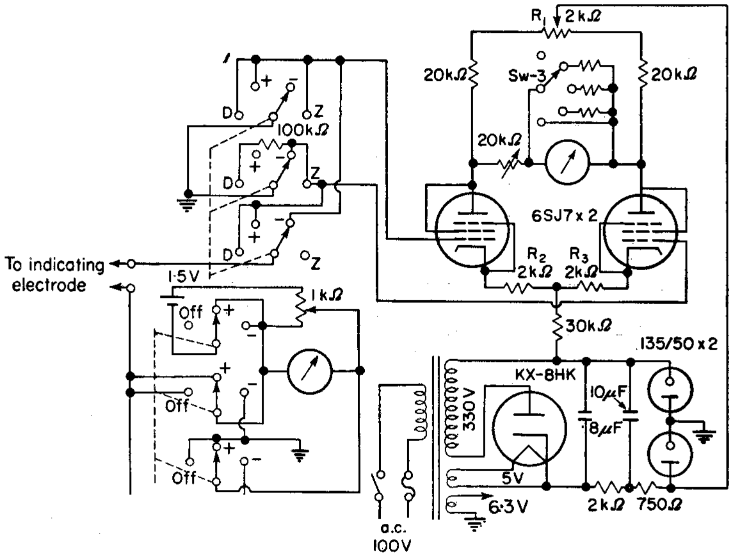


FIG. 3.—Circuit diagram for indicator system.

EXPERIMENTAL AND RESULTS

1. *Titration curve*

The reaction of bromine with iron^{II} is very slow in sulphuric acid solution, requiring several hours for the reaction of the bromine generated in five minutes, as shown in curve A, Fig. 4. Various other solutions of the compositions cited in Table I were examined.

Table I shows the pH values and the voltages at the end-point for the various compositions. The titration curves were obtained by plotting each indicated voltage after electrolytic oxidation for 20 sec at an electrolytic current of 10 mA. The solution being titrated was prepared by adding 2 ml of 0·01M ferrous ammonium sulphate to 100 ml of the cited electrolytic solution. Fig. 4 shows the titration curves. The titration curve of B is very similar to that of A and the titration curve of C to that of D. The titration curves of E and G almost coincide with that of F. Therefore only the curves of A, D, and F are shown in Fig. 4.

Probably because of precipitation of ferric hydroxide, the titrated solution gradually becomes brownish during the titration and more and more turbid with increase of sodium hydroxide (the increase of pH). Fig. 4 shows that the indicated voltages of all the solutions coincide very well after passing the end-point. Therefore it is concluded

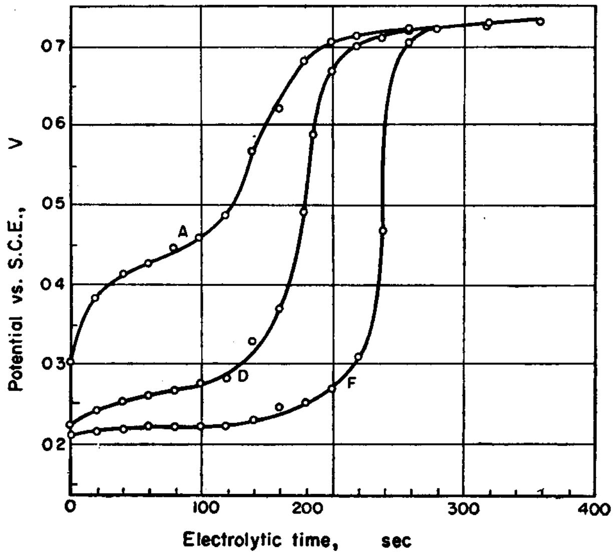


FIG. 4.—Titration curve for iron^{II} against electro-generated bromine
A: 0·1*M* KBr + 1*N* H_2SO_4.
D: 0·1*M* KBr + 1*N* CH_3COOH, 100 ml + 1*N* NaOH, 20 ml.
F: 0·1*M* KBr + 1*N* CH_3COOH, 100 ml + 1*N* NaOH, 40 ml.

that the oxidation-reduction potential Fe^{2+}/Fe^{3+} moves to a lower voltage in acetic acid-sodium acetate than in sulphuric acid, although that of Br_2/Br^- is the same in both solutions. This should be in interpreting the much greater reactivity of iron^{II} with bromine in acetic acid-sodium acetate solution than in sulphuric acid solution.

TABLE I. RELATIONSHIP BETWEEN THE END-POINT AND THE COMPOSITION OF ELECTROLYTE

Electrolyte	Composition of electrolyte	pH	Potentiometric end-point, *V*(vs. S.C.E.)
A	$\left\{\begin{matrix}0\cdot1M\text{-KBr}\\1N\ H_2SO_4\end{matrix}\right\}$ 100 ml + 1*N* NaOH 0 ml	0·6	0·6
B	$\left\{\begin{matrix}0\cdot1M\text{-KBr}\\1N\ CH_3COOH\end{matrix}\right\}$ 100 ml + 1*N* NaOH 0 ml	2·15	0·6
C	$\left\{\begin{matrix}0\cdot1M\text{-KBr}\\1N\ CH_3COOH\end{matrix}\right\}$ 100 ml + 1*N* NaOH 10 ml	3·65	0·5
D	$\left\{\begin{matrix}0\cdot1M\text{-KBr}\\1N\ CH_3COOH\end{matrix}\right\}$ 100 ml + 1*N* NaOH 20 ml	4·0	0·5
E	$\left\{\begin{matrix}0\cdot1M\text{-KBr}\\1N\ CH_3COOH\end{matrix}\right\}$ 100 ml + 1*N* NaOH 30 ml	4·2	0·5
F	$\left\{\begin{matrix}0\cdot1M\text{-KBr}\\1N\ CH_3COOH\end{matrix}\right\}$ 100 ml + 1*N* NaOH 40 ml	4·4	0·5
G	$\left\{\begin{matrix}0\cdot1M\text{-KBr}\\1N\ CH_3COOH\end{matrix}\right\}$ 100 ml + 1*N* NaOH 50 ml	4·6	0·5

2. *Reaction velocity*

The reactivity of the generated bromine with iron^{II} was examined with respect to solutions of the various compositions cited in Table I. Two ml of 0·01*M* ferrous ammonium sulphate were added to 100 ml of the electrolytic solution. Bromine was generated by electrolysing for 140 sec at 10 mA and the change of the indicating voltage up to a definite voltage was observed. The results are shown in Fig. 5. Curves B, C, E, and G are not shown, because curve B approximates to A, curve C is intermediate between curves A and D (nearer D), curve E is intermediate between curves D and F, and curve G approximates to curve F. From the result described above, it is apparent that the reaction velocity (the reciprocal of the time for return to the initial voltage) becomes greater with increase of added sodium hydroxide.

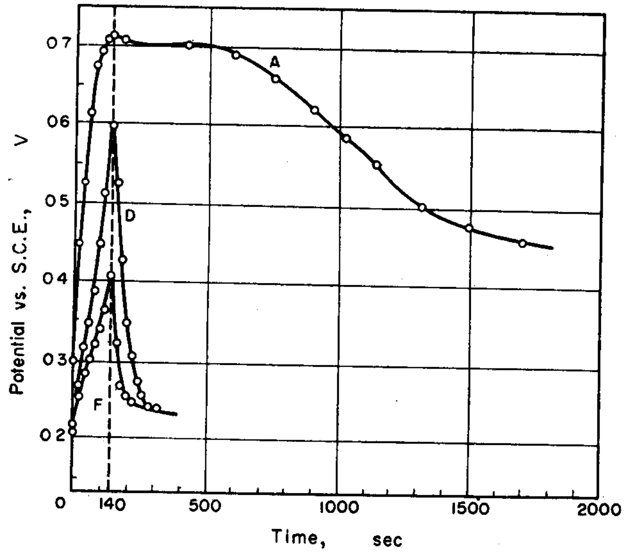


FIG. 5.—Potential change in iron^{II} solution after electro-generation of a quantity of bromine
A: $0{\cdot}1M$ KBr + $1N$ H_2SO_4.
D: $0{\cdot}1M$ KBr + $1N$ CH_3COOH, 100 ml + $1N$ NaOH, 20 ml.
F: $0{\cdot}1M$ KBr + $1N$ CH_3COOH, 100 ml + $1N$ NaOH, 40 ml.

3. *Coulometric titration* (*potentiometric method*)

The above preliminary experiments indicate the possibility of coulometric titration of iron^{II} by electro-generated bromine. This was further investigated by using two electrolytic solutions, *i.e.* one solution (*a*) composed of $0{\cdot}1M$ potassium bromide, $1N$ acetic acid and $0{\cdot}2N$ sodium hydroxide, and the other solution (*b*) composed of $0{\cdot}1M$ potassium bromide, $1N$ acetic acid and $0{\cdot}4N$ sodium hydroxide. In the electrogeneration of bromine the current efficiencies were respectively 98·3% (*a*) and 89·0% (*b*) at 10 mA, when measured by titration with sodium arsenite standard solution.

The procedure used was as follows; Place 100 ml of the electrolytic solution in the electrolytic cell and remove dissolved oxygen by passing nitrogen gas for 5 min (the effect of the dissolved oxygen is not great in practice). Connect the electrolytic electrodes to the constant-current supply source and the indicating and reference electrodes to the vacuum tube potentiometer, closing the electric circuit for 2 sec to confirm the absence of reacting substance by an instantaneous jump of the indicating voltage. After this confirmation, add the sample solution and begin to generate bromine for its coulometric titration. Continue the titration until the indicating voltage rises above 0·5 V vs. S.C.E. and does not return to that voltage. Typical results are shown in Table II.

Table II shows that the errors are always positive and relatively smaller (average error 5·6%) in 0·2*N* sodium hydroxide than in 0·4*N* sodium hydroxide. On the other hand the error becomes greater in more dilute sodium hydroxide solution, so that the desirable concentrations in the electrolytic solution is 0·2*N* sodium hydroxide. The calibration curve is shown in Fig. 6, which shows a linear relationship between coulombs (the electrolytic time at constant current) and the concentration of iron^{II}, if the electrolytic solution contains 0·2*N* sodium hydroxide, 0·1*M* potassium bromide and 1*N* acetic acid. Provided that the coulomb value is corrected by a factor of 0·9466 as a titration factor, the coulometrically titrated value of iron^{II} has only an error ranging within ±1%

TABLE II. COULOMETRIC TITRATION OF Fe^{2+} WITH ELECTRO-GENERATED BROMINE AT 9·92 mA ELECTROLYTIC CURRENT (POTENTIOMETRIC END-POINT DETECTION)

Electrolyte	No. of trials	Taken, *meq* × 10^3	Found, *meq* × 10^3	Error, %	Standard deviation, %
0·1*M* KBr +	4	8·851	9·488	+7·19	1·53
0·2*N* NaOH +	4	17·702	18·576	+4·94	1·58
1*N* CH_3COOH	4	35·404	37·418	+5·68	0·69
	4	53·106	56·076	+5·59	0·51
	4	88·51	92·78	+4·82	0·44
0·1*M* KBr +	4	19·282	23·263	+20·65	2·28
0·4*N* NaOH +	2	38·564	49·137	+27·42	—
1*N* CH_3COOH	2	57·846	80·593	+39·32	—
	1	77·128	108·760	+41·01	—

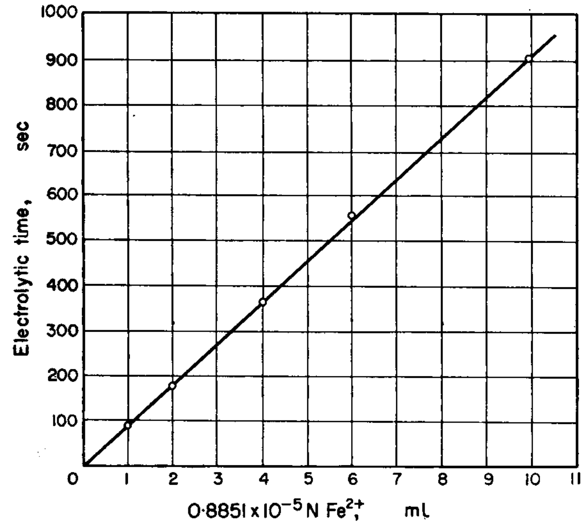


FIG. 6.—Relationship between quantity of iron^{II} and bromine generating time.

4. *Coulometric titration* (*dead-stop method*)

The vacuum-tube potentiometer used allows the use of a dead-stop method for the end-point detection. By changing the switch, the electric current between the indicating electrodes is, as shown in Fig. 7, passed through the fixed resistance (100 KΩ), which voltage drop can be read with a vacuum tube potentiometer. The indicating electrodes are platinum plates, 15 × 15 mm^2 and 10 × 5 mm^2, between which the voltage of 0·4 ~ 0·5 V is applied. (The applied voltage is far less than 0·4 V when the indicating current is running, because of the voltage depression due to the resistance of 100 KΩ.) The cathode acts as an indicating electrode. The indicating current flows because of depolarisation in the presence of iron^{II}, stops because of the polarisation at the end-point, and passes again because of depolarisation caused by liberated bromine after the end-point. Therefore the titration curve is sharply V-shaped at the end-point, this corresponding to the minimum of the titration curve.

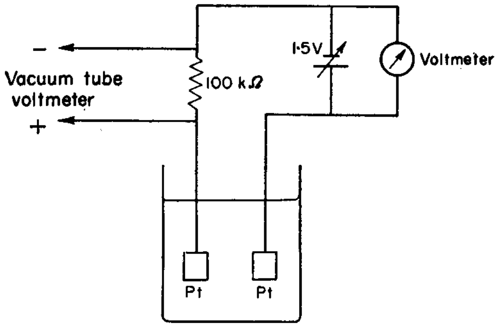


FIG. 7.—Schematic diagram for amperometric detection of end-point.

TABLE III. COULOMETRIC TITRATION OF Fe^{2+} WITH ELECTROGENERATED BROMINE (AMPEROMETRIC END-POINT DETECTION)

Taken, *meq* × 10^3	Found, *meq* × 10^3	Error, %
8·644	9·098	+5·25
8·851	9·350	+5·69
17·288	17·990	+4·06
17·392	18·092	+4·02
17·702	18·609	+5·11
34·576	35·979	+4·06
54·175	51·864	+4·46

Table III shows the result when iron^{II} is titrated with bromine generated at 10 mA in an electrolyte containing 0·1*M* KBr, 1*N* CH_3COOH and 0·2*N* NaOH.

Zusammenfassung—Die Reaktion zwischen Eisen (II) und Brom verläuft in einem Medium von Essigsäure-Natriumazetat viel glatter als in Schwefelsäure. Dies bewirkt einen sehr gut ausgeprägten Sprung in der potentiometrischen Titrationskurve. Die Kurve sowie die Reaktionsgeschwindigkeiten der Reaktionen wurden studiert. Es wurde gezeigt dass Eisen(II)-Mengen von 0·01 bis 0·1 Milliäquivalenten coulometrisch mit etwa 1 % Fehler titriert werden können, wenn die Lösung 0·1 m in Kaliumbromat, 1 n in Essigsäure und 0·2 n in Natronlauge ist.

Résumé—L'ion ferreux réagit sur le brome plus facilement en milieu acide acétique-acétate de sodium qu'en milieu acide sulfurique; il en résulte une variation nette du potentiel au point équivalent. Les courbes de titrage et les vitesses de cette réaction ont été étudiées, et les auteurs ont montré qu'il était possible de titrer de 0,0 à 0,1 milliéquivalent de fer ferreux par coulométrie à environ 1% près si la solution électrolytique contient du bromate de potassium 0,1 M, de l'acide acétique N et de la soude 0,2 N.

REFERENCES

[1] N. H. Furman, W. D. Cooke and C. N. Reilley, *Analyt. Chem.*, 1951, **23**, 945.

[2] P. S. Tutundžić and S. Mladenović, *Analyt. Chim. Acta*, 1955, **12**, 382, 390.

[3] T. Takahashi, K. Kimoto and H. Sakurai, *Rep. of Research Institute of Industrial Science*, Univ. of Tokyo, 1955, **5**, 122.

Talanta, 1960, Vol. 5, pp. 213 to 215. Pergamon Press Ltd. Printed in Northern Ireland

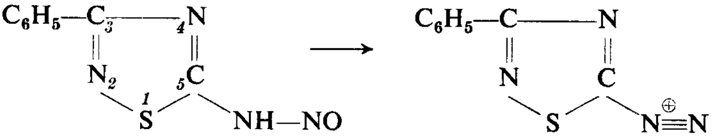
UN RÉACTIF DÉFINI DE DIAZOCOPULATION, LE 3-PHENYL 5-NITROSAMINO 1,2,4-THIODIAZOLE OU PHENITRAZOLE

Maurice Pesez, Jaroslav Bartos et Jean-François Burtin
Centre de Recherches Roussel-Uclaf, Paris, France

(*Reçu le* 23 *Mai* 1960)

Résumé—Le 3-phényl 5-nitrosamino 1,2,4-thiodiazole ou *phénitrazole* permet de réaliser des diazocopulations dans des conditions parfaitement définies. En milieu acide, il se déshydrate en effet en un diazoïque que l'on condense d'emblée sur des phénols ou des amines aromatiques. Ce réactif permet encore de révéler les aldéhydes dont les phénylhydrazones correspondantes conduisent à des formazans. Les colorations obtenues autorisent le plus souvent des dosages à l'échelle du centième de milligramme.

Parmi les 5-nitrosamino 1,2,4-thiodiazoles connus, le dérivé 3-phénylé, I, offre l'avantage d'une stabilité satisfaisante, contrairement à ses analogues méthylé ou méthoxylé[2]. Ces nitrosamines se déshydratent en milieu acide pour conduire aux sels de diazonium correspondants[2,3]. Ainsi, le composé I, que nous proposons de nommer *phénitrazole*, fournit le diazoïque II dont la réactivité a déjà été mise à profit pour réaliser des condensations sur les pyrroles[6].



I
Phénitrazole

II

Selon nos recherches, l'emploi du phénitrazole se révèle avantageux en analyse. En effet, par simple déshydratation effectuée directement dans le milieu de condensation, ce réactif nous a permis de réaliser des diazocopulations dans des conditions parfaitement définies, contrairement aux solutions de diazoïques usuelles dont la composition est difficile à reproduire. De plus, avec ce sel de diazonium, on n'observe pas de coloration des témoins.

Les *phénols*, par action du phénitrazole en présence d'acide perchlorique, forment des azoïques dont la coloration est observée en milieu alcalin (Tableau I). Dans le cas du phénol ordinaire, la comparaison des résultats obtenus avec les réactifs usuels et avec le nouveau réactif est en faveur de ce dernier. Ainsi, pour obtenir une densité optique de 0,3 (cuve de 1 cm), il faut mettre en jeu 15 à 30 μg de phénol avec les diazoïques de la *p*-nitraniline ou de l'acide sulfanilique et seulement 5 μg avec le phénitrazole. L'emploi du phénitrazole conduit par ailleurs à une méthode quantitative permettant des dosages à l'échelle du centième de milligramme.

TABLEAU I. APPLICATION DIRECTE AUX PHENOLS ET AUX ARYLAMINES

	Coloration	λ max., mμ	Prise d'essai pour obtenir une densité optique de 0,3 en cuve de 1 cm, μg
A-Phénols			
o-Aminophénol	rose	515	21
m-Aminophénol	rouge	520	7
p-Aminophénol	rose	515	45
Gaïacol	rouge-violet	530	5
Hydroquinone	brun	420	65
α-Naphtol	violet	550	7
β-Naphtol	violet	540	12
Phénol	rouge	515	4
Phloroglucinol	rouge	500	10
Pyrocatéchol	violet	530	12
Résorcinol	rouge orangé	500	5
Salicylaldéhyde	jaune	380	40
B-Arylamines et divers			
Aniline*	orangé	495	28
Diméthylaniline	rose violacé	535	6
Méthylaniline*	rose	510	27
Carbazole*	bleu	590	7
Indole*	orangé	470	9

* 5 minutes de contact à 0° en milieu acide.

Des colorations sont également obtenues à partir des *arylamines* (Tableau I) tandis que les alcoylamines ne sont pas révélées. Parmi les composés hétérocycliques que nous avons essayés, seuls l'indole et le carbazole ont réagi. L'histidine, l'histamine, la théophylline, la caféine, l'adénine, la thymine et la guanine, qui se condensent avec les sels de diazonium usuels, ne développent pas de coloration dans le cas présent.

Enfin, le phénitrazole, par action des phénylhydrazones, se prête à la condensation en formazans déjà décrite pour d'autres sels de diazonium[4,5]. Les *aldéhydes* peuvent être ainsi décelés et dosés (Tableau II), les cétones et sucres usuels étant sans action.

TABLEAU II. APPLICATION INDIRECTE AUX ALDEHYDES

Aldéhydes	Coloration	λ max., mμ	Prise d'essai pour obtenir une densité optique de 0,3 en cuve de 1 cm, μg
Acétaldéhyde	Orangé	490	44
Acide glyoxylique (sel de sodium)	Orangé	490	40
Benzaldéhyde	Violet	550	23
Formaldéhyde	Orangé	490	3
Furfuraldéhyde	Orangé	510	22
Glyoxal (monohydrate)	Orangé	490	14
Propionaldéhyde	Orangé	490	105
Vanilline	Violet	565	92

PARTIE EXPERIMENTALE

(avec Mlles G. CLEMENT et S. VENARD)

Le 3-phényl 5-amino thiodiazole, et son dérivé nitrosé (phénitrazole) sont préparés selon Goerdeler.[1,2]

Phénols et arylamines

A 1 cm³ de solution alcoolique du phénol, on ajoute 1 cm³ de solution alcoolique à 0,4 pour cent de phénitrazole et 1 cm³ d'acide perchlorique (55° Bé). Après 5 minutes de repos à température ordinaire, on refroidit dans la glace et ajoute 3 cm³ de solution aqueuse à 20 pour cent de soude également glacée. On effectue la mesure sur photomètre après 5 minutes à température ordinaire.

Aldéhydes

Le réactif est obtenu par mélange de volumes égaux d'acide perchlorique (55° Bé) et de solution alcoolique à 0,4 pour cent de phénitrazole. On maintient à 0° pendant 5 minutes avant emploi.

A 1 cm³ de solution alcoolique d'aldéhyde, on ajoute 0,5 cm³ de solution aqueuse à 0,5 pour cent de chlorhydrate de phénylhydrazine, abandonne pendant 20 minutes à température ordinaire, refroidit à 0°, ajoute 1 cm³ de réactif puis, après 5 minutes à 0°, 3 cm³ de solution aqueuse à 20 pour cent de soude. La lecture sur photomètre est effectuée après 5 minutes de repos à 0°.

Summary—3-Phenyl-5-nitrosamino-1:2:4-thiodiazole, or *phenitrazole*, allows diazo coupling to be carried out in precisely defined conditions. In acid medium it dehydrates to a diazo compound which may be condensed directly with phenols or aromatic amines. The reagent enables the detection of aldehydes of which the corresponding phenylhydrazones lead to formazans. The colorations obtained allow the determination of amounts of the order of hundredths of a milligram.

Zusammenfassung—3-Phenyl-5-nitrosamino-1,2,4-thiodiazol (Phenitrazol) gestattet Diazokupplung unter genau definierten Bedingungen. In saurem Medium dehydriert die Verbindung zu einer Diazoverbindung, die direkt mit Phenolen oder aromatischen Aminen kondensieren kann. Das Reagens ermöglicht die Bestimmung von Aldehyden, deren entsprechende Phenylhydrazone zur Bildung von Formazanen führen. Die erhaltene Färbung gestattet die Bestimmung von Mengen in der Grössenordnung einiger Hundeertstel Milligramm.

REFERENCES

[1] J. Goerdeler, *Ber.*, 1954, **87,** 66.
[2] J. Goerdeler et K. Deselaers, *ibid.*, 1958, **91,** 1025.
[3] J. Goerdeler et H. Haubrich, *ibid.*, 1960, **93,** 397.
[4] E. Pittarelli, *Archivio farmacol. sper.*, 1920, **30,** 148.
[5] L. Rosenthaler, *Pharm. Acta Helv.*, 1946, **21,** 217; *Pharm. Ztg.*, 1953, **89,** 242.
[6] A. Treibs et R. Zimmer-Galler, *Ann.*, 1959, **627,** 166.

Talanta, 1960, Vol. 5, pp. 216 to 220. Pergamon Press Ltd. Printed in Northern Ireland

SUR UN PRINCIPE DE COLORIMETRIE EN MILIEU NON AQUEUX. SON APPLICATION A L'ANALYSE ORGANIQUE FONCTIONNELLE

MAURICE PESEZ et JAROSLAV BARTOS
Centre de Recherches Roussel-Uclaf, Paris, France

(*Reçu le* 23 *Mai* 1960)

Résumé—En milieu non aqueux, il est possible de caractériser la fonction hydroxyle, le carbonyle ou le groupe amine primaire aliphatique. On procède à la formation d'un dérivé (ester, hydrazone ou arylamine) présentant des groupes nitrés aromatiques puis, sans extraction ni élimination de l'excès de réactif, on développe par une base organique en diméthylformamide une coloration caractéristique. Des dosages peuvent être ainsi effectués sur quelques centièmes de milligramme.

L'ÉTUDE des réactions colorées en absence d'eau n'a été l'objet, jusqu'ici, que de recherches fragmentaires. On peut, à titre d'exemple, citer le cas des malonylurées que l'on identifie sous forme de complexes métalliques obtenus en milieu anhydre. De même, en présence de bases, les dérivés nitrés aromatiques conduisent, selon le solvant, à des absorptions variables en position et en intensité.[1]

Il nous est apparu possible de donner une extension plus large à la notion de colorimétrie en milieu non aqueux et de l'appliquer à l'analyse organique fonctionnelle. Le but de nos essais a été de procéder à la formation d'un dérivé puis, par l'emploi d'un solvant, de développer d'emblée une coloration, sans extraction préalable ni élimination de l'excès de réactif.

Nous décrivons ici ces colorimétries nouvelles. Les exemples rapportés intéressent la fonction hydroxyle, le carbonyle et le groupe amine primaire aliphatique. Les dérivés retenus (esters, hydrazones, arylamines) présentent des groupes nitrés aromatiques que l'on révèle par la pipérazine ou l'hydrate de benzyltriméthylammonium. A partir des amines, il est également possible de former des bases de Schiff comportant un reste diméthylaminé aromatique sensible à l'action du nitrométhane. L'effet du solvant apparaît alors décisif. Ainsi en diméthylformamide, les esters dinitrobenzoïques se colorent par la pipérazine tandis que l'acide dinitré lui-même n'est pas révélé; en alcool, il n'apparaît aucune coloration ni avec l'acide ni avec ses esters.

Alcools primaires et secondaires

L'estérification par le chlorure de 3,5-dinitro benzoyle suivie d'une réaction avec l'acétone a déjà été mise à profit pour doser colorimétriquement les alcools.[2] Mais cette méthode exige, en particulier, une séparation préalable et quantitative de l'ester.

Aprés acylation en présence de pyridine, une solution de pipérazine dans le diméthylformamide développe une coloration rouge (510 mμ) qui n'est pas observée en absence de corps hydroxylés. Dans les mêmes conditions, les amines ne sont pas révélées et les phénols ne conduisent qu'à une coloration fugace.

La méthode peut être quantitative (Tableau I). Il convient alors d'effectuer les

TABLEAU I

Alcools	Prise d'essai pour obtenir une densité optique de 0,3 à 510 mμ en cuve de 1 cm, μg
Ethanol	9
Butanol-1	15
Butanol-2	17
Cholestérol	75
Epi-déhydroandrostérone	65
Testostérone	60

lectures photométriques à température constante pour éviter tout phénomène de thermochromie. En pratique, 50 μg de 3,5-dinitrobenzoate d'éthyle conduisent, dans nos conditions opératoires, à une densité optique de 0,65 à 0° et de 0,15 à 50°, en cuve de 1 cm.

Composés carbonylés

Les *p*-nitrophénylhydrazones sont colorées en milieu alcalin et l'intensité de la coloration varie avec le solvant.[1b] Selon nos essais, l'hydrate de benzyltriméthylammonium en solution dans le diméthylformamide permet de rendre la réaction sélective. On obtient des colorations rouges ou violettes et des dosages peuvent être effectués sur quelques centièmes de mg (Tableau II).

Amines primaires aliphatiques

On sait que l'on forme des dérivés dinitrophénylés par action du 1-fluoro 2,4-dinitro benzène sur le groupe amine primaire. Nous avons observé que l'arrangement *m*-dinitré peut alors être révélé et dosé en milieu non aqueux par l'hydrate de benzyltriméthylammonium qui fournit une coloration rouge orangé (Tableau III). Dans les mêmes conditions, les amines secondaires (diéthyl-, dipropyl- et dibenzyl-amine) ne réagissent que faiblement. Les amines aliphatiques tertiaires et les aryl-amines ne sont pas décelées.

Si l'on condense le *p*-diméthylamino cinnamaldéhyde sur les amines primaires aliphatiques, en choisissant le nitrométhane comme solvant, on observe des colorations orangées. Cette réaction permet également des dosages sur 5 à 20 μg (Tableau III).

PARTIE EXPERIMENTALE

(avec Mlle G. CLEMENT)

ALCOOLS PRIMAIRES ET SECONDAIRES

Réactifs

Solution à 5 pour cent de chlorure de 3,5-dinitrobenzoyle dans le benzène.

Solution à 25 pour cent d'hexahydrate de pipérazine dans le diméthylformamide.

Mode opératoire

La prise d'essai dissoute dans 0,1 ml de mélange à parties égales de pyridine et de benzène, est ajoutée à 0,1 ml de solution de chlorure de 3,5-dinitrobenzoyle puis abandonnée pendant vingt minutes à 18–22°. On introduit ensuite 0,1 ml de pyridine à la même température puis, après cinq minutes, 5 ml de solution de pipérazine également portée à 18–22°. La lecture est effectuée à 510 mμ.

Tableau II

Composés carbonylés	Temps de chauffage à 70°, *min*	Couleur	λ max., $m\mu$	Prise d'essai pour obtenir une densité optique de 0,3 en cuve de 1 cm, μg
Aldéhydes				
Acétaldéhyde	30	rouge	510	40
Diphénylacroléine	20	bleu violet	570	10
Formaldéhyde	20	rouge	500	8
Glyoxal (monohydrate)	30	bleu	690	3
Pipéronal	20	violet	540	8,5
Propionaldéhyde	30	rouge	510	50
Salicylaldéhyde	20	violet	550	7,5
Vanilline	20	bleu violet	570	9,5
Sucres				
Glucose	20	rouge	510	50 → 0,04*
Ribose	20	rouge	510	50 → 0,06
Cétones simples				
Acétone	30	rouge	510	6
Acétophénone	30	violet	540	26
Acétylacétate d'éthyle	30	rouge	510	50 → 0,1
Acétylacétone	30	rouge	510	50 → 0,03
Benzile	30	violet	550	80
Benzophénone	30	rouge	510	50 → 0,08
Camphre	30	rouge	510	50 → 0,05
Cyclohexanone	20	rouge	510	10,5
Cyclopentanone	30	rouge	510	16,5
Diacétyle	30	violet-bleu	560 680	17,5 13,5
α-Ionone	30	violet	540	19
Méthyléthylcétone	30	rouge	510	10
Cétones stéroïdes				
Acide déhydrocholique	30	rouge	510	42
Androstane 17β-ol 3-one	30	rouge	510	30
$\Delta^{1,4}$-Androstadiène 3,17-dione	30	bleu-violet	560	25
Δ^{4}-Androstène 3,17-dione	20	violet	540	18
Cortisone	20	violet	540	22,5
1-Déhydrocortisone	30	violet	555	24
Déhydro *épi*-androstérone	30	rouge	510	50 → 0,08
1-Déhydrohydrocortisone	30	violet	555	30
Dexaméthasone	30	violet	560	33
Hydrocortisone	20	violet	540	23
Progestérone	20	violet	540	18,5
Testostérone	20	violet	540	19
Δ^{1}-Testostérone (acétate)	30	violet	540	35

* Avec une prise d'essai de 50 μg, la densité optique est de 0,04.

TABLEAU III

Amines	Prise d'essai pour obtenir une densité optique de 0,3 en cuve de 1 cm	
	Réaction au 1-fluoro 2,4-dinitrobenzène (495 mμ)	Réaction au diméthylaminocinnamaldéhyde (475 mμ)
Ethylamine	8 μg	12 μg
Propylamine	8 μg	7,5 μg
Benzylamine	22 μg*	20 μg
Cyclohexylamine	22 μg	18 μg
Ethanolamine	11 μg	11 μg

* $\lambda_{max.} = 525$ mμ dans le cas de la benzylamine.

COMPOSÉS CARBONYLÉS

Réactifs

Solution à 0,040 g pour cent de *p*-nitrophénylhydrazine dans l'éthanol absolu contenant 0,1 pour cent d'acide chlorhydrique concentré.

Solution fraîchement préparée à 0,4 pour cent d'hydroxyde de benzyltriméthylammonium dans le diméthylformamide, obtenue en diluant à 1 pour cent dans le solvant la solution aqueuse à 40 pour cent d'hydroxyde d'ammonium quaternaire.*

Mode opératoire

A 0,5 ml de solution dans l'éthanol du composé carbonylé, on ajoute 0,5 ml de réactif à la *p*-nitrophénylhydrazine et chauffe à 70° pendant dix à trente minutes. On refroidit puis dilue par 9 ml de solution de benzyltriméthylammonium dans le diméthylformamide.

AMINES PRIMAIRES ALIPHATIQUES

(*a*) *Par le* 1-*fluoro* 2,4-*dinitrobenzène*

Réactifs

Solution à 0,025 pour cent de 1-fluoro 2,4-dinitrobenzène dans le diméthylformamide.

Solution fraîchement préparée à 0,4 pour cent d'hydroxyde de benzyltriméthylammonium dans le diméthylformamide, obtenue en diluant à 1 pour cent dans le solvant la solution aqueuse à 40 pour cent d'hydroxyde d'ammonium quaternaire.*

Mode opératoire

A 1 ml de solution d'amine dans le diméthylformamide, on ajoute 0,5 ml de solution de fluorodinitrobenzène, abandonne pendant dix minutes à température ordinaire et ajoute 4,5 ml de solution de benzyltriméthylammonium et 0,1 ml d'eau. La lecture est effectuée après cinq minutes de repos, à 495 mμ.

(*b*) *Par le diméthylaminocinnamaldéhyde*

Dans 2 ml de solution d'amine dans le nitrométhane (ou dans 0,1 ml d'éthanol en ajoutant 2 ml de nitrométhane), on introduit 2 ml de solution à 0,05 pour cent de diméthylaminocinnamaldéhyde dans le nitrométhane, chauffe pendant vingt-cinq minutes au bain-marie bouillant, refroidit et complète à 10 ml avec du nitrométhane. La lecture est effectuée à 475 mμ.

---

* On peut également utiliser une solution à 30–35 pour cent d'hydroxyde obtenu à partir de bromure ou d'iodure d'ammonium quaternaire. A 5,5 g de bromure ou à 6,6 g d'iodure, en solution dans 10 cm^3 d'eau, on ajoute 5 g de Ag_2O. Après une heure d'agitation, on filtre, abandonne pendant 24 heures puis on ajoute 0,5 g de noir décolorant, agite pendant 5 minutes et filtre de nouveau.

Summary—In non-aqueous medium it is possible to characterise the hydroxyl, the carbonyl and the aliphatic primary amino groups, by formation of a derivative (an ester, hydrazone or arylamine) containing nitro groups. Without either extraction or elimination of the excess of reagent, a characteristic coloration is developed in dimethylformamide by using an organic base. Determinations are possible on the hundredths of a milligram scale.

Zusammenfassung—In nichtwässrigen Medium ist es möglich Hydroxyl-Carbonyl- und primäre aliphatische Aminogruppen durch Bildung eines Derivates (Ester, Hydrazon oder Arylamin), das eine Nitrogruppe enthält, zu charakterisieren. Ohne extraction oder Entfernung des Reagensüberschusses wird in Dimethylformamid eine charakteristische Färbung erzielt, wenn eine organische Base angewendet wird. Bestimmung im Hundertstel-milligrammbereich sind möglich.

REFERENCES

[1] Voir en particulier:
(*a*) J. P. Heotis et J. W. Cavett, *Analyt. Chem.*, 1959, **31**, 1977;
(*b*) E. Sawicki, T. R. Hauser et T. W. Stanley, *ibid.*, 1959, **31**, 2063;
(*c*) G. N. Smith, *ibid.*, 1960, **32**, 32.

[2] A. E. Kellie, E. R. Smith et A. P. Wade, *Biochem. J.*, 1953, **53**, 578.

Talanta, 1960, Vol. 5, pp. 221 to 230. Pergamon Press Ltd. Printed in Northern Ireland

A NEW SELECTIVE METALLOCHROMIC REAGENT FOR THE DETECTION AND CHELATOMETRIC DETERMINATION OF CALCIUM

R. A. CLOSE* and T. S. WEST
Chemistry Department, University of Birmingham, Edgbaston, Birmingham 15, England

(*Received* 30 *May* 1960)

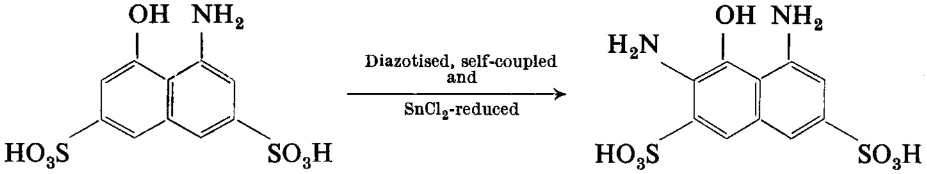
Summary—A new reagent, Calcichrome, which gives a highly sensitive colour reaction with calcium ions in alkaline solution, has been synthesised. Neither barium, strontium nor magnesium react with the reagent, which is therefore proposed as a selective spot-test reagent for calcium. In addition, Calcichrome may be used as a metallochromic indicator for the accurate complexometric titration of calcium in the presence of at least twelve-fold amounts of barium. *Trans*-1:2-diamino*cyclo*hexane-N:N:N′:N′-tetra-acetic acid is used as titrant since it is the only complexan available which is sufficiently selective in its reactivity towards calcium and barium.

FEW satisfactory methods are available for the detection and determination of calcium in the presence of the other alkaline-earth elements and magnesium. Glyoxal-bis (2-hydroxyanil) is the only reagent known to us which can be used, without chemical separation, for the detection of calcium in the presence of barium and strontium.[1] All three alkaline earths give a red precipitate with the reagent, but only the calcium complex is extracted from aqueous solutions into a chloroform phase.

In the course of an extensive survey of the complexometric indicator properties of polyhydroxyazo dyes, part of which has already been published,[2,3] we have observed certain relationships between molecular structure and indicator action. In the course of subsequent investigations based on this experience we isolated the self-coupling reaction product of diazotised H-acid (8-hydroxyl-1-aminonaphthalene-3:6-disulphonic acid) and examined its indicator properties. Whilst more work requires to be done on the structure of this reagent, the present paper describes the synthesis, properties and some of the applications of this new reagent which is specific for calcium within the alkaline earth group. Thus we have used it as a spot-test for the detection of calcium in the presence of barium and strontium and for the titration of calcium in the presence of a large excess of soluble barium salts.

DISCUSSION

The self-coupling reaction product of diazotised H-acid was first described in the early German literature. In Friedländer's compilation[4] the opinion was expressed that the composition of the product was such that one or possibly two diazotised H-acid

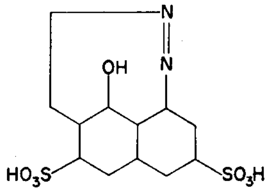


---

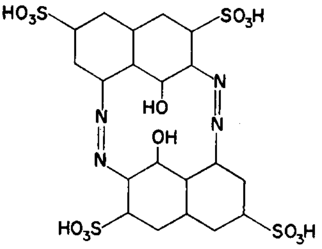
* Present address: The Clayton Aniline Company, Manchester, England.

units were involved. It was reported that reduction with stannous chloride yielded only 1:7-diamino-8-naphthol-3:6-disulphonic acid. No other product could be isolated.

From the above evidence self-coupling had definitely taken place; moreover it was also observed that once the diazonium salt had been made alkaline, acidification yielded only a reversible blue to red colour-change and no trace of the original diazonium salt. Friedländer therefore proposed two possible structures:—

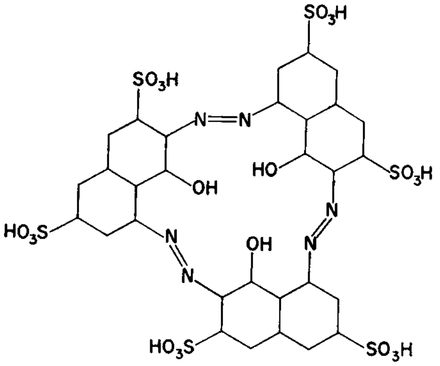


A



B

However, consideration of the stereochemistry involved in these structures suggested to us that their existence was highly improbable and this was borne out when attempts were made to build molecular models of such compounds. We have found, however, that it is easily possible for a scale model molecule to be formed in which three diazotised H-acid units are coupled together by 1–7 azo linkages. This produces a virtually planar ring structure in which the hydroxyl groups are closely crowded together in the centre of the molecule.



Probable stucture

A preliminary series of experiments designed to establish the structure of such a molecule, *cyclo*-tris-7-(1-azo-8-hydroxynaphthalene-3:6-disulphonic acid), has yielded some results which substantiate the hypothesis of formation of a trimer of diazotised H-acid, but more refined experiments are required before a definite conclusion can be stated. Some of this evidence is presented in outline below, but meanwhile, the practical significance of this new metallochromic reagent justifies publication of its synthesis, an account of its reactions with cations, and details of its application to certain analytical problems.

SYNTHESIS

1-Amino-8-naphthol-3:6-disulphonic acid may be diazotised in hydrochloric acid solution and self-coupled by pouring the solution into strong sodium hydroxide, when a deep-blue solution is obtained. Acidification of the reaction mixture with hydrochloric acid changes the colour of the solution to red and precipitation of the crude product is virtually complete after 12 hr. For use as an indicator or a spot reagent, the compound may be purified sufficiently by suspending in methanol and gassing out with HCl. The filtered solution may then be evaporated to crystallisation under reduced pressure on a water bath. Purification is also obtained by dissolution of the crude product in water, and precipitation and isolation of the lead salt. The latter is suspended in water and the bulk of the lead is precipitated therefrom as $PbCl_2$; the last traces are removed with H_2S, which in turn is removed by passage of nitrogen, and the product is obtained by concentration of the filtered aqueous solution under reduced pressure. The product thus obtained which contains only a very small amount of sodium, and is free from lead and chloride, is believed to be the virtually pure free acid form of the reagent.

It is thought that a superior purification procedure may be possible and this will be reported later when details are given of the structure of the compound.

ACID-BASE AND METALLOCHROMIC REACTIONS

The chemical properties of the reagent, *cyclo*-tris-7-(1-azo-8-hydroxynaphthalene-3:6-disulphonic acid), hereafter referred to as Calcichrome, were examined with a 0·5% aqueous solution of the reagent. The reagent is coloured crimson in the pH range 2–8·5, purple at pH 10–11·5, blue at pH 13 and dark red in strong alkali: This observation agrees with our supposition that the molecule contains three ionisable protons which would not be expected to dissociate fully till a high pH had been attained.

The metallochromic properties of the reagent were examined with 37 cations each in six different buffers corresponding to pH 2, 4·6, 7, 10, 11·5, and 13. The ions concerned were Al, As^{III}, Ag, Ba, Be, Bi, Ca, Cd, Ce^{III} and Ce^{IV}, Co, Cr^{III}, Cu^{I} and Cu^{II}, Fe^{II} and Fe^{III}, Ga, Hg^{I} and Hg^{II}, In, La, Mg, Mn, Ni, Pb, Sb, Sn^{II} and Sn^{IV}, Sr, Th, Ti^{III}, U^{IV} and U^{VI}, V^{IV} and V^{V}, Zn, Zr. These tests were carried out in small test tubes containing 1 ml of distilled water and 2 drops of 0·1 *N* solutions of the metal ions. Two drops of pH adjusting solution were added and the contents were mixed and treated with 2 drops of Calcichrome. The colour of the solution was noted and if it differed from that produced by the buffer alone, 3 drops of 0·1*M* EDTA were added and any colour change recorded. The essential points are noted in Table I.

Only eight ions yield coloured products with the reagent under these conditions and in strongly alkaline solutions, pH 13, *only* calcium forms a coloured product. Neither magnesium nor the other two alkaline earths give a colour reaction with Calcichrome under these conditions and consequently this reaction can be used as the basis of a specific spot-test procedure for Ca^{2+} in the presence of other ions. Ordinary strontium salts usually contain sufficient calcium to yield a faint pink colour but spectrographically pure strontium salts yield no colour.

SPECIFIC SPOT-TEST FOR CALCIUM

With a $1 \times 10^{-4}M$ solution of Calcichrome in water and the procedure recommended below it was shown that on a spot plate unequivocal detection of calcium by

Table I

Metal ion	pH	Colour Change	
		Metal ion	EDTA (excess)
Ba	10	Red	Purple
	11·5	Red	Purple
Ca	10	Red	Purple
	11·5	Red	Purple
	13	Red	Blue
Cd	11·5	Red	Purple
Cu^{I} and Cu^{II}	4·6	Purple	Red
	7	Purple	Red
La	10	Red	Purple
	11·5	Red	Purple
Mg	10	Red	Purple
	11·5	Red	Purple
V^{IV}	4·6	Blue	Red
	7	Blue	Red
Zn	10	Red	Purple
	11·5	Red	Purple

the naked eye under normal laboratory conditions could be obtained with 0·25 μg at a dilution limit of 1:1,000,000. When the alkalinity of the test medium is greater than $4 \times 10^{-2}N$ there is a loss of sensitivity, and when less than $2 \times 10^{-2}N$ the blanks give a purple rather than a blue colour, with consequent loss of colour contrast. At one stage a solution of the reagent in 0·1N NaOH was used in order to simplify the procedure but this was abandoned when this formulation of the reagent was found to deteriorate after a few days.

Precipitates of some heavy metal hydroxides adsorb the reagent and give a purple colour even in the absence of calcium, but it was found that by treatment with hydrogen sulphide in acetone these interferences could be overcome within certain limits. Some cations inhibit the colour formation with the calcium quite markedly when present in large excess, though they themselves do not form coloured products. Thus, the following molar proportions of ions interfere in this way: Ba, 35: Mg, 20: Na (chloride), 1000. Almost complete inhibition was also caused by the following molar proportions of the anions PO_4^{3-}, 5: $(COO)_2^{2-}$, 10: SO_4^{2-}, 800; fluoride does not appear to interfere.

The recommended procedure can be used to detect 1 part of calcium at the $10^{-4}M$ level in the presence of 8 parts each (molar proportion) of Ba, Sr, Cu, Zn, Cd, Mg, *i.e.*, a total of 48 parts of the other ions present in the sample solution. An identical test could be produced if the H_2S–in–acetone treatment were replaced by acetone and thioacetamide, but if the acetone-sulphide is omitted both test and blank solutions give purple colours. The function of the acetone is discussed in the following section.

REACTION OF CALCICHROME WITH Ca^{2+} IONS

Fig. 1 shows the absorption spectra of the metal-free indicator and its calcium solution at pH $\approx$ 13. From this it will be observed that the addition of calcium produces a hypsochromic shift of the wavelength of maximum absorption equivalent to *ca.* 80 mμ. Only a cursory examination has so far been made to verify the exact nature of the molecule itself and its calcium chelate since difficulty was experienced in obtaining a sample of the dye of sufficient purity to give an accurate ultimate analysis in view of its rather high molecular weight. A preliminary examination by Job's method (*cf.* Fig. 2) shows however that the ratio of calcium ions to H-acid units in the molecule corresponds to 1:3. This may be interpreted as some indication that the cyclic trimer structure is most likely. We attribute the absence of colour reaction of Calcichrome with barium and strontium in part to the known tendency of these ions to form weaker complexes than calcium, but more largely to the size of the chelate "cage" at the centre of the molecule, the larger ionic radii of these ions, and their consequent inability to approach the closely crowded hydroxyl groups.

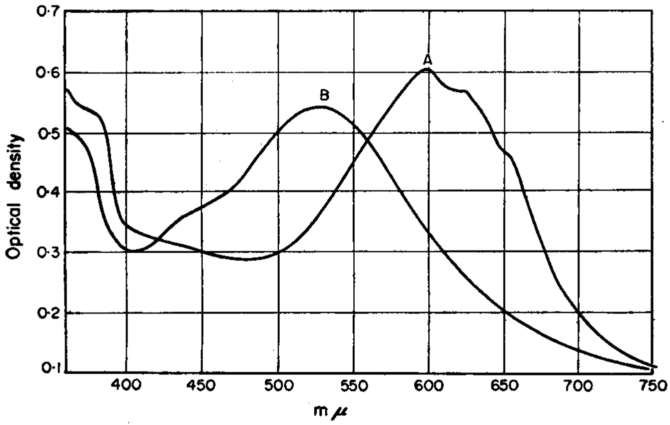


FIG. 1. Absorption spectra at pH > 12
(a) Metal-free reagent
(b) Calcium chelate

TITRATION OF CALCIUM IN PRESENCE OF BARIUM

There is now no lack of suitable indicators for the complexometric titration of calcium, but none is sufficiently selective in its behaviour to permit the titration of calcium in the presence of the other alkaline earths. The reactions of Calcichrome suggest that it should be applicable to the problem. However, because of the unselective reactivity of EDTA it would appear that a specific indicator would do little to solve the problem since the complexan will react with the other alkaline earths before the calcium has been completely titrated. The logarithms of the instability constants of the calcium and barium chelates of EDTA are 10·6 and 7·8 respectively. An examination of published log K values for other complexans shows that for *trans*-1:2-diamino*cyclo*hexanetetra-acetic acid (CDTA) the log K values for the calcium and barium chelates are 12·5 and 7·99 respectively. This separation of 4·51

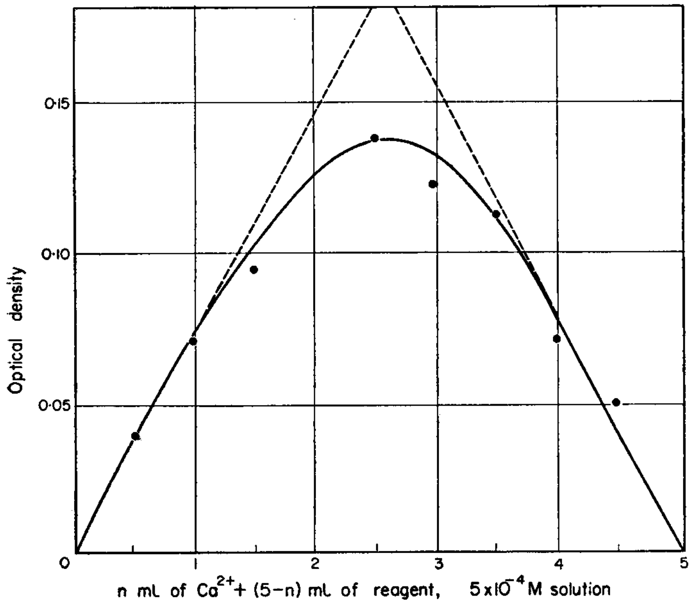


FIG. 2. Corrected plot of continuous variations experiment on Ca^{2+} chelate of reagent pH ≈ 12. $\lambda = 520$ mμ

TABLE II. RECOVERY OF 10·00 ml OF $2 \times 10^{-2}M$ Ca^{2+} IN PRESENCE OF Ba^{2+}

$2 \times 10^{-2}M$ $BaCl_2$ added, *ml*	Ba^{2+}/Ca^{2+} ratio	Recovery of Ca^{2+}, *ml*	Quality of end-point
0·00	0	10·00 10·00 10·00	Colour change complete over 3 drops. Rapid and sharp end-points.
5·00	0·5	10·00 10·02 10·00	Colour change complete over 3 drops. Rapid and sharp end-points.
10·00	1	10·00 10·00 10·04	Colour changes over 4 drops. Fairly rapid and sharp.
25·00	2·5	10·00 10·00 10·02	Colour changes over 5 drops. Sluggish but still sharp.
25·00 ml of $1 \times 10^{-1}M$ Ba^{2+}	12·5	10·04 10·00 10·00	Colour changes over 5 drops. Sluggish but still sharp.

units is better than that to be obtained with any other available complexan and consequently we have used it as a titrimetric reagent.

First of all the indicator action was examined in the EDTA titration of $2 \times 10^{-2}M$ and $10^{-2}M$ calcium solutions, and compared against Acid Alizarin Black SN (AABSN, Colour Index Mordant Black 25) which in our experience is the best calcium indicator currently available for dilute solution work.[3] Both indicators furnished identical titres though the end-point with Calcichrome was not as sharp as with AABSN. The latter gave a 1-drop colour change, whereas Calcichrome changed colour over 4 drops with the $1 \times 10^{-2}M$ solution. Even though it can be used for calcium in strongly alkaline solutions Calcichrome is not very suitable for the titration of calcium in the presence of magnesium. Solutions of calcium were next titrated with $2 \times 10^{-2}M$ CDTA with satisfactory results, and subsequently with calcium solutions containing varying amounts of barium. The results of these experiments are summarised in Table II. When the barium was present in fairly large proportions there was a tendency for sluggish end-points to be obtained and for the recovery to be very slightly high. As the colour showed signs of changing just before the end-point, the titrant was added dropwise at 10-sec intervals over the last few drops. Despite this sluggishness, however, there was no difficulty in obtaining a specific and accurate titration of calcium in the presence of a twelve-fold amount of barium.

TITRATION OF CALCIUM IN PRESENCE OF STRONTIUM

Since we could find no data relating to the stability constant of the CDTA-Sr^{2+} chelate we repeated the above experiments in an attempt to determine calcium in the presence of strontium. However, high recoveries were obtained and it was apparent that an appreciable amount of strontium was titrating with calcium. Several other complexans were examined without success, namely N:N′-bis-hydroxyethylethylenediamine-N:N′-diacetic acid (HEEDDA), N-hydroxyethyl-ethylenediamine-N:N′:N′-triacetic acid (HEEDTA), 1:2-diamino*cyclo*pentane-N:N:N′:N′-tetra-acetic acid (CPDTA)[5] and 1:2-diamino*cyclo*heptane-N:N:N′:N′-tetra-acetic acid (CHDTA).[5]

Attempts were made to overcome the interference of strontium in the calcium titration by precipitating the former as its insoluble sulphate. A procedure based essentially on that of Scott and Furman[6] was therefore applied, in which ammonium sulphate was employed as the reagent. It was found that the results for calcium were virtually quantitative whether or not the strontium sulphate was removed by filtration (*cf.* Table III). The resultant large concentration of electrolyte in the solution caused some inhibition of the indicator action, but this was overcome to a certain extent by addition of acetone. This expedient was adopted since it has been observed that the addition of miscible organic solvents stabilises complexes in solution whereas the addition of electrolyte has a weakening effect.[7] Thus we sought to balance the two effects against each other.

Precipitation with sodium sulphate and sulphuric acid yielded less reproducible results, but precipitation from homogeneous solutions *via* hydrolysis of sulphamic acid, with its resultant larger crystals of strontium sulphate, yielded slightly superior results though the gain in accuracy was small relative to the much greater time factor involved. Consequently only the ammonium sulphate procedure is reported here. Because of its obvious limitation in terms of absolute precision and accuracy this last procedure is not included as a recommended method for the determination of calcium in the presence of strontium, but rather as a rapid procedure which gives a tolerably good result when the time factor is more important than accuracy.

Table III. Recovery of calcium in presence of strontium by CDTA titration with Calcichrome as indicator

$2 \times 10^{-2}M$ calcium solution taken, *ml*	$2 \times 10^{-2}M$ strontium solution added, *ml*	$2 \times 10^{-2}M$ calcium solution found, *ml*
10·00	0·00	10·00
5·00	5·00	4·85 5·00 5·05 5·05 5·30
10·00	5·00	9·70 10·00 9·86 9·80
15·00	5·00	14·85 15·05 15·00 14·95 15·05

TITRATION OF CALCIUM IN PRESENCE OF OTHER METALS

It was found that 0·5 molar proportions of zinc, lead, arsenic and antimony did not affect the accuracy of the calcium determination provided sufficient sodium hydroxide was added to form their amphoteric salts.

CONCLUSIONS

Whilst a fair amount of work remains to be done to establish firmly the exact structure of this new metallochromic reagent for calcium, the above experiments provide a highly selective and sensitive reagent for the detection of calcium. They also illustrate the necessity to use a selective complexan in conjunction with a specific indicator to obtain true specificity of titration. To the best of our knowledge the above method is the only direct titrimetric procedure which has been devised for the accurate titration of calcium in the presence of soluble barium.

EXPERIMENTAL

Synthesis of Calcichrome

5*N* hydrochloric acid (500 ml) is cooled in ice to below 5° and treated with a 30% solution of sodium nitrite (23 ml). The mixture is stirred continuously and kept below 5° whilst a suspension of 1-amino-8-naphthol-3:6-disulphonic acid monosodium salt sesquihydrate (H-acid) (37 g) in water (150 ml) is added in small portions over a period of 15 min. The reaction mixture is stirred for a further 30 min, and then the suspension of the yellow diazonium salt is poured in a thin stream with constant stirring into cold 4*N* sodium hydroxide (1 litre). Self-coupling takes place immediately, but the mixture should be stirred for a further 30 minutes to ensure complete reaction. To the alkaline solution is added sufficient concentrated hydrochloric acid to make it just acid; the colour changes to red and after 12 hr the impure product is filtered off and dried over solid sodium hydroxide. The impure product consists of the acid sodium salt with some sodium chloride. It may be rendered pure enough for reagent use by the following method.

The impure product is stirred with ethanol (1 litre) and hydrogen chloride gas is bubbled gently through the mixture to saturation. The free acid reagent dissolves in the alcohol and the residue of sodium chloride is removed by filtration. The solution is evaporated under vacuum on a water bath and when the product separates out it may be filtered off at the pump, sucked dry and finally dried *in vacuo* over sodium hydroxide.

Spot test for calcium

Reagents: 1N Sodium hydroxide: 0·1N Sodium hydroxide: Acetone saturated with washed and dried H_2S: 0·1% *Calcichrome Solution* (*ca.* 1 × $10^{-4}M$) aqueous.

(*a*) *Direct Procedure:* Place 4–5 drops of test solution on the spot-plate, add 1 drop (2 if necessary as shown by blank) of 0·1*N* sodium hydroxide and 1 drop of Calcichrome reagent solution. Prepare a blank similarly with 4–5 drops of water in place of the test solution. The latter should have a blue colour free of any trace of red. The presence of calcium will be revealed by a definite red coloration.

(*b*) *Procedure for Calcium in presence of ions which interfere with or inhibit the reaction as used above:* Place in a small centrifuge-tube test solution (1·0 ml), acetone saturated with hydrogen sulphide (0·5 ml) and 1 *N* sodium hydroxide (0·2 ml). Shake the mixture for 10 sec and centrifuge to give a clear solution. Place 5 drops (0·2 ml) of the supernatant solution on a spot-plate and to this add 1 drop of 0·1*N* sodium hydroxide to give a final alkalinity of approximately 3 × $10^{-2}N$. Add 1 drop of the reagent solution to the test spot and stir with a small glass rod. After 10 sec compare the colour of the spot with that of a "blank" spot in which the test solution is replaced by distilled water. The presence of calcium in the test solution is indicated by the pink colour of the spot; the "blank" is pale blue.

The acetone saturated with hydrogen sulphide may be replaced by pure acetone (0·5 ml) and thioacetamide (0·05 g).

Complexometric titration of calcium in presence of barium

Reagents: 2 × $10^{-2}M$ *CDTA*: 6·88 g of free acid dissolved in 50 ml of 1*N* sodium hydroxide and made up to 1 litre. Standardise against pure 2 × $10^{-2}M$ calcium chloride solution. *Indicator solution,* 0·5% in water: *Sodium hydroxide,* 1*N*:

Procedure: The test solution should be approximately 2 × $10^{-2}M$ with respect to the concentration of calcium. Pipette 10·00 ml of test solution into a 250-ml conical flask. Make the volume up to 100 ml by the addition of distilled water, and to the solution add 1*N* sodium hydroxide (10 ml) and 3 drops of indicator solution. Titrate the solution against the standard CDTA to the pink to blue end-point. Add the titrant slowly when approaching the end-point. Variations of the above volumes may be made so long as the sodium hydroxide concentration is maintained at *ca.* 0·1*N*.

Rapid titration of calcium in presence of strontium (method of limited precision)

Reagents: 2 × $10^{-2}M$ solutions of *Calcium chloride, Strontium chloride, CDTA: Ammonium sulphate,* 0·2*M*: *Calcichrome indicator solution,* 0·5% *aqueous: Acetone: Sodium hydroxide,* 1*N*.

Procedure: Pipette measured amounts of 2 × $10^{-2}M$ solutions of calcium and strontium chlorides into a 250-ml conical flask and dilute the contents to 50 ml. Bring the contents of the flask to boiling point and add 5 ml of 0·2*M* ammonium sulphate dropwise to the boiling solution over a period of *ca.* 2 min. Simmer the mixture for a further 10 min then allow to cool for 30 min. Add 20 ml of acetone, 6 ml of 1*N* sodium hydroxide and 4–5 drops of indicator solution. Finally titrate the solution to the sluggish pink to blue end-point.

Acknowledgments—We are grateful to the Clayton Aniline Company for the provision of a research grant to one of us (R. A. C.) and wish to express our thanks to Professor R. Belcher for many helpful suggestions.

Zusammenfassung—Ein neues Reagens, Calcichrome, wurde synthetisiert. Das Reagens gibt eine hochempfindliche Farbreaktion mit Calcium in alkalischer Lösung. Barium, Strontium und Magnesium reagieren nicht. Das Reagens wird daher zum selektiven Tüpfelnachweis von Calcium vorgeschlagen. Zusätzlich kann Calcichrome als metallochromer indicator zur komplexometrischen Bestimmung von Calcium in Gegenwart von wenigstens zwölffachem Überschuss an Barium verwendet werden. Trans-1,2-diaminocyclohexantetraessigsäure wird als Titrationsmittel verwendet, da es das einzige erhältliche Komplexan ist, das hinreichende Selektivität in Bezug auf die Reaktion mit Calcium und Barium zeigt.

Résumé—L'auteur a fait la synthèse d'un nouveau réactif—Calcichrome—qui donne une réaction colorée très sensible avec les ions calcium en solution alcaline. Ni le baryum, ni le strontium, ni le magnésium ne réagissent sur le réactif, qui est, pour cette raison, proposé comme réactif sélectif d'essai par touches du calcium. De plus le Calcichrome peut être utilisé comme indicateur métallochromique pour le titrage complexométrique précis du calcium en présence de quantités au moins 12 fois plus grandes de baryum. L'acide trans-1-2-diaminocyclohexane-N-N-N′-N′-tétracétique est utilisé comme agent titrant car il est le seul complexant convenable qui soit suffisamment sélectif dans sa réactivité vis à vis du calcium et du baryum.

REFERENCES

[1] D. Goldstein and C. Stark-Mayer, *Analyt. Chim. Acta*, 1958, **19**, 437.

[2] R. Belcher, R. A. Close and T. S. West, *Chemist-Analyst*, 1957, **46**, 86; *Idem, ibid.*, 1958, **47**, 2.

[3] R. A. Close and T. S. West, *Analyt. Chim. Acta*, 1960, **23**, 261.

[4] Friedländer, *Fortschritte der Teerfarbenfabrikation*, 1894–97, **4**, 610.

[5] W. Hoyle, Unpublished work, *cf.* W. Hoyle and T. S. West, *Talanta*, 1959, **2**, 158; 1959, **3**, 47.

[6] W. W. Scott and N. H. Furman, *Standard Methods of Chemical Analysis.* Van Nostrand, N.Y., 1939, 901.

[7] G. Schwarzenbach and H. Ackermann, *Helv., Chim. Acta*, 1948, **31**, 1029.

Talanta, 1960, Vol. 5, pp. 231 to 237. Pergamon Press Ltd. Printed in Northern Ireland

PRECIPITATION OF METAL 8-HYDROXYQUINOLATES FROM HOMOGENEOUS SOLUTION—II

THORIUM

KAZUYOSHI TAKIYAMA*, EUGENE D. SALESIN and LOUIS GORDON†
Department of Chemistry and Chemical Engineering, Case Institute of Technology,
Cleveland 6, Ohio, U.S.A.

(*Received* 7 *June* 1960)

Summary—A comparison has been made of the precipitation of thorium with 8-hydroxyquinoline by the direct method of addition of reagent and by precipitation from homogeneous solution by generation of the reagent from 8-acetoxyquinoline. The latter reagent produces a thorium precipitate with superior physical characteristics. Separation studies using cerium^{III} as a diverse ion also indicate the superiority of the method using 8-acetoxyquinoline. Further studies of thorium 8-hydroxyquinolate, precipitated by either method, indicate that ignition to thorium oxide is a reliable way to conclude the determination. Methods involving weighing or brominating the 8-hydroxyquinolate generally furnish erroneous results.

INTRODUCTION

8-HYDROXYQUINOLINE is a widely used reagent for the precipitation of many metals. In 1929 it was recommended for thorium,[1] 2–100 mg, the determination being concluded either by weighing or brominating the 8-hydroxyquinolate. The formula[2,3] of the thorium chelate is reported to be $Th(C_9H_6NO)_4{\cdot}(C_9H_6NOH)$. At 110° the chelate is said to retain its molecule of crystallisation.[2,4] There is some question about the temperature at which the molecule of crystallisation is removed because the temperature ranges reported for weighing $Th(C_9H_6NO)_4$ are 150–160°,[5] 160–170°,[1,2] and 275–345°.[4]

The present investigation was undertaken to study the precipitation of thorium from homogeneous solution using 8-acetoxyquinoline as a source of 8-hydroxyquinoline and to compare it with the conventional precipitation method. A further objective of the investigation was to study the usual methods used to conclude the determination, *i.e.*, weighing or brominating the precipitate or ignition to thorium oxide.

EXPERIMENTAL

Reagents

Unless otherwise specified, all chemicals were reagent grade.

Thorium: About 5 g of $Th(NO_3)_4{\cdot}4H_2O$ (J. T. Baker Chemical Company, Phillipsburg, N.J.) were dissolved in 200 ml of water to which were added 10 ml of concentrated hydrochloric acid and 25 g of ammonium chloride. The resulting solution was filtered and diluted to 400 ml and 5% hexamethylenetetramine[6] solution (freshly prepared) was added dropwise, until pH 6 was reached. The thorium precipitate was washed with hot 1% ammonium chloride solution, dissolved in a slight excess of hydrochloric acid, and the solution diluted to 2 litres. The concentration of thorium was determined by precipitation with hexamethylenetetramine[6] followed by ignition to the oxide.

---

* Present address: Institute for Chemical Research, Kyoto University, Takatsuki, Osaka, Japan.
† To whom requests for reprints should be addressed.

Rare earths: The source of cerium was either $Ce(NO_3)_3\,6H_2O$ (Eimer and Amend Company, New York, N.Y.) or $(NH_4)_2Ce(NO_3)_6$ (G. F. Smith Chemical Company, Columbus, Ohio). From these compounds, cerium^{III} chloride solutions were prepared. Solutions of yttrium chloride and lanthanum chloride were prepared from yttrium oxide (Research Chemicals Inc., Burbank, Calif.) and lanthanum oxalate (Lindsay Light and Chemical Company, West Chicago, Ill.).

8-*Hydroxyquinoline:* The solution used was made by dissolving 2·5 g of the reagent (Matheson, Coleman, and Bell Division of Matheson Company, East Rutherford, N.J.) in 6 ml of glacial acetic acid and diluting with water to 100 ml.

8-*Acetoxyquinoline:* This reagent was prepared by the method of Salesin and Gordon[7] for use in the present investigation but has since become available from Burdick and Jackson Laboratories, 1953 S. Harvey St., Muskegon, Michigan.

Precipitation of thorium with 8-*acetoxyquinoline*

Preliminary investigations were made to determine the appropriate concentrations of reagents, the temperature of reaction, and the pH, which would result in the quantitative precipitation of thorium 8-hydroxyquinolate in a form with desirable physical characteristics. The quantity of 8-acetoxyquinoline used was three times the stoichiometric amount required.

Below pH 4·0, no precipitate formed, and at pH 4·5, precipitation was not quantitative. The rate of precipitation increased with pH and with temperature. At pH 6·5, the precipitate became somewhat gelatinous. Desirable results were obtained by precipitation in the pH range, 5·0–6·0, and at 50°; the precipitate was obtained in the form of spherical orange-coloured particles. At room temperature and at pH 5·5, smaller particles more uniform in size and more yellow in colour were obtained. Yttrium, lanthanum, and cerium^{III} were found to precipitate at a pH somewhat above 6·0. The best results for the precipitation of thorium for analytical purposes were obtained using pH 5·0 and 50°, and by increasing the quantity of 8-acetoxyquinoline to four times the stoichiometric amount required.

Photomicrographs of thorium 8-hydroxyquinolate are shown in Fig. 1.

Procedure: Dissolve 8-acetoxyquinoline (four times the stoichiometric quantity required for the thorium) in 20 ml of 1:1 acetic acid. Add a solution of thorium containing 10–50 mg and dilute to 100–500 ml, the final volume being proportional to the quantity of thorium present. Adjust the pH to 5·0 with 1:1 ammonium hydroxide and then warm the solution at 50° for 2 hr. Cool, filter, and wash the precipitate with a minimum of cold water. Ignite to thorium oxide.

Precipitation of thorium with 8-*hydroxyquinoline*

Method used: Five ml of 2*N* acetic acid were added to the solution containing 10–50 mg of thorium in a volume of 100–500 ml, the final volume being proportional to the quantity of thorium present. Then 8-hydroxyquinoline solution, 6 ml for each 10 mg of thorium present, was added. The solution was then heated to 90° and 50 ml of 2*N* ammonium acetate solution was added with continuous stirring. The solution was cooled to room temperature before filtering.

Determination of thorium in the precipitate

Because, as will be discussed later, there was some question regarding the composition of the precipitate, it was desirable in many of the determinations to minimise solubility losses due to the use of wash solution. Thus, precipitates were frequently transferred to a filter with the repeated use of the filtrate itself. After complete transfer to the filter medium, the precipitate was then washed with two small portions of cold water before either being weighed or brominated. In other cases, transfer and washing of the precipitate were effected wholly with a minimum of cold water. At 110° precipitates were dried for 3–5 hr; at higher temperatures they were dried for approximately 10 hr.

Where bromination was used, the titrimetric procedure[8] given in *Analytical Chemistry of the Manhattan Project* was used.

In some cases, precipitation of a known amount of thorium was effected with a known excess either of 8-hydroxyquinoline or 8-acetoxyquinoline. After precipitation, the reaction mixture was diluted in a volumetric flask and an aliquot of the supernatant liquid, obtained by filtration through a dry filter, was analysed for residual reagent by bromination and titration. From these results, the composition of the precipitate could be determined.

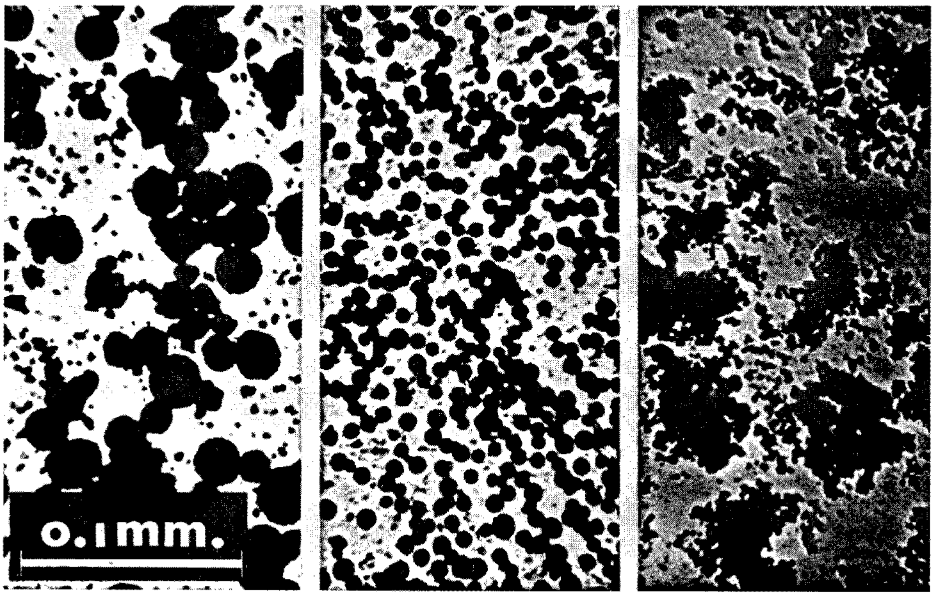


FIG. 1.—Photomicrographs of thorium 8-hydroxyquinolate (all photomicrographs are at same magnification.)
(*a*) method of PFHS at pH 5·0 and at 50°.
(*b*) method of PFHS at pH 5·5 and at room temperature.
(*c*) conventional method of precipitation.

Separation of thorium and cerium

Thorium was precipitated in the presence of cerium^{III} and the precipitate was decomposed with a mixture of 10 ml of concentrated nitric acid and 3 ml of concentrated perchloric acid by heating to fumes of the latter. The cerium in the resulting solution was then determined colorimetrically with *o*-phenanthroline[9] using a Beckman DU spectrophotometer with 1-cm cells.

RESULTS AND DISCUSSION

The composition of the precipitate, determined as previously described by using known quantities both of thorium and the reagent is shown in Table I. The uncertain composition of the precipitate is quite obvious; in particular, there appears to be less than the one molecule of crystallisation of 8-hydroxyquinoline as has been previously reported by others. The results shown in Table I are in general confirmed by the more usual determinations in which the precipitates were separated by filtration. Parts A and B of Table II show less than one molecule of crystallisation regardless of whether the precipitate is analysed by bromination without previously drying, or weighed after being dried at 110°.

TABLE I. COMPOSITION OF THE THORIUM PRECIPITATE

Formula assumed = $Th(C_9H_6NO)_4{\cdot}(C_9H_6NOH)_x$

Precipitation with 8-*hydroxyquinoline* (6 *determinations*)

x = 1·16, 0·89, 0·91, 0·97, 0·83, 1·01

Precipitation with 8-*acetoxyquinoline* (2 *determinations*)

x = 0·80, 0·87

As is also shown by the high results of Part B of Table II, further drying at 165° did not remove all of the 8-hydroxyquinoline of crystallisation. The exception is the one conventional precipitation with 14 mg of thorium, but as will be seen subsequently there is a somewhat slightly different response to drying shown by precipitates obtained by the two different methods of precipitation.

When the drying temperature was changed to 180°, the results obtained were quite satisfactory, as is shown in Part C of Table II. Somewhat better results are indicated for the PFHS method, but the results are not conclusive.

The results of Part D of Table II and their summary in Table III confirm the previous observation that satisfactory results can be obtained by drying the precipitate at 180°. Again, the slightly lower results obtained for the conventionally produced precipitate are evident. The degradation of the precipitate is apparent if the precipitate is dried at 190° or higher. It is difficult to correlate the results obtained here at 295° and at 345° with the recommendation of 275–345°[4] as a drying temperature even though the latter derives from thermogravimetric data. It is often inadvisable to compare a thermogravimetric observation with results obtained by a conventional weighing procedure. However, it would appear from the overwhelming evidence obtained in the present study not only that the thermogravimetric experiment ought to be repeated, but particularly that the recommendation of 275–345° as a drying temperature be ignored where a conventional drying and weighing procedure is to be employed. On the other hand, the close tolerance required for drying the precipitate, *i.e.* within a narrow range close to 180°, is certainly something of a handicap.

With either method of precipitation, excellent results were obtained as shown in Table IV when the precipitate is ignited to thorium oxide.

TABLE II. DETERMINATION OF THORIUM BY WEIGHING AND/OR BROMINATION OF THE 8-HYDROXYQUINOLATE

A. By bromination of the precipitate[a] *without prior drying*

Method of precipitation	Th taken (*mg*)	Difference found (*mg*)	
		$Th(C_9H_6NO)_4{\cdot}(C_9H_6NOH)$	Th
PFHS	69·9	−11·2	−2·8
PFHS	14·0	−1·8	−0·5
PFHS	14·0	−2·8	−0·7
Conventional	14·0	−11·6	−2·8
Conventional	14·0	−6·5	−1·6
Conventional	14·0	−3·6	−0·9
Conventional	14·0	−1·5	−0·4
Conventional	14·0	−1·4	−0·4
Conventional	14·0	+2·4	+0·6
Conventional	28·0	−2·9	−0·8

B. By weighing the precipitate[b] *dried first at* 110 ± 1° *and later at* 165 ± 5° *followed by bromination*

Method of precipitation	Th taken (*mg*)	Difference found (*mg*)					
		110°		165°			
				Weighing		Bromination	
		$Th(C_9H_6NO)_4{\cdot}(C_9H_6NOH)$	Th	$Th(C_9H_6NO)_4$	Th	$Th(C_9H_6NO)_4$	Th
PFHS	69·9	−19·5	−4·9	+14·7	+4·2	+14·7	+4·2
PFHS	69·9	−17·7	−4·4	+14·6	+4·1	+20·7	+5·9
PFHS	69·9	−17·3	−4·3	+15·7	+4·5	+19·3	+5·5
Conventional	14·0	−3·3	−0·8	−1·7	−0·5	−1·3	−0·4
Conventional	14·0	−3·5	−0·9	—	—	—	—
Conventional	14·0	−4·0	−1·0	—	—	—	—

C. By weighing the $Th(C_9H_6NO)_4$ *precipitate*[b] *dried at* 180 ± 5° *followed by bromination*

Method of precipitation	Th taken (*mg*)	Difference found (*mg* of Th)	
		By weighing	By bromination
PFHS	14·0	0·0	0·0
PFHS	14·0	−0·1	−0·1
PFHS	14·0	+0·1	—
PFHS	14·0	−0·1	—
PFHS	14·0	−0·6	—
PFHS	28·0	+0·1	—
Conventional	14·0	−0·3	0·0
Conventional	14·0	−0·4	—
Conventional	14·0	−0·2	—
Conventional	28·0	−0·3	−0·5
Conventional	28·0	−0·3	−0·1

D. By weighing the precipitate[b] *after consecutive drying at various temperatures*

Method of precipitation	Th taken (*mg*)	Difference found (*mg*)					
		110 ± 1°		180 ± 5°		190 ± 5°.	
		$Th(C_9H_6NO)_4\cdot(C_9H_6NOH)$	Th	$Th(C_9H_6NO)_4$	Th	$Th(C_9H_6NO)_4$	Th
PFHS	20·1	−3·9	−0·9	−0·3	−0·1	−0·9	−0·3
PFHS	20·1	−3·9	−0·9	+0·1	0·0	−0·8	−0·2
PFHS	20·1	−4·5	−1·0	−0·2	−0·1	−1·2	−0·3
PFHS	2·0	−0·1	0·0	−0·1	0·0	—	—
PFHS	1·0	+1·0	+0·2	−0·1	0·0	—	—
Conventional	20·1	−1·3	−0·3	−0·8	−0·2	−2·0	−0·6
Conventional	20·1	−4·4	−1·1	−1·0	−0·3	−2·2	−0·6
Conventional	20·1	−1·8	−0·4	0·0	0·0	−1·7	−0·5

Difference found (*mg*)								Method of precipitation
200 ± 5°.		245 ± 5°.		295 ± 5°.		345 ± 5°.		
$Th(C_9H_6NO)_4$	Th	$Th(C_9H_6NO)_4$	Th	$Th(C_9H_6NO)_4$	Th	$Th(C_9H_6NO)_4$	Th	
−2·0	−0·6	−6·2	−1·8	−38·4	−11·0	−46·5	−13·3	PFHS
−1·8	−0·5	−5·7	−1·6	−33·6	−9·6	−46·2	−13·2	PFHS
−2·2	−0·6	−8·0	−2·3	−21·2	−6·1	−45·3	−12·9	PFHS
−2·9	−0·8	−4·2	−1·2	—	—	—	—	PFHS
—	—	—	—	—	—	—	—	PFHS
−3·7	−1·1	−10·8	−3·1	−46·7	−13·4	−47·2	−13·5	Conventional
−3·7	−1·1	−9·7	−2·8	−35·5	−10·2	−46·5	−13·3	Conventional
−2·9	−0·8	−8·5	−2·4	−34·5	−9·9	−46·5	−13·3	Conventional

[a] Precipitate washed thoroughly with cold water.

[b] Precipitate transferred with filtrate to minimize possible solubility losses and finally washed with two small portions of cold water.

TABLE III. AVERAGE RATIO, THEORETICAL QUANTITY OF 8-HYDROXYQUINATE EXPECTED: EXPERIMENTAL QUANTITY FOUND AT VARIOUS DRYING TEMPERATURES

20·1 mg Thorium taken (from Table II, D).

Temperature, °*C*	Ratio	
	PFHS	Conventional
110	1·052	1·032
180	1·001	1·009
190	1·014	1·029
200	1·029	1·051
245	1·10	1·16
295	1·80	2·25
345	2·91	3·00

TABLE IV. DETERMINATION OF THORIUM BY IGNITION OF 8-HYDROXYQUINOLATE[a] TO THORIUM OXIDE

Method of precipitation	Thorium taken (*mg*)	Difference (*mg* of Th)
Conventional	14·0	0·00
Conventional	14·0	0·00
PFHS	14·0	0·1
PFHS	69·9	0·3
PFHS	69·9	0·0
PFHS	139·8	1·0

[a] See note *b* of Table II.

The separation of thorium and cerium is quite satisfactory, as the results of Table V indicate. In view also of the observation that lanthanum and yttrium do not precipitate until a pH slightly greater than 6·0 is reached, it would seem that the PFHS method could furnish an excellent separation of thorium from many of the rare earths. While the separation of thorium from other diverse ions was not studied, the present method can be expected to give better results than are obtainable with the conventional use of 8-hydroxyquinoline.

TABLE V. SEPARATION OF THORIUM FROM CERIUM[a]

Method of precipitation	Thorium taken (*mg*)	Cerium taken (*mg*)	Cerium found in precipitate (*mg*)
Conventional	50·3	50	0·082
PFHS	50·3	50	0·043
Conventional	50·3	250	0·37
PFHS	50·3	250	0·18
PFHS	50·3	500	0·28

[a] Precipitate washed thoroughly with cold water.

CONCLUSIONS

The information of the present study indicates that ignition of thorium 8-hydroxyquinolate to the oxide is a reliable method of concluding the determination. While the PFHS method indicates that good results can also be obtained by drying the 8-hydroxyquinolate at 180 ± 5°, the close control of temperature represents a disadvantage. In general, with this one exception, it would seem best to avoid methods of concluding the determination of thorium which involve weighing or brominating the 8-hydroxyquinolate.

The separation of thorium from the rare earths using PFHS appears promising.

Zusammenfassung—Die Thorium-oxinat niederschläge, nach zwei verschiedenen Fällungsmethoden erhalten, wurden verglichen. Die physikalischen Eigenschaften des Oxinatniederschlages erhalten durch homogene Fällung mittels Hydrolyse von 8-Acetoxychinolin sind wesentlich günstiger als die eines Niederschlages erhalten durch direkte Fällung mittels Oxin. Trennungen von Cer als Fremdion zeigten ebenfalls die Uberlegenheit des Niederschlages aus homogener Lösung. Weitere Untersuchungen ergaben, dass die Veraschung des Niederschlages zu Thoriumoxyd ein zuverlässiger Weg zum Abschluss der Analyse ist. Direktes Auswägen des Oxinates oder massanalytische Bestimmung mittels Brom führen im allgemeinen zu fehlerhaften Resultaten.

Résumé—Les auteurs ont fait une comparaison de la précipitation du thorium par la 8-hydroxyquinoléine, d'une part par la méthode directe d'addition du réactif, d'autre part par précipitation en solution homogène par production du réactif à partir de 8-acetoxyquinoléine-Ce dernier réactif donne un précipité de thorium qui a des caractéristiques physiques supérieures. Des études de séparation utilisant le cérium (III) indiquent aussi la supériorité de la méthode employant la 8-acétoxyquinoléine. Des études ultérieures du 8-hydroxyquinolate de thorium, précipité par l'une ou l'autre méthode, indiquent que la calcination à l'état d'oxyde de thorium est un procédé sûr pour terminer le dosage. Les méthodes faisant intervenir des pesées ou la bromuration du 8-hydroxyquinolate donnent généralement des résultats erronés.

REFERENCES

F. Hecht and W. Reigh-Rohrwig, *Monatsh. Chem.*, 1929, **53–54**, 596.
F. J. Frere, *J. Amer. Chem. Soc.*, 1933, **55**, 4362.

[3] F. Hecht and W. Ehrmann, *Z. analyt. Chem.*, 1935, **100**, 98.
[4] M. Borrel and R. Paris, *Analyt. Chim. Acta*, 1950, **4**, 267.
[5] H. H. Willard and H. Diehl, *Advanced Quantitative Analysis*. D. van Nostrand Co., New York, 1952, p. 76.
[6] A. S. Ismail and H. F. Harwood, *Analyst*, 1939, **62**, 185.
[7] E. D. Salesin and L. Gordon, *Talanta*, 1960, **4**, 75.
[8] C. J. Rodden, *Analytical Chemistry of the Manhattan Project*. McGraw-Hill Book Co., New York, 1950, p. 187.
[9] L. Gordon and A. M. Feibush, *Analyt. Chem.*, 1955, **27**, 1050.

Talanta, 1960, Vol. 5, pp. 238 to 249. Pergamon Press Ltd. Printed in Northern Ireland

PHOTOMETRIC DETERMINATION OF TELLURIUM WITH BISMUTHIOL II

JOSEF JANKOVSKÝ and OTAKAR KŠÍR
Institute for Ore Research, Prague, Czechoslovakia

(*Received* 14 *June* 1960)

Summary—A method for the photometric determination of tellurium based on the extraction of the yellow-coloured complex of tellurium with bismuthiol II is presented. The described method permits the determination of as little as 0·01 % of tellurium in ores directly without preliminary separation. After the isolation of the element by reduction with tin^{II} chloride even smaller amounts can be determined.

INTRODUCTION

TELLURIUM is the least abundant of the sulphur group of the elements, its percentage in the earth's crust being estimated[41] to the extent of $1 \cdot 10^{-6}$%. Although it is found native, in most cases it is in the form of its compounds. In its minerals, which are rare, tellurium occurs as the tellurite, tellurate, and most frequently as the telluride. Its affinity to various metals decreases in the following order:[42]

Au—Ag—Hg—Bi—Ni—Pb—Cu.

Tellurium is found associated with selenium, especially in sulphide ores from which it is transferred to ashes during metallurgical processing and to anode slimes during the electrolytical refining of metals. These ashes and slimes constitute the chief sources for its production.[40]

Colorimetric procedures for the determination of small amounts of tellurium in ores are usually preceded by the isolation of the element from a large sample by reduction to the elemental state. Gravimetric and titrimetric procedures are unsuitable for such small amounts.

The first colorimetric method was elaborated by Pierson,[38] who reduces tellurium compounds to the element with mercury^{I} chloride and estimates the amount of tellurium present by comparing the colour of the mercury^{I} chloride with standards similarly prepared. Volkov[48] and Zemel[50] precipitate the element with tin^{II} chloride in the form of a coloured sol in the presence of a protective colloid; Johnson, Kwan and Westlake[18] recommend hypophosphorous acid for reduction. Johnson and Andersen[16] measure the tellurium sol in the ultraviolet region in which the measurement is more sensitive. The coloured halides of quadrivalent tellurium have been also used for determination. Hanson, Bradbury and Carlton[13] measure the solutions of tellurium in concentrated hydrochloric acid, Fletcher and Wardle[10] employ hydrobromic acid, while Johnson and Kwan[17] carry out their measurements in hydriodic acid. Geiersberger and Durst[11] utilise the brown coloration of a solution of caesium iodotellurite for determination. Metallic tellurium dissolves in concentrated sulphuric acid to give the purple addition compound $Te \cdot SO_3$, and this was used by Wiberley, Bassett, Burrill and Lyng[49] for the colorimetric determination of the element. Scott and Leonard[43] recommend the measurement of the absorption of telluric acid in the ultraviolet region. Some organic reagents have been also proposed for the determination. Thus, Jílek and Vřešťál[15] apply thiourea, which yields a yellow solution with tellurium. The photometric procedure of Gotô and Kakita[12] is based on the extraction of the yellow complex of tellurium with diethyldithiocarbamate; Bode[1] performs the above reaction in the presence of EDTA and potassium cyanide. Shcherbov and Ivankova[46] extract the complex of chlorotellurous acid and rhodamine B and determine tellurium fluorometrically. Ingamells and Sandell[14] use an indirect procedure based on an induced reaction of the element with ferri-phenanthroline.

The present paper is devoted to the reaction of tellurium with bismuthiol II (mercaptophenylthiolthiadiazolone), which was applied to the photometric determination of the element.

Bismuthiol II was introduced to analytical chemistry by Dubský, Okáč and Trtílek[7] as a micro reagent for the detection of bismuth, and its reactions were further studied by the same authors.[5,6,8,9] Later, the reagent was utilised for the gravimetric determination of mercury,[47] bismuth,[20,21] lead,[26] palladium,[22] platinum,[23] silver,[27,34] thallium,[28] copper,[29] cadmium,[30] arsenic,[31] and antimony,[31] for the separation of arsenic, antimony, and tin[31] from each other, for the separation of gold[23] and silver[32] from the platinum metals, and for certain separations within the platinum group.

Titrimetric procedures using bismuthiol II are based on several principles: bismuth,[24] lead,[33] and cadmium[30] can be determined by dissolving the isolated precipitate of the element with bismuthiol II in EDTA and back-titrating the excess of the latter with a standard solution of a magnesium salt, using Eriochrome Black T as indicator. Analogously, the precipitates of palladium[24] and silver[33] can be dissolved in potassium cyanide, the excess of which is back-titrated with silver nitrate and potassium iodide as indicator. Bismuthiol II may be used as a titrimetric reagent in the amperometric determination of silver,[3] lead,[3] mercury,[3] copper,[4] and cadmium.[4] Bismuth[4] is determined indirectly by back-titrating the excess of bismuthiol II with a mercury^{II} salt. The excess of a standard solution of bismutiol II can be titrated oxidimetrically with iodine monochloride[2] using potentiometric indication as, for instance, in the determination of copper and silver.

As a colorimetric reagent bismuthiol II was used only in the case of bismuth[20] and palladium.[25] In both methods the colour intensity of coloured complexes held in solution by a protective colloid is measured. Extraction-photometric procedures have not been described up to now. Although a number of the above cited papers describe the effect of nearly all elements, the behaviour of selenium and tellurium towards bismuthiol II has not been reported.

EXPERIMENTAL

Apparatus

The absorption spectrum of the yellow-coloured complex was investigated with a Zeiss universal spectrophotometer in 1-cm cells, using a hydrogen lamp and NaCl-prism.

All other measurements were carried out with an Elpho-Pulfrich photometer in 2-cm cells using a tungsten lamp, an EGS photocell and a violet 415-mμ filters with a spectral band of 31 mμ.

The pH of the buffer solutions was measured with an Ionoscop potentiometer with a built-in Weston element. A platinum indicating electrode and a saturated calomel reference electrode were used in the quinhydrone method.

Reagents

Tellurium stock solution: 0·1000 g of crushed metallic tellurium (Johnson, Matthey and Sons, London) was dissolved, with warming, in 10 ml of concentrated nitric acid; the resulting solution was evaporated on a water bath to dryness. The residue was taken up with concentrated hydrochloric acid (200 ml in total) and distilled water, cooled to 20°, and diluted to 1000 ml. From this stock solution, containing 100 μg of tellurium per ml, the working solution was prepared by diluting 200 ml to 1000 ml with distilled water. The working solution contains 20 μg of tellurium per ml.

Selenium solution: 0·14 g of selenium dioxide (Johnson, Matthey and Sons, London) was dissolved in water and made up to 100 ml with distilled water. 1 ml corresponds to approximately 1 mg of selenium.

Bismuthiol II solution: 1 g of bismuthiol II (the potassium salt of 5-mercapto-3-phenyl-2-thiol-1:3:4-thiadiazolone-2, p.a.; Lachema, m.p. 244–247°) was dissolved in distilled water and diluted to 100 ml. The solution was saturated for about 5 min with nitrogen from a cylinder and stored in a tightly stoppered bottle. The nitrogen was previously freed from traces of oxygen by absorption in an alkaline solution of pyrogallol containing 5 g of pyrogallol and 20 g of potassium hydroxide in 100 ml.

Thymol blue solution: 0·1 g of solid indicator plus 1 pellet of sodium hydroxide were dissolved, with warming, in about 20 ml of water and diluted to 100 ml in the usual manner.

Acetate buffer solution: 123 g of anhydrous sodium acetate (pure, remelted; Lachema) was dissolved in about 200 ml of boiling water, treated with 485 ml of glacial acetic acid (p.a.; Lachema), cooled, and diluted to 1000 ml with distilled water.

Tin^{II} chloride solution: 50 g of tin^{II} chloride dihydrate (p.a. Lachema) was boiled with 40 ml of hydrochloric acid (1:1) until the solution became clear. The solution was cooled and made up to 100 ml with distilled water.

Hydrobromic acid: The commercial product (40–48%) was redistilled with the addition of about 1 g of hydrazine sulphate per litre. The constant boiling acid was collected and stored in a dark bottle.

RESULTS

During preliminary tests it was found that, with bismuthiol II in feebly acid solution, tellurium and selenium yield yellow precipitates. A buffered acetic acid solution, however, remained clear and colourless. Tellurium, and partially also selenium, could be extracted with organic solvents in the form of yellow solutions.

In the present paper the extractibility of the tellurium complex was used for its photometric determination. Benzene was selected as the most suitable extraction agent.

Determination of the absorption maximum

The yellow coloured complex in benzene was measured at different wavelengths in a 1-cm cell with a spectrophotometer, using water in the reference cell. From Fig. 1 it can be seen that the maximum absorption of the yellow complex is attained at 335 mμ. However, at this wavelength the absorption of the blank is also maximal. For this reason all subsequent measurements were carried out in the visible region of the spectrum, which does not require an expensive spectrophotometer and is more suitable for routine work. All other measurements were made with an Elpho-Pulfrich photometer and a violet 415-mμ filter.

Influence of pH of the solution

To neutralised solutions of tellurium (100 μg), acetate or monochloracetate buffer mixtures and a solution of the reagent were added. The resulting solutions were extracted with a 10-ml portion of benzene. The readings of the extracts are plotted against the pH of the buffer solution used. As can be seen from Fig. 2 the extinction increases with decreasing pH and is maximal at pH values lower than 4·3. At pH 4·0 about 0·5 hr after the addition of the reagent a yellow precipitate of the complex is gradually formed in the aqueous phase. At higher acidities the precipitate was formed almost immediately and caused lower extinction readings of the benzene extract.

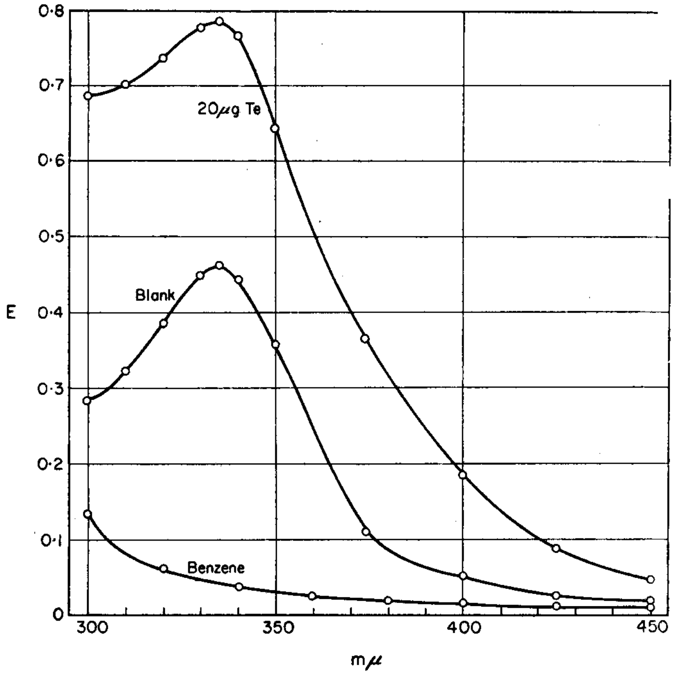


FIG. 1.—Dependence of extinction upon wavelength.

It was necessary, therefore, to extract immediately after the addition of the reagent. From Fig. 2 it is evident that the extinction is maximal in the range of pH 4·3 to 3·3. The formation of an analogous complex of selenium with bismuthiol II is shifted to higher acidities. At a pH of 4·15, which was selected as most suitable, the extinction is maximal, interference by selenium is slight, and no precipitation takes place in the aqueous phase. A buffer solution possessing this pH can be obtained by mixing acetic acid and sodium acetate in the molar ratio 8·5: 1·5. Ten ml of the buffer solution, which is 10M in acetate, were used in all subsequent measurements.

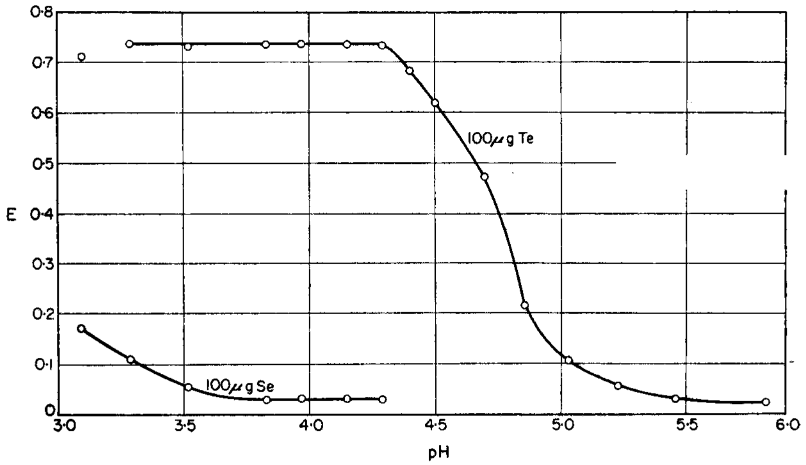


FIG. 2.—Dependence of extinction upon pH.

Influence of concentration of the reagent

To 50 ml of solution, representing 100 μg of tellurium, 10 ml of buffer solution and a freshly prepared solution of the reagent in amounts ranging from 0·2 to 4 ml were added. The solution was extracted with 10 ml of benzene and the extract measured against water. As can be seen from Fig. 3 maximum extinction is attained by the use of 2 ml of a 1 % solution of the reagent and it does not change upon further addition of the reagent. The apparent slight tendency to enhance the extinction is caused by the somewhat higher extinction of the blank. Further, it was found that the consumption of reagent increases with an increasing volume of the aqueous phase. Aqueous solutions of bismuthiol II are subject to gradual oxidation by air, resulting in the formation of a turbidity or even a precipitate. This decomposition of the reagent does not substantially influence the determination. In all subsequent measurements 3 ml of a 1 % solution of the reagent were used, which is sufficient even if the volume of the aqueous phase is 100 ml. It is feasible to pass nitrogen through the freshly prepared solution and to stopper the flask tightly after each withdrawl of reagent or to repeat the bubbling from time to time. A solution through which nitrogen had been passed and which was kept in a tightly stoppered flask remained clear and usable for 6 months.

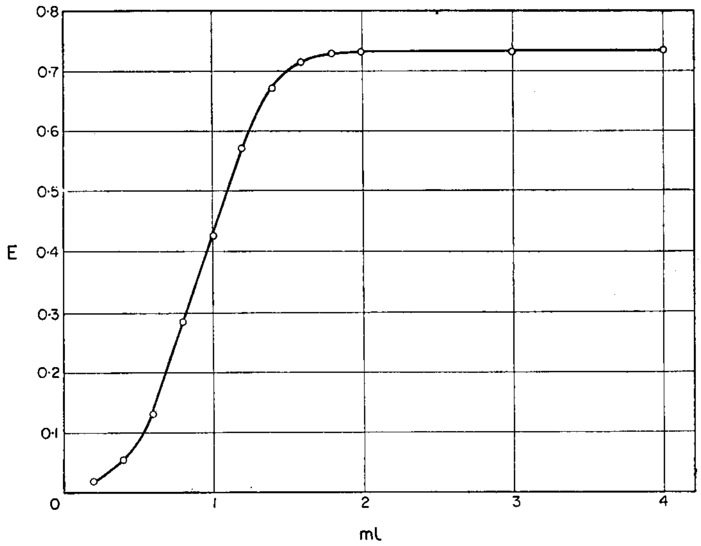


FIG. 3.—Dependence of extinction upon amount of reagent added.

Stability of coloration

The stability of coloration of the yellow complex of tellurium with bismuthiol II was investigated by measuring its extinction at regular intervals. A benzene extract of the complex, corresponding to 100 μg of tellurium, did not exhibit the slightest change during 3 hr. However, all vessels in which the complex is kept must be completely air-tight to avoid the volatilisation of benzene. Practically the same extinction reading was obtained if the extract was left in contact with the aqueous layer in the separatory funnel for 3 hr.

Effect of number of extractions on the coloured complex

Fifty ml of solution, containing 100 μg of tellurium, were treated with 10 ml of acetate buffer mixture, 3 ml of 1 % solution of bismuthiol II, and extracted with 10 ml of benzene. After the separation of the phases, the aqueous layer was extracted with another 10 ml of benzene. The second extract exhibited the same extinction as the blank which is proof that the complex of tellurium with bismuthiol II is extracted quantitatively by a single extraction. To obtain quickly a quite clear extract, the benzene layer was filtered through a small filtering funnel in the stem of which a plug of glass wool has been inserted. (Alternatively, a clear benzene extract can be obtained by centrifuging.) The extraction was performed in separatory funnels whose stems have been shortened to approximately 1 cm.

General procedure

To approximately 50 ml of a feebly acid solution in a 100-ml separatory funnel, containing 0–100 μg of tellurium, add 1 ml of a 10 % solution of EDTA and 5 drops of a 0·1 % solution of thymol blue and neutralise with ammonium hydroxide (1 :1) until the indicator turns yellow. Treat with 10 ml of acetate buffer solution, swirl, add 3 ml of a 1 % solution of bismuthiol II and extract for 1 min with 10 ml of benzene added from a pipette (the pipette is filled by means of a rubber bulb possessing a single conical vent). Allow the phases to separate, draw off the aqueous layer and discard it. Pour the benzene layer through the neck of the separatory funnel into a small filtering funnel into the stem of which a plug of glass wool has been inserted, and collect the clear filtrate directly into a dry 2-cm photometric cell. Obtain the extinction with a suitable photometer, using a violet filter and distilled water in the reference cell.

Calibration curve

For the construction of the calibration curve treat 0, 1, 2, 3, 4, and 5 ml of the working solution, containing 20 μg of tellurium per ml, as indicated above. The calibration curve obtained in the visible region of the spectrum by the use of a 415-mμ filter does not exactly follow linearity but it is quite reproducible (Fig. 4).

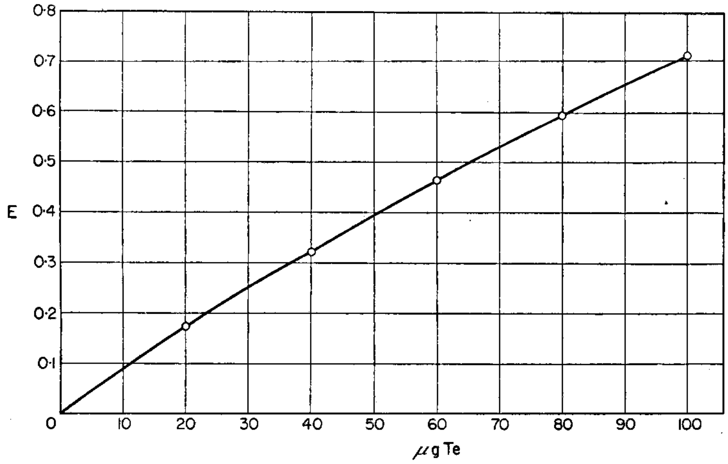


FIG. 4.—Calibration curve of tellurium with bismuthiol II in 10 ml of benzene.

Influence of foreign ions

Solutions containing 100 μg of tellurium and generally 10 mg of a foreign element were treated with 1 ml of a 10% solution of EDTA to avoid precipitation of elements

TABLE I.—DETERMINATION OF 100 μg OF TELLURIUM IN THE PRESENCE OF FOREIGN IONS

Element	Amount of element, *mg*	Form added	Te found, μg	Relative error, %
Ag*	10	$AgNO_3$	—	—
	1**		96	−4
	0·1**		99	−1
Al	10	$KAl(SO_4)_2\cdot 12H_2O$	101	+1
As	10	K_3AsO_3	99·5	−0·5
	10	$Na_2HAsO_4\cdot 7H_2O$	99·5	−0·5
Au*	0·1	$HAuCl_4\cdot 4H_2O$	107	+7
Ba	10	$BaCl_2\cdot 2H_2O$	100	±0·0
Be†	10	$BeSO_4\cdot 4H_2O$	102	+2
Bi	10	$Bi(NO_3)_3\cdot 5H_2O$	101·5	+1·5
Ca	10	$CaCl_2\cdot 6H_2O$	101·5	+1·5
Cd	10	$CdSO_4\cdot 8/3H_2O$	100	±0·0
Ce	10	$CeCl_3$	100	±0·0
Co	10	$CoCl_2\cdot 6H_2O$	101·5	+1·5
Cr†	10	$CrCl_3$	98·5	−1·5
Cs	10	$CsCl$	100	±0·0
Cu	10	$CuSO_4\cdot 5H_2O$	102	+2
Dy	10	$DyCl_3$	101	+1
Er	10	$ErCl_3\cdot 6H_2O$	100	±0·0
Eu	10	$Eu_2(SO_4)_3\cdot 8H_2O$	100·5	+0·5
Fe	10	$FeCl_3\cdot 6H_2O$	100	±0·0
	50§		101	+1
Ga	10	$Ga_2(SO_4)_3$	101	+1
Gd	10	$GdCl_3$	101	+1
Ge	10	$GeCl_4$	99·5	−0·5
Hf	10	$Hf(SO_4)_2$	100	±0·0
Hg*	10	$HgCl_2$	—	—
	0·1		96·5	−3·5
Ho	10	$HoCl_3\cdot 6H_2O$	100	±0·0
In	10	$In_2(SO_4)_3$	100	±0·0
Ir¶	1	$IrCl_4$	98	−2
K	10	K_2SO_4	100	±0·0
La	10	$LaCl_3$	99	−1
Li	10	$Li_2SO_4\cdot H_2O$	100	±0·0
Lu	10	$LuCl_3$	100·5	+0·5
Mg	10	$MgCl_2\cdot 6H_2O$	100	±0·0
Mn	10	$MnSO_4\cdot 5H_2O$	102·5	+2·5
Mo	10	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	100	±0·0
Na	10	$NaCl$	100	±0·0
Nb¶	1	oxalate	100·5	+0·5
Nd	10	$NdCl_3\cdot 6H_2O$	100	±0·0
NH_4	10	NH_4NO_3	100	±0·0
Ni	10	$NiCl_2\cdot 6H_2O$	101·5	+1·5
Os*	1	OsO_4	—	—
	0·1		97	−3
Pb	10	$Pb(NO_3)_2$	102	+2
Pd*	1	$PdCl_2$	—	—
	0·1		99·5	−0·5
Pr	10	$PrCl_3\cdot 6H_2O$	100	±0·0

TABLE I (CONTINUED)

Element	Amount of element, *mg*	Form added	Te found, *μg*	Relative error, %
Pt*	1	$PtCl_4 \cdot 8H_2O$	—	—
	0·1		105	+5
Rb	10	RbCl	100	±0·0
Re	10	Re_2O_7	100	±0·0
Rh	1	$RhCl_3 \cdot 4H_2O$	97·5	−2·5
Ru	1	$RuCl_3$	102	+2
Sb†	10	$SbCl_3$	101·5	+1·5
Sc	10	$ScCl_3$	101·5	+1·5
Se	5	SeO_2	112	+12
	4		109	+9
	3		108	+8
	2		105	+5
	1		102	+2
Sm	10	$SmCl_3 \cdot 6H_2O$	99	−1
Sn	10	$(NH_4)_2SnCl_6$	99	−1
Sr	10	$SrCl_2$	100·5	+0·5
Ta¶	1	oxalate	100·5	+0·5
Tb	10	$TbCl_3$	100	±0·0
Th	10	$Th(NO_3)_4 \cdot 4H_2O$	99·5	−0·5
Ti†	10	$TiCl_4$	101	+1
Tl*	10	Tl_2SO_4	—	—
	0·5		99·5	−0·5
Tm	10	$TmCl_3 \cdot 7H_2O$	101	+1
U	10	$UO_2(NO_3)_2 \cdot 6H_2O$	100	±0·0
V	1	NH_4VO_3	101	+1
W†	10	$Na_2WO_4 \cdot 2H_2O$	102	+2
Y	10	$YCl_3 \cdot 6H_2O$	99	−1
Yb	10	$YbCl_3 \cdot 6H_2O$	100	±0·0
Zn	10	$ZnSO_4 \cdot 7H_2O$	101·5	+1·5
Zr	10	$ZrOCl_2 \cdot 8H_2O$	100.0	±0·0
Phosphate	100‡	$NH_4H_2PO_4$	100·5	+0·5
Nitrate	5000‡	NH_4NO_3	100	±0·0
Oxalate	1000‡	$H_2C_2O_4 \cdot 2H_2O$	100	±0·0
Sulphate	4000‡	K_2SO_4	100	±0·0

* precipitates
† 100 mg of oxalic acid added
‡ weight of compound added
¶ amount of ammonia required for neutralisation added to buffer solution
§ 5 ml of a 10% solution of EDTA added
** 0·5 ml of HCl (1 : 1) added; reagent added after 10 min

of the hydrogen sulphide group by the reagent and the hydrolysis of certain elements during neutralisation. To some ions, which are easily hydrolysed even in the presence of EDTA, a small quantity of ammonium oxalate was added. In the case of niobium, tantalum and iridium, the amount of ammonium hydroxide required for neutralisation (determined in a separate aliquot) was added directly to the buffer solution to avoid local over-alkalisation. The solutions were treated further as described in the general procedure. From the results listed in Table I it is seen that under the above conditions, besides tellurium, only selenium is extracted in the form of a yellow complex. In comparison with tellurium, its rate of extraction is low and can often be neglected. Oxidising ions such as Au^{III}, Pt^{IV}, V^{V}, nitrites and other oxidising anions were found to yield a yellow extract, since the coloured oxidation product of bismuthiol II is also extracted. Under the conditions described, *i.e.* even in the presence of EDTA, the following elements are precipitated by bismuthiol II: Ag^{I}, Au^{III}, Hg^{II}, Os^{VIII}, Pd^{II}, Pt^{IV}, and Tl^{I}. Larger amounts of these elements must be removed. Among a number of anions investigated, fluoride, tartarate, citrate, and dithionite could not be used as screening agents, because low results for tellurium ensue in their presence.

Application of the method

Since the determination of tellurium with bismuthiol II is sensitive and in the presence of EDTA selective, tellurium can be determined in a number of cases directly without preliminary separations. Using an aliquot corresponding to 100 mg, the method may be applied to the determination of as little as 0·01 % of the element in ores, especially pyrites.

With ores low in tellurium it is feasible to isolate tellurium by reduction to the element with tin^{II} chloride in the presence of a small amount of selenium (1 mg) as collector.

Selenium and mercury can be removed from the obtained precipitate as the volatile bromides by evaporation with hydrobromic acid and bromine.[10,35,37] No loss of tellurium occurred if the evaporation was carried out on a water bath in the presence of a small amount of sulphuric acid.

After decomposition with sulphuric acid, silver and thallium may be removed as the insoluble chlorides by the addition of hydrochloric acid. Contrary to silver, any thallium that survives does not affect the determination. If the final solution contains only a small amount of chlorides (0·5 ml of HCl 1:1), the remaining silver is precipitated approximately 10 min after neutralisation and addition of the buffer solution.

The behaviour of gold in the analysis of auriferous pyrites and concentrates is rather interesting. Since the gold content at times amounted to 500 g/t, it was necessary to deal with its removal. Several procedures are recommended in the literature to effect its removal already during decomposition. The statements concerning their applicability are, however, often conflicting. According to Volkov[48] gold is not dissolved by attack with nitric acid but dissolves during the evaporation with sulphuric acid necessary for the subsequent isolation of tellurium and selenium with tin^{II} chloride. For this reason the above author proposes to decompose the sample with nitric acid, to filter off the insoluble residue, and only then to fume off the filtrate with sulphuric acid. Zemel,[50] on the other hand, states that gold is dissolved by the action of nitric acid but it is again precipitated during the evaporation with sulphuric acid which causes its reduction.

On checking these procedures it was found that the finely dispersed gold in the ore partially dissolves in nitric acid even when diluted 1:1. Further, it was found that tervalent gold is reduced to the element if its solutions are evaporated to white fumes of sulphuric acid. This procedure cannot, however, be used for quantitative purposes. In our opinion the precipitation of elemental gold is not to be attributed to a reducing effect of sulphuric acid but to the thermal decomposition of auric acid. This observation is in agreement with the experiments of Polukarov[39] who recommends isolation of the gold by selective reduction with hydrazine sulphate. Other authors also prefer to remove gold by a preliminary separation step with, for instance, ferrous sulphate,[45] nitrite,[19] or hydroquinone.[44]

Gold is known to remain quantitatively in the insoluble residue after the decomposition of ores with sulphuric acid, which fact has been used for its isolation and gravimetric determination.[36] Experiments showed that this mode of attack, in which telluride is oxidised to tellurite by sulphuric acid, is quantitative for tellurium and it may be used for the determination of the element. Thus, it is possible to remove all of the gold and to obtain the tellurium quantitatively as the sulphate by a single operation. A sulphuric acid solution is not only needed for the reduction of tellurium to the elemental state but is also suitable for its direct determination.

Platinum metals which interfere with the determination of tellurium were not contained in the analysed ores and, therefore, their removal has not been dealt with.

Based on the above facts the following procedure can be recommended for the analysis of sulphide ores.

Decomposition of ores

Transfer 1 g of a 200-mesh sample to a 200-ml conical flask, and add, with constant rotating, 7 ml of concentrated sulphuric acid, cover with a clock glass and heat on a sand bath, first moderately for about 5 min, then to boiling with occasional swirling. Decomposition is complete when the mixture assumes a light coloration and part of the sublimed sulphur is condensed in the upper part of the flask. After about 30 min remove from the sand bath, cool, carefully add approximately 50 ml of water, and boil until the soluble sulphates have dissolved (about 10 min).

Direct determination of tellurium

This procedure may be used for the determination of as little as 0·01 % of tellurium, provided the ore does not contain excessive amounts of selenium or other interfering elements.

Pour the sulphuric acid solution into a 100-ml calibrated flask, cool, dilute to the mark, and mix. Filter the solution through a dry filter paper of close texture and discard the first few ml. Transfer 10 ml of the clear filtrate, by means of a pipette, to a 100-ml separatory funnel, dilute to about 50 ml with distilled water, add 5 ml of a 10% solution of EDTA and proceed as outlined in the general procedure. From the extinction reading obtained subtract that produced by a blank carried through all of the steps of the procedure.

Determination of tellurium after its separation

This procedure is suitable for the determination of amounts as low as 0·001 % of tellurium, even if appreciable amounts of selenium and other interfering elements are present.

Decompose 1 g of the sample with the aid of sulphuric acid in the manner already described, boil with water until soluble salts have dissolved, cool, filter through a filter paper of close texture into a 250-ml low-form beaker, and wash the insoluble residue with distilled water until the volume of the filtrate is 70–80 ml. Treat the filtrate with 10 ml of hydrochloric acid (1:1), then collect any precipitated silver (or thallium) on a small filter paper and wash moderately with water. Dilute the filtrate to 100–120 ml, add 1 ml of a 0·14% solution of selenium dioxide, heat to boiling and precipitate by the dropwise addition of a 50% solution of tin^{II} chloride until the yellow colour of iron^{III} chloride is removed (the solution assumes a light colour which can be seen even if the solution is turbid by precipitated selenium and tellurium), then add 1 ml in excess (in most cases a total amount of only 2–3 ml is required). Cover the beaker with a clock glass and heat on a water bath for 3 to 4 hr. Remove from the bath and let stand at room temperature overnight. Filter the precipitated selenium and tellurium with suction through a porcelain filtering crucible, wash with hydrochloric acid (1:9) containing 1 ml of a 50% solution of tin^{II} chloride per litre, and finally with water. To the precipitate in the filtering crucible add 5 ml of concentrated hydrobromic acid and 3 to 5 drops of 30% hydrogen peroxide. Since the precipitate tends to creep, moisten the walls of the crucible with the same acid by means of a short stirring rod. When solution is complete, filter into the original beaker. Again add 5 ml of hydrobromic acid and a few drops hydrogen peroxide to the crucible and filter and wash with distilled water. Treat the filtrate with 1 ml of sulphuric acid(1:1) and evaporate on a water bath until only sulphuric acid is left. Dilute with a few ml of water, again add 5 ml of hydrobromic acid and 3 to 5 drops of hydrogen peroxide and evaporate as before. Dilute, cool, transfer the solution to a 100-ml separatory funnel, dilute to approximately 50 ml, add in the following order, 0·5 ml of hydrochloric acid (1 : 1), 1 ml of a 10% solution of EDTA, and proceed as indicated in the general procedure. If silver is present, the reagent is added 10 min after the addition of the buffer solution. From the obtained extinction reading subtract that produced by a blank carried through all of the steps of the procedure.

In case the sample contains more than 100 μg of tellurium, transfer the sulphuric acid solution to a 100-ml calibrated flask, and take a corresponding aliquot for the determination.

The presented method was checked by a modified procedure of the iodide method of Johnson and Kwan.[17] Table II shows some results obtained with both procedures of the present method *i.e.* directly and after separation of tellurium. It can be seen that the results are quite reproducible and in good agreement with the mean value of the check method.

TABLE II.—DETERMINATION OF TELLURIUM IN ORES

Sample No.	Tellurium found, %		
	With bismuthiol II		With iodide
	After separation	Directly	
1	0·016 0·018	0·018 0·019	0·017
2	0·025 0·024	0·026 0·027	0·025
3	0·014 0·015	0·013 0·016	0·014
4	0·015 0·015	0·017 0·016	0·016

Acknowledgement—The author thanks Mr. Harry Matschina, Prague, for the translation of the present paper.

Zusammenfassung—Ein photometrisches Verfahren zur Bestimmung des Tellurs beruhend auf der Extraktion des gelben Komplexes von Tellur mit Bismuthiol II wird beschrieben. Das Verfahren ermöglicht es, Tellur bis herab zu 0·01 % direkt nach dem Aufschluss mit Schwefelsäure ohne vorangehende Trennung zu bestimmen, Nach Isolierung des Tellurs mit Zinn(II)-chlorid können noch kleinere Mengen bestimmt werden.

Résumé—L'auteur décrit une méthode de dosage photométrique du tellure, fondée sur l'extraction du complèxe jaune du tellure avec le bismuthiole II. La méthode permet le dosage de quantités aussi faibles que 0·01 % de tellure dans les minerais directement après décomposition, sans séparations préliminaires. Après isolement du tellure par le chlorure stanneux des quantités encore plus faibles peuvent être dosées.

REFERENCES

[1] H. Bode, *Z. analyt. Chem.*, 1955, **144**, 90.
[2] J. Čihalík and J. Růžička, *Chem. Listy*, 1957, **51**, 264.
[3] J. Čihalík and J. Voráček, *ibid.*, 1956, **50**, 1750.

[4] *Idem, ibid.*, 1957, **51**, 278.

[5] J. V. Dubský and A. Okáč, *Chem. Obzor*, 1935, **10**, 83; 107; 123; *Z. analyt. Chem.*, 1935, **100**, 408.

[6] J. V. Dubský, A. Okáč and J. Trtílek, *Mikrochemie*, 1935, **17**, 332.

[7] *Idem, Chem. Obzor*, 1934, **9**, 171; 203; *Z. analyt. Chem.*, 1934, **96**, 412.

[8] J. V. Dubský, A. Okáč, B. Okáč and J. Trtílek, *Chem. Obzor*, 1934, **9**, 173; 189; *Z. analyt. Chem.*, 1934, **98**, 184.

[9] J. V. Dubský and J. Trtílek, *Chem. Listy*, 1935, **29**, 33.

[10] N. W. Fletcher and R. Wardle, *Analyst*, 1957, **82**, 743.

[11] K. Geiersberger and A. Durst, *Z. analyt. Chem.*, 1952, **135**, 11.

[12] H. Gotô and Y. Kakita, *Japan Analyst*, 1954, **3**, 299.

[13] M. W. Hanson, W. C. Bradbury and J. K. Carlton, *Analyt. Chem.*, 1957, **29**, 490.

[14] C. O. Ingamells and E. B. Sandell, *Microchem. J.*, 1959. **3**, 3.

[15] A. Jílek and J. Vřešťál, *Chem. Zvesti*, 1952, **6**, 497.

[16] R. A. Johnson and B. R. Andersen, *Analyt. Chem.*, 1955, **27**, 120.

[17] R. A. Johnson and F. P. Kwan, *ibid.*, 1951, **23**, 651.

[18] R. A. Johnson, F. P. Kwan and D. Westlake, *ibid.*, 1953, **25**, 1017.

[19] V. Lenher, G. B. L. Smith and D. C. Knowles, *Ind. Eng. Chem. Analyt.*, 1934, **6**, 43.

[20] A. K. Majumdar, *J. Indian Chem. Soc.*, 1942, **21**, 347.

[21] A. K. Majumdar and M. M. Chakrabartty, *Z. analyt. Chem.*, 1957, **154**, 262.

[22] *Idem, ibid.*, 1957, **155**, 1.

[23] *Idem, ibid.*, 1957, **155**, 7.

[24] *Idem, ibid.*, 1957, **156**, 103.

[25] *Idem, Sci. and Culture*, 1957, **23**, 46.

[26] A. K. Majumdar and B. R. Singh, *Z. analyt. Chem.*, 1957, **154**, 413.

[27] *Idem, ibid.*, 1957, **155**, 81.

[28] *Idem, ibid.*, 1957, **155**, 86.

[29] *Idem, ibid.*, 1958, **161**, 81.

[30] *Idem, ibid.*, 1958, **161**, 257.

[31] *Idem, ibid.*, 1958, **161**, 261.

[32] *Idem, ibid.*, 1957, **155**, 166.

[33] *Idem, ibid.*, 1957, **156**, 265.

[34] M. Malínek, *Chem. Listy*, 1955, **49**, 1400.

[35] F. E. McKenna and D. H. Templeton, Natl. Nuclear Energy Ser., Div. VIII, 1, *Anal. Chem. Manhattan Project*, 1950, p. 303.

[36] K. A. Nenadkevich, *Trudy Inst. geologicheskikh Nauk*, 1940, vyp. 53; J. N. Knipovich and J. V. Morachevskiy, *Analiz mineralnovo syrya*, Leningrad, 1956, p. 867.

[37] F. D. L. Noakes, *Analyst*, 1951, **76**, 542.

[38] G. G. Pierson, *Ind. Eng. Chem. Anal.*, 1934, **6**, 437.

[39] A. N. Polukarov, *Zavodskaya Lab.*, 1959, **25**, 905.

[40] K. Rankama and T. G. Sahama, *Geochemistry*, 1959, p. 755.

[41] A. A. Saukov, *Geochemie*, ČSAV Publishers, Prague, 1954, p. 49.

[42] V. V. Shcherbina, *Bull. Acad. Sci. U.R.S.S.*, *Classe math. nat.*, *Ser. geol.*, 1937, **5**, 965.

[43] L. W. Scott and G. W. Leonard, *Analyt. Chem.*, 1954, **26**, 445.

[44] J. Seath and F. E. Beamish, *Ind. Eng. Chem. Analyt.*, 1937, **9**, 373.

[45] M. J. Shubin, *Zavodskaya Lab.*, 1934, **3**, 677.

[46] D. P. Shcherbov and A. J. Ivankova, *ibid.*, 1958, **24**, 1346.

[47] V. Šedivec, *Chem. Listy*, 1951, **45**, 171.

[48] S. T. Volkov, *Zavodskaya Lab.*, 1936, **5**, 1429.

[49] S. E. Wiberley, L. G. Bassett, A. M. Burrill and H. Lyng, *Analyt. Chem.*, 1953, **25**, 1586.

[50] V. K. Zemel, *Zavodskaya Lab.*, 1936, **5**, 1433.

Talanta, 1960, Vol. 5, pp. 250 to 253. Pergamon Press Ltd. Printed in Northern Ireland

THE ANALYSIS OF BERYLLIUM AND BERYLLIUM OXIDE—IV

THE DETERMINATION OF COBALT

J. O. HIBBITS, A. F. ROSENBERG and R. T. WILLIAMS
Aircraft Nuclear Propulsion Department, General Electric Company
Cincinnati 15, Ohio, U.S.A.

(*Received* 7 *June* 1960)

Summary—A method is described for the determination of cobalt in beryllium or beryllium oxide by extraction of the cobalt thiocyanate complex with acetylacetone (2:4-pentanedione). The method is accurate to ±2% or 2 μg of cobalt, whichever is greater. Of the 68 elements investigated only manganese and chromium interfere in 10 mg amounts. No interference was observed when 1 g of each had been removed by ion-exchange or volatilisation (of chromium only) before extraction.

INTRODUCTION

A CHEMICAL method is presented which is specific for cobalt within the limits investigated. No interference was caused by at least 10-mg amounts of 66 elements. The presence of 5 or 10 mg of manganese or chromium caused a slight interference, giving results approximately 6% high for 100 μg of cobalt. One g of manganese and/or chromium has been successfully removed by ion-exchange, resulting in no observable interference. This method is accurate to ±2% or 2 μg of cobalt, whichever is greater.

The method adopted is a modification of one presented by Brown and Steinbach.[2] The sample is dissolved as previously described,[1] citric acid is added to prevent the precipitation of beryllium, and the pH is adjusted to 4·0 ± 0·1. This solution is extracted with acetylacetone (2:4-pentanedione) to remove beryllium and other elements. After removal of the organic phase, sodium thiocyanate is added to the aqueous phase and the cobalt thiocyanate complex extracted with acetylacetone. The absorbance of the organic extract, measured at 625 mμ, is a linear function of the cobalt concentration, at least from 0–8 μg of cobalt per ml, and is constant for at least 2 weeks.

EXPERIMENTAL

Apparatus

Cary Model 14 Recording Spectrophotometer and 50-mm cells.

International Clinical Centrifuge and 15-ml glass-stoppered centrifuge tubes. Beckman pH meter, Model H-2, and combination 14-cm electrode (single probe).

Reagents

De-ionised water, used throughout.

Standard cobalt solution: dissolve 250 mg of cobalt in 6*M* sulphuric acid with 5 drops of nitric acid added initially. Cool and dilute to 1 litre. Dilute this solution to obtain a solution containing 10 μg of cobalt per ml.

Acetylacetone, (2:4-pentanedione): B.P. 136–139°. The acetylacetone as obtained from the supplier may have a slight yellow colour, probably due to small amounts of iron. This material can be used without further treatment, except for the preparation of the sodium thiocyanate solution and the extraction of the cobalt thiocyanate complex. It is recommended that the acetylacetone be distilled for these uses. It is economical to recover the used acetylacetone by distillation.

Sodium thiocyanate solution, 6M: dissolve 486 g of reagent grade sodium thiocyanate in 380 ml of water, filter immediately and dilute the filtrate to 1 litre with distilled acetylacetone (350 ml).

Citric acid, 50% (w/v).

Hydrochloric acid, (Sp. gr. 1·19, 12*M*).

Nitric acid (Sp. gr. 1·42, 15*M*).

Perchloric acid, 70%.

Sulphuric acid, (Sp. gr. 1·84, 18*M*).

Sodium hydroxide, 50% w/v.

Dowex 1-X8, (50–100 mesh).

Procedure

Dissolve a sample containing about 100 μg of cobalt according to the directions previously given.[1] (If more than 5 mg of manganese or manganese and chromium are known to be present, the solution should be evaporated to dryness and taken up in 9*M* hydrochloric acid. Pass this solution through a column 14 cm high by 1 cm diameter of Dowex 1-X8 in the chloride form. Wash the column with three 15-ml portions of 9*M* hydrochloric acid. Discard the eluate and washings. Wash the column with four 15-ml portions of 0·1*M* sulphuric acid. Collect this eluate and carry it through the following procedure. If more than 1 mg of chromium and less than 1 mg of manganese are present, volatilise the chromium as chromyl chloride in the usual manner and evaporate to dryness. Chromium slowly forms an extractable acetylacetonate which interferes with the determination of cobalt. Thus, it is advisable to complete the analysis as rapidly as possible, when the presence of trace amounts of chromium is suspected.)

Add sufficient acid to have present 5 ml of hydrochloric acid and 10 ml of sulphuric acid. Add 5 ml of 50% citric acid and adjust the pH to 4·0 ± 0·1 with 50% sodium hydroxide. If necessary, heat to redissolve any precipitated beryllium, cool, re-adjust the pH and transfer to a 250-ml separatory funnel. Extract by shaking for 1·5 min with 20-ml portions of acetylacetone until the acetylacetone remains colourless. Discard the organic layers. Check the pH and re-adjust to 4·0 ± 0·1. Again extract with 20-ml portions of acetylacetone until the organic phase is colourless. Add 30 ml of 6*M* sodium thiocyanate and 25 ml of distilled acetylacetone. Shake for 1·5 min. Allow the phases to separate, discard the aqueous phase and drain the organic phase into a 25-ml calibrated flask and dilute to 25 ml with acetylacetone. Centrifuge in glass-stoppered tubes and measure the absorbance at 625 mμ in 50-mm cells, using acetylacetone in the reference cell. Determine the cobalt concentration by reference to a standard curve obtained by carrying known amounts of cobalt through the above procedure. A blank and standard should be carried through the entire procedure. If the absorbance of the sample does not fall on the calibration curve, the sample may be diluted with acetylacetone or the absorbance may be measured using a shorter cell length.

Extraction of the cobalt thiocyanate complex

The cobalt thiocyanate is extracted from an aqueous phase containing 2·5 g of citric acid, 5 ml of 12*M* hydrochloric acid, 7 ml of 18*M* sulphuric acid, sufficient 50% sodium hydroxide to make the pH = 4·0, and 30 ml of 6*M* sodium thiocyanate, in a volume of 175–200 ml. This solution is nearly saturated with acetylacetone.

The cobalt thiocyanate is extracted with 25 ml of acetylacetone. The effect of salt concentration on the solubility of acetylacetone in water makes it necessary to dilute the extract containing the cobalt thiocyanate complex to a definite volume with additional acetylacetone. In spite of the unfavourable phase ratio more than 98% of the cobalt complex is extracted in this manner. The distribution coefficient of the cobalt thiocyanate complex between these two phases is 580 ± 22. This value is independent of the initial cobalt concentration, at least between 0·1 and 5·3 μg/ml.

Brown and Steinbach[2] reported the use of various sources of thiocyanate ion, such as barium, potassium, and ammonium thiocyanates. The first two reagents were unsuitable in this method since they gave precipitates of their sulphates. Ammonium thiocyanate was considered unsuitable because of its lack of purity and instability in acid media. Sodium thiocyanate was used because it overcame these difficulties.

Measurement of the cobalt thiocyanate complex

The colour of the cobalt thiocyanate complex in acetylacetone is stable for at least 2 weeks, whereas it fades in a few hr in some of the more commonly used solvents including acetone, methyl *iso*butyl ketone, or chloroform. The molar absorptivity of the cobalt complex at 625 mμ was found to be 1877 ± 11. The absorbance is a linear function of concentration, at least from 0–8 μg of cobalt per ml acetylacetone.

The absorbance of the cobalt thiocyanate complex is independent of the aqueous thiocyanate concentration between 1·0 and 1·5*M*. Below 1·0*M* thiocyanate the absorbance decreases with decreasing thiocyanate concentration.

Effect of other elements

In testing the effect of other elements on the determination of cobalt by the procedure described, the elements were added to a solution containing the appropriate amounts of beryllium sulphate, sulphuric, hydrochloric and citric acids. Brown and Steinbach tested their method in the presence of unreported amounts of only 8 different metal ions. It was, therefore, deemed necessary to investigate the effects of other possible impurities. No interference was caused by the presence of 10-mg amounts of Al, Sb^{III}, Sb^{V}, As^{III}, As^{V}, Ba, Bi, B, Br, Cd, Ca, Ce^{IV}, Cs, Cu^{II}, Dy, Er, Eu, Gd, Ga, Ge, Au, Hf, Ho, In, I, Ir, Fe^{III}, La, Pb, Li, Lu, Mg, Hg^{II}, Mo^{VI}, Nd, Ni, Nb, Pd^{IV}, P(as $PO_4^{\equiv}$), Pt^{IV}, K, Pr, Re, Rh, Rb, Sm, Sc, Se^{IV}, Si, Sr, Ta, Te^{IV}, Tb, Tl^{I}, Th, Tm, Sn^{II}, Ti^{III}, Ti^{IV}, W^{VI}, U^{VI}, V^{V}, Yb, Y, Zn, or Zr; 100 mg of F^-, 10 ml of 3*M* nitrate, 10 ml of 2*M* perchlorate, or 10 ml of 2*M* acetate. Results are about 6% high when 10 mg of chromium or manganese are present. Therefore, if either or both of these last two elements are present, they should be removed as described.

Apparently, all of the elements investigated which form coloured thiocyanates are removed by the preliminary acetylacetone extraction except nickel, cobalt and platinum. The nickel thiocyanate is not soluble in acetylacetone and does not, therefore, interfere with the determination of cobalt. Some or all of the platinum thiocyanate is extracted with acetylacetone. It does not absorb at 625 mμ, at least at the level investigated; however, it changes the colour of the extract from blue to green.

APPLICATION OF THE METHOD

A sample of beryllium oxide analysed for cobalt using this procedure was found to contain less than 1 ppm of cobalt. When 1-g samples of this oxide were "spiked" with 100 μg of cobalt, recoveries of 100% ± 2% were obtained indicating the applicability of this method in the presence of large amounts of beryllium.

Blank values corresponding to 0–1 μg of cobalt were obtained with the amounts of reagents used during the analysis.

Results obtained when the method was applied to New Brunswick Atomic Energy Commission Laboratory standard samples of beryllium and beryllium oxide are shown in Table I.

TABLE I.—ANALYSIS OF NBL STANDARDS

Sample	Co found, *ppm*		Average, *ppm*	Nominal Co present[c], *ppm*
Be 85	4·0,	4·3	4·15[a]	4
86	21·7,	20·9	21·3[b]	22
87	6·9,	6·8	6·85	7
88	8·4		8·4	8
BeO 72–1	7·3,	7·2	7·25	7·2
–2	3·6,	3·6	3·6	3·6
–3	1·8,	1·8	1·8	1·8
–4	0·76,	0·65	0·70	0·72
–5	0·0 ,	0·0	0·0	0·0

[a] Analysis of 10-g samples gave 5·2 and 5·2 ppm of Co.

[b] Analysis of 5-g samples gave 22·7 and 24·7 ppm of Co.

[c] Nominal values for BeO are based on additions to base material, for Be on chemical analysis.

Zusammenfassung—Eine Methode zur Bestimmung von Cobalt in Beryllium oder Berylliumoxyd durch Extraktion von Cobalthiocyanat mit Acetylacetone (2:4-Pentandion) wird beschrieben. Die Methode ist auf ± 2% oder 2 Mikrogramm genau, was immer der höhere Wert ist. Von 68 studierten Fremdionen stören lediglich Mangan und Chrom in Mengen von 10 mg. Keine Störungen wurden festgestellt wenn 1 g deise beideu Ionen durch Ionenaustauscher oder Verfluchtigen (im Falle von Chrom) vor der Extraktion entfernt wurden.

Résumé—Les auteurs décrivent une méthode de dosage du cobalt dans le beryllium ou l'oxyde de beryllium par extraction du complexe thiocyanate de cobalt par l'acétylacétone (2–4 pentanedione). La méthode est précise à ±2% près ou jusqu'à 2 microgrammes de cobalt. Parmi les 68 éléments étudiés, seuls le manganèse et le chrome gênent pour des quantités de 10 mg. Aucune gêne n'est observée quand 1 g de chacun de ces corps a été éliminé par échange d'ion ou volatilisation (du chrome seulement) avant l'extraction.

REFERENCES

[1] J. O. Hibbits, W. F. Davis, and M. R. Menke, *Talanta*, 1960, **4**, 61.
[2] W. B. Brown and J. F. Steinbach, *Analyt. Chem.* 1959, **31**, 1805.

Talanta, 1960, Vol. 5, pp. 254 to 259. Pergamon Press Ltd. Printed in Northern Ireland

ANALYTICAL APPLICATIONS OF XYLENOL ORANGE—V*

A SPECTROPHOTOMETRIC STUDY OF THE BISMUTH-XYLENOL ORANGE COMPLEX

K. L. CHENG
RCA Laboratories, Princeton, N.J., U.S.A.

(*Received* 28 *June* 1960)

Summary—The red bismuth-Xylenol Orange complex has been studied spectrophotometrically. It offers a sensitive and selective reaction for determining traces of bismuth. The complex has an absorption maximum at 540 to 545 mμ and requires a rather narrow acidity range (0·08 to 0·15*N*) for maximum colour development. It is a 1:1 complex and has a formation constant of $2{\cdot}8 \times 10^5$ under the conditions studied. Chloride masks the complex.

XYLENOL Orange forms a red coloured complex with bismuth in an acid medium. The coloured complex is stable and can be used as a basis for the determination of traces of bismuth. This paper reports on the conditions for the colour development of the complex, its composition, its formation constant, and the interference. Since only chloride masks the bismuth-Xylenol Orange complex,[1] bismuth may be determined selectively based on this specific masking.

APPARATUS AND REAGENTS

Standard bismuth solution

Appropriate standard solutions were prepared from a stock bismuth solution in 1*N* sulphuric acid. The stock solution from pure bismuth metal was standardised by EDTA titration.[2] From the stock solution, a 20 μg per ml bismuth solution was prepared in 0·1*N* sulphuric acid solution containing 0·15 g of tartaric acid per litre.

Other apparatus and reagents are the same as those reported previously.[1]

PROCEDURE

Calibration curve

Pipette 20 to 100 μg of bismuth into a 25-ml calibrated flask. Add 4 ml of 0·05% Xylenol Orange in 0·1*N* sulphuric acid, dilute to the mark with 0·1*N* sulphuric acid and mix. Measure the absorbance at 545 mμ using the reagent blank. Beer's law is followed. The molar absorptivity was found to be 24,000.

RESULTS

Absorption spectra

The spectra for Xylenol Orange and its bismuth complex are shown in Fig. 1. The maximum absorption of the complex is at 540 to 545 mμ.

Effect of acidity

Fig. 2 shows that the optimum sulphuric acid concentration for the colour development of the bismuth complex is 0·08 to 0·15*N*. In general, perchloric acid

---

* Part IV: *Talanta*, 1959, **3**, 147.

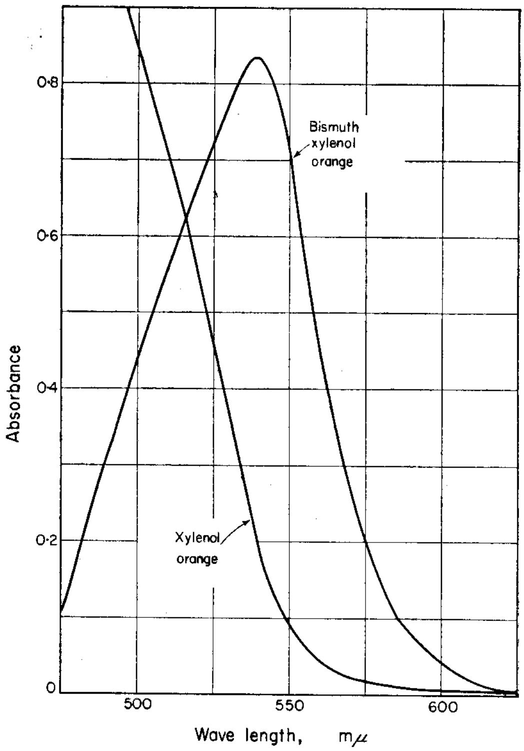

Bismuth
xylenol
orange
Xylenol
orange
Absorbance
0·8
0·6
0·4
0·2
0
500
550
600
Wave length, mμ

FIG. 1.

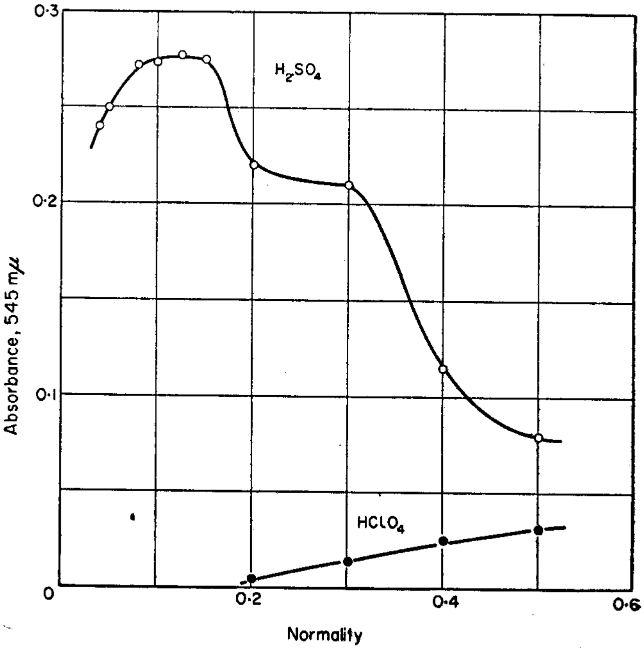

H_2SO_4
$HClO_4$
Absorbance, 545 mμ
0·3
0·2
0·1
0
0·2
0·4
0·6
Normality

FIG. 2.

inhibits the formation of the bismuth-Xylenol Orange complex; however, the absorbance increases slightly above 0·2N perchloric acid. As expected, hydrochloric acid can completely mask the formation of the bismuth-Xylenol Orange complex.

Effect of amount of Xylenol Orange

Fig. 3 shows that for 120 μg of bismuth, 3 to 4 ml of 0·05% Xylenol Orange solution are required. Contrary to the previous cases of the colour development of the Xylenol Orange complexes of zirconium, hafnium, and iron, large amounts (more than 4 ml of 0·05%) of Xylenol Orange do not tend to decrease the absorbance.

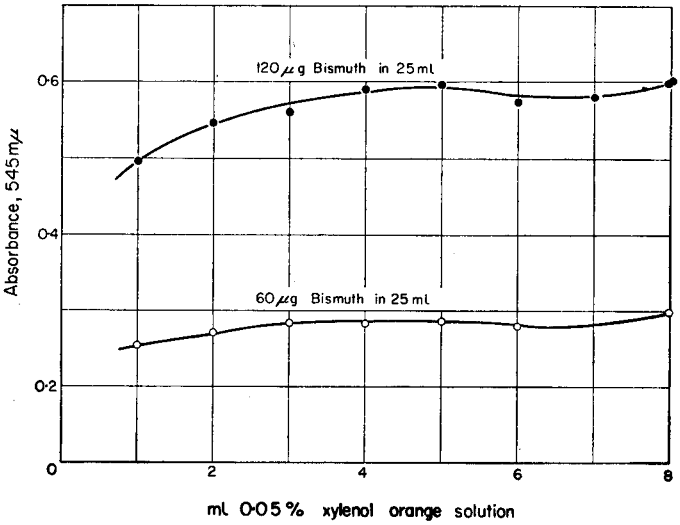


FIG. 3.

Complex formation

Like zirconium, hafnium, and iron, bismuth also forms a 1:1 complex with Xylenol Orange as indicated by Job's method (Fig. 4). The formation constant was calculated from the curves shown in Fig. 4, based on the method used previously.[3] It was found to be $2{\cdot}8 \times 10^5$ in 0·1N sulphuric acid. Because of its low formation constant, it is easily understood why Xylenol Orange has been successfully used as an indicator in the EDTA titration of bismuth in a rather acidic medium.

Effect of chloride

It is well known that halides form quite strong complexes with bismuth. Approximately 14 millimoles of chloride are required to completely mask 40 μg of bismuth, and 16 millimoles for 100 μg of bismuth. Since chloride does not affect the colour of the Xylenol Orange complexes of zirconium, hafnium, and iron, tin, etc., such specific masking by chloride may be used to determine bismuth in the presence of other metals which also give coloured complexes with Xylenol Orange. For instance, the determination of bismuth in the presence of zirconium may be conducted by measuring the change in the absorbance of the sample solution caused by the addition of chloride. The change is equivalent to the bismuth present (see Table I).

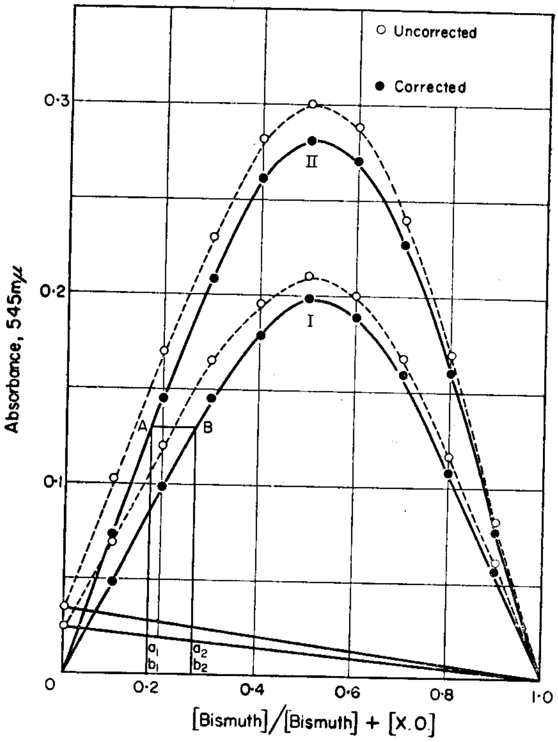


FIG. 4.

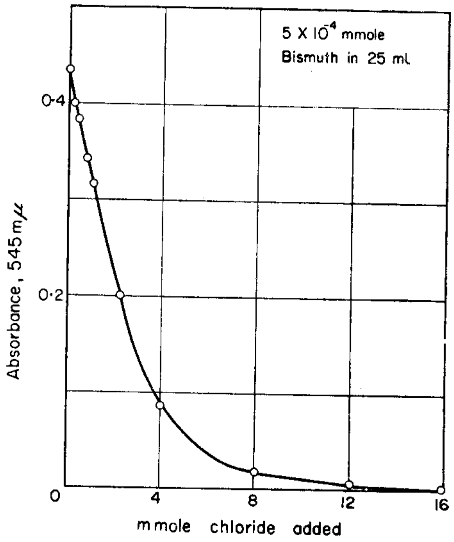


FIG. 5.

Effect of tartaric acid

Fig. 6 shows that tartaric acid has a slight effect on the absorbance. Citric acid shows a similar effect. Both tartaric acid and citric acid mask the Xylenol Orange

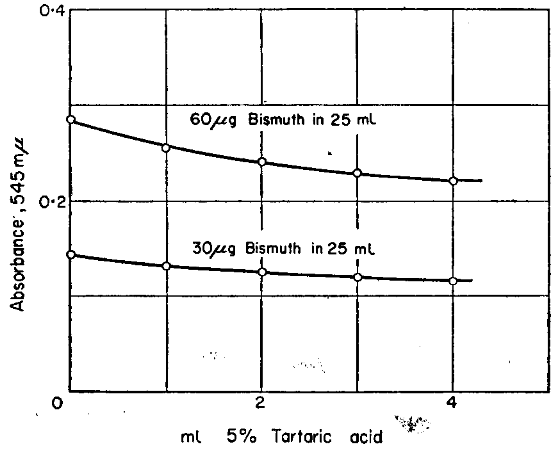


FIG. 6.

complexes of zirconium, hafnium, tin, and antimony (Xylenol Orange is insensitive to antimony). In the case of determining bismuth in the presence of tin, citric acid or tartaric acid may be added as a masking agent; however, approximately the same amount of citric acid or tartaric acid should also be added to the standard bismuth solution in order to compensate for its effect.

TABLE I. EFFECT OF FOREIGN IONS

Taken: 40 μg of bismuth

Ion	Amount added	Bismuth recovery, %	Remark
Aluminium	1 mmole	100·0	
Manganese^{II}	1 mmole	100·1	
Niobium	5×10^{-4} mmole	100·5	1 mmole citric acid added
Niobium	5×10^{-4} mmole	244	no citric acid added
Molybdenum^{VI}	0·1 mg	191	no H_2O_2 added
Molybdenum^{VI}	0·1 mg	101·1	3 ml 30% H_2P_2 added
Antimony^{III}	1×10^{-3} mmole	130	
Antimony^{III}	1×10^{-3} mmole	99·5	1 mmole citric acid added
Tin^{II}	5×10^{-4} mmole	265	
Tin^{II}	5×10^{-4} mmole	101·5	1 mmole citric acid added
Iron^{III}	40 μg	99·2	2 ml 1% ascorbic acid added
Zirconium	10 μg	180	
Zirconium[a]	10 μg	102·5	

[a] When determining bismuth in the mixture of bismuth and zirconium, two equal aliquots were used; to one was added 14 mmoles of chloride and to the other no chloride was added. The bismuth was calculated based on the difference between the two absorbances obtained.

Interference study

Only a few metals in a $0{\cdot}1N$ sulphuric acid medium produce a red colour with Xylenol Orange.[1] Table I indicates the extent of the effect of these interfering ions on the determination of bismuth. Some of the interfering metals can be completely or partially masked by appropriate masking agents. Fluoride and thioglycollic acid show a slight masking effect on the bismuth-Xylenol Orange complex.

The Xylenol Orange solution and its bismuth complex are stable for at least 1 week without appreciable change. The dithiocarbamate method for bismuth[4] is sensitive and highly selective, but its bismuth complex is not very stable. It was found that the Xylenol Orange method is simple and sensitive for the determination of traces of bismuth in bismuth-manganese thin film used in the electronic industry.

Zusammenfassung—Der rote Wismut-Xylenolorange-Komplex wurde photometrisch untersucht. Er bildet die Grundlage zu einer empfindlichen und selektiven Wismutbestimmung. Der Komplex zeigt ein Absorptionsmaximum bei 540–545 mμ und benötigt einen ziemlich nahen Aciditätsbereich (0·08–0·15 n) zur höchsten Farbentwicklung. Der Komplex hat die Zusammensetzung 1:1 und eine Bildungskonstante von $2{\cdot}8 \times 10^5$ (unter den studierten Bedingungen). Chlorid maskiert.

Résumé—Le complexe rouge bismuth-xylénol orange a été étudié par spectrophotométrie. Il offre une réaction sensible et sélective pour le dosage de traces de bismuth. Le complexe a un maximum d'absorption à 540–545 mμ et nécessite un domaine d'acidité assez étroit (0,08 à 0,15 N) pour obtenir une coloration maximum. C'est un complexe 1-1 qui a une constante de formation de $2{,}8 \cdot 10^5$ dans les conditions indiquées. Le chlorure masque le complexe.

REFERENCES

[1] K. L. Cheng, *Talanta*, 1959, **2**, 61.
[2] *Idem, Analyt. Chem.*, 1954, **26**, 1977.
[3] *Idem, Talanta*, 1959, **2**, 266.
[4] *Idem, Analyt. Chem.*, 1955, **27**, 24.

Talanta, 1960, Vol. 5, pp. 260 to 263. Pergamon Press Ltd. Printed in Northern Ireland

THE FLUOROMETRIC DETERMINATION OF *o*-PHTHALIC ACID

GLEN A. THOMMES* and ELMER LEININGER
Kedzie Chemical Laboratory, Michigan State University, East Lansing
Michigan, U.S.A.

(*Received* 15 *July* 1960)

Summary—A fluorometric procedure for the determination of *o*-phthalic acid by conversion to fluorescein is described. The optimum amount of *o*-phthalic acid for application of the method is 50–5000 μg. The determination can be carried out with a relative error of less than 5% even when significant quantities of common *o*-phthalic acid contaminants are present.

THE condensation of 1:2-dicarboxylic acids with resorcinol to yield dyes of the fluorescein type has been noted by Feigl[1] and the fluorescent compounds formed have been used for the qualitative identification of 1:2-dicarboxylic acid structures.

Barr[2] has made a successful quantitative application of this type of reaction in developing fluorometric procedures for the determination of succinic and malic acids.

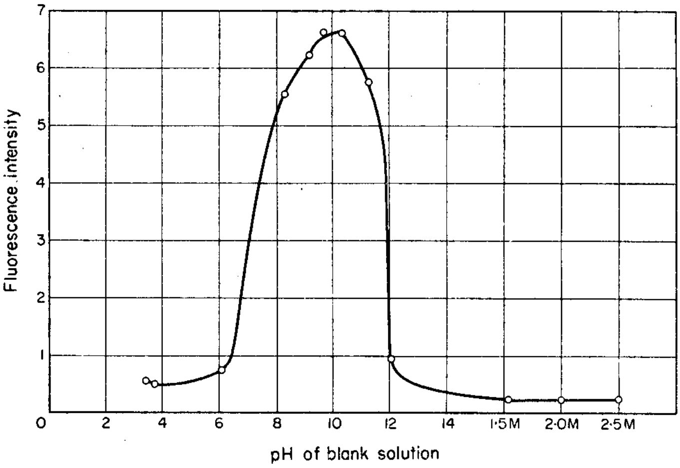


FIG. 1.—Effect of pH on blank fluorescence.

In attempting to apply this reaction to the quantitative determination of *o*-phthalic acid, difficulty was encountered in controlling the deep blue blank fluorescence resulting from the reaction between resorcinol and concentrated sulphuric acid. The fluorescence resulting from this reaction is so intense that the reaction has been recommended by Denigés[3] as a qualitative test for the identification of resorcinol. Fortunately, however, the blank fluorescence intensity is highly dependent upon pH (Fig. 1) while the greenish-yellow fluorescence of fluorescein solutions is completely pH independent above pH 6 (Fig. 2). Consequently, if the fluorescence intensity

---

* Present address: E. I. du Pont de Nemours and Co., Inc., Photo Products Department, Parlin, New Jersey, U.S.A.

measurements are made in strongly alkaline solution, the blank fluorescence is almost completely suppressed and does not interfere with the determination.

Both Feigl and Barr recommend the use of freshly sublimed resorcinol as a means of minimising blank fluorescence. This procedure did not appreciably lower the blank fluorescence in strongly alkaline (2*M* NaOH) solution as is shown by the comparative results in Table I. The samples used in this study were 1·0-ml aliquot portions of an *o*-phthalic acid solution containing 1·0 mg per ml.

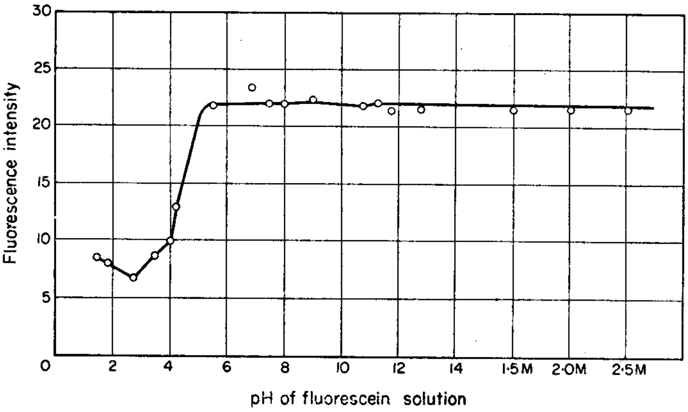


FIG. 2.—Effect of pH on sample fluorescence.

The difference noted between the average results obtained is deemed insignificant because it is within the limits of reproducibility of the method.

The elimination of the sublimation procedure from the method reduces the time required for the over-all procedure by approximately two and one-half hours.

TABLE I. SUBLIMED RESORCINOL VS UNSUBLIMED

Freshly Sublimed		Unsublimed (C.P.)	
Sample fluorescence*	Blank fluorescence*	Sample fluorescence*	Blank fluorescence*
14·3	0·12	14·5	0·21
14·5	0·11	14·3	0·21
14·5	0·12	14·5	0·15
14·3	0·20	14·5	0·19
14·5	0·30	14·0	0·24
14·5	0·20	14·5	0·24
14·5	0·22	14·2	0·18
Ave. = 14·44	Ave. = 0·18	Ave. = 14·36	Ave. = 0·20

* Instrument readings.

REAGENTS AND INSTRUMENTS

The reagents required are: chemically pure resorcinol, pure concentrated sulphuric acid and a solution of approximately 2*M* sodium hydroxide.

The direct reading fluorometer used was constructed in this laboratory employing the line operated

Photovolt Electronic Photometer, model 501-M, in conjunction with a cell compartment and lamp-housing constructed along the lines suggested by C. E. White.[4] The photometer was equipped with the Photovolt "C" phototube which has maximum sensitivity in the range 300–600 mμ.

The primary filter employed was the Corning No. 5840 and the secondary filter combination consisted of the Green Corning Filter No. 4015 used in conjunction with the ultraviolet filter from the Lumetron Model 402-EF instrument. This filter was employed to prevent scattered ultraviolet light from striking the photocell.

EXPERIMENTAL PROCEDURE

An aqueous solution of *o*-phthalic acid should be used. Therefore, if a solid sample is to be determined, dissolve a weighed amount in a measured volume of water, using a small amount of sodium hydroxide to effect solution if necessary.

A 1·0-ml aliquot of the aqueous sample solution is pipetted into a 5-ml beaker and 0·04 ml of pure concentrated sulphuric acid is added with a graduated 1-ml pipette. Approximately 5–10 mg of chemically pure resorcinol is added, the mixture is thoroughly stirred to promote solution of the resorcinol, and the samples are placed in an oven (125°), for 1·5 hr. At the completion of this reaction period, the samples are removed from the oven and allowed to cool to room temperature. The reaction products in the beaker are taken up in distilled water and quantitatively transferred to a 200-ml volumetric flask. If a high concentration of *o*-phthalic acid is present in the sample, some difficulty may be encountered in dissolving the reaction products. However, addition of a small amount of dilute sodium hydroxide readily effects solution. Dilution to 200 ml is made with distilled water and a 10-ml aliquot portion of this solution is transferred to a 100-ml volumetric flask. Dilution to 100 ml is made with $2M$ sodium hydroxide. This solution is then used for the fluorescence intensity measurement. The double dilution is used to minimise blank fluorescence, which is significant in more concentrated solution.

To obtain the fluorescence intensity of the sample, the fluorometer is adjusted to give a zero reading with distilled water and the fluorescence intensity of the sample solution is read relative to this setting. If a null-point type instrument, such as the Lumetron model 402-EF, is used for the fluorescence intensity measurements, a standard solution must be used to obtain a 100% setting. A fluorescein solution, of appropriate concentration for the range being studied, is sufficiently stable for this purpose.

After the fluorescence intensity of the solution has been measured, the quantity of *o*-phthalic acid treated originally is found by comparison of the intensity value with a calibration curve.

No correction is applied for blank fluorescence because it is relatively constant and is incorporated in the calibration curve. However, it is wise to prepare a blank as a control for each group of samples determined.

The calibration curve is prepared by treating *o*-phthalic acid solutions of known concentrations as described above, and determining their fluorescence intensities. Primary standard grade potassium acid phthalate can conveniently be used to prepare standard solutions for preparation of the calibration curve.

DISCUSSION AND RESULTS

The optimum concentration range that can be covered by the method is 50–5000 μg of *o*-phthalic acid per 1-ml aliquot reacted. With samples containing less than 50 μg the contribution of the blank fluorescence becomes significant and poor reproducibility of sample fluorescence results. Above 5000 μg the linearity of the fluorescence versus concentration plot falls off rapidly and poor reproducibility again results.

The results obtained with some prepared unknowns are shown in Table II. The samples were in all cases aqueous solutions of *o*-phthalic acid, and where contaminants were added, the aqueous *o*-phthalic acid solution was saturated with the contaminant.

The contaminants selected are those which might be expected as by-products if *o*-phthalic acid were prepared by oxidation of impure *o*-xylene or naphthalene. The results indicate that none of the contaminants grossly affect the method. However, the presence of α-naphthoquinone causes an orange-red colour in the reaction solution

TABLE II

Contaminant	Taken, μg	Found. μg	% Error
None	140	139	−0·7
None	219	227	+3·6
None	579	585	+1·0
None	1080	1090	+0·9
m- and *p*-Phthalic acid	500	494	−1·2
Benzoic acid	1000	990	−1·0
α-Naphthoquinone	1000	975	−2·5
Benzoic acid and α-naphthoquinone	1000	950	−5·0

which is accompanied by a slight decrease in fluorescence intensity and leads to consistently low results. This effect is particularly noticeable in solutions saturated with both benzoic acid and α-naphthoquinone.

Zusammenfassung—Ein fluorimetrische Methode zur Bestimmung von o-Phthalsäure durch Überführung in Fluorescein wird beschrieben. Der optimale Mengenbereich ist 50–5000 μg. Die Bestimmung kann auf 5% genau ausgeführt werden, selbst wenn beträchtliche Mengen der in o-Phthalsäure überlicherweise anwesende Verunreingungen vorhanden sind.

Résumé—Les auteurs décrivent une méthode fluorométrique de dosage de l'acide o-phtalique par transformation en fluorescéine. La quantité optimum d'acide o-phtalique pour l'application de cette méthode est de 50–5000 μg. Le dosage peut être effectué avec une erreur relative de moins de 5 pour cent même quand des quantités importantes d'impuretés courantes de l'acide o-phtalique sont présentes.

REFERENCES

[1] F. Feigl, *Qualitative Analysis by Spot Tests*. Nordheim Publishing Co., Inc., New York, 1939, p. 299.
[2] C. G. Barr, *Plant Physiology*, 1948, **23**, 443–454.
[3] G. Denigés, *Rev. Asoc. Bioquim. Argentina*, 1949, **14**, 3–8.
[4] C. E. White, *Selected Topics in Modern Instrumental Analysis*, D. F. Boltz, Editor. Prentice-Hall Inc., New York, 1952, p. 83.

Talanta, 1960, Vol. 5, pp. 264 to 266. Pergamon Press Ltd. Printed in Northern Ireland

PRELIMINARY COMMUNICATION

Indirect neutron absorptiometry

(*Received* 4 *August* 1960)

It is possible to utilise the absorption of neutrons for analysis just as the absorption of electromagnetic radiation is used for other methods. In the past few years, some work of this type has been reported in the literature[1–6] but in general this method has had little acceptance except for the analysis of boron.

The tendency for an element to absorb thermal neutrons is indicated by a "thermal neutron absorption cross-section". Table I lists these cross-sections for the 20 elements which are the best neutron absorbers. It is interesting to note that most of these elements, particularly those with the highest cross-sections, are rather exotic elements not often encountered in the majority of analytical laboratories.

TABLE I. THERMAL NEUTRON ABSORPTION CROSS-SECTIONS[7]

Element	Cross-section, *barns*
Gadolinium	46,000
Samarium	5,500
Europium	4,600
Cadmium	2,550
Dysprosium	1,100
Boron	750
Iridium	430
Mercury	380
Indium	190
Rhodium	150
Thulium	118
Hafnium	105
Lutetium	108
Gold	98
Rhenium	84
Lithium	71
Holmium	64
Silver	62
Neodymium	46
Terbium	44

The application of neutron absorptiometry to the analysis of boron appears to have filled a need for a rapid, non-destructive, and on occasion "in-line"[8,9] method for macro amounts of this element. From Table I we see, however, that there are several elements for which the method would be much more sensitive and for which there would be less potential interference. Indeed, the element gadolinium would be some 60 times more sensitive than boron and almost 10 times better than any other element in the periodic system.

We are studying a technique for utilising this unique neutron absorption property in the analysis of common elements such as fluorine. This technique, which we call "Indirect Neutron Absorptiometry", is analogous to radiometric analysis in that neutron absorbing elements are utilised in the determination of elements which do not themselves absorb neutrons.

In a typical procedure, fluoride ions in solution are precipitated with an excess of gadolinium ions. Gadolinium ions adsorbed on the precipitate are washed off or eliminated by a dissolution and reprecipitation. Neutron absorption measurements are then made either on the dissolved precipitate or on the liquid residue. The neutron-absorbing gadolinium measured thus represents a stoichiometric amount of fluoride.

The sensitivity obtainable is quite dependent upon the geometry of the neutron source, sample container and neutron detector within the assembly. At present a modified Nuclear-Chicago Neutron Howitzer is being used with a 5-curie plutonium-beryllium source. This permits a bottled liquid sample to be placed between the source and the detector. We are, however, assembling a modified apparatus in which the sample solution is contained in a Marinelli-type beaker surrounding the small neutron detector tube. This should eliminate much of the scattered neutron radiation which now reaches the detector without "seeing" the sample. By improving the geometry we should also increase the sensitivity of the method.

Preliminary results indicate that the idea of indirect neutron absorptiometry is sound and that values reproducible to within a few per cent can be obtained rapidly by this technique. Even with relatively poor geometry it is possible to analyse for milligram amounts of fluoride and it should be possible to improve this sensitivity with the new apparatus being assembled. This method should also be applicable to the analysis of other ions which form insoluble compounds with gadolinium. It may even be possible to analyse for potassium as the tetraphenylborate by this technique.

Indirect neutron absorptiometry is a non-destructive method which utilises encapsulated sources only and does not require handling of radioactive solutions. In this respect it presents no more problems than the thousands of thickness, density and level gauges used routinely in industry at the present time. Furthermore, it utilises the same principles of absorptiometry already so familiar to the analytical chemist—only the type of radiation is different.

Work is continuing on this method to elaborate the areas of analysis in which it will be most useful. Detailed evaluation of procedures and equipment will establish limits of sensitivity, as well as point up problems of contamination, manipulation, and the like. It appears now, however, that this indirect approach to neutron absorption has considerable potential for the average analytical laboratory.

Acknowledgement—The author enjoyed many fruitful discussions with G. W. Leddicotte and J. E. Strain on the general topic of neutron absorption during a leave at Oak Ridge National Laboratory in the Spring of 1960. The work was partially supported by the U.S. Atomic Energy Commission.

W. Wayne Meinke

Department of Chemistry
University of Michigan
Ann Arbor, Michigan, U.S.A.

Summary—A preliminary account is given of the use of the neutron absorption of suitable elements (such as gadolinium) for the determination of non-absorbing elements (such as fluorine) by measuring the absorption of a dissolved precipitate (in the case quoted, gadolinium fluoride). This indirect determination by neutron absorption gives reproducible results rapidly and non-destructibly. The applications of the method are being studied.

Zusammenfassung—Eine Vorläufige Mitteilung über die Anwendung von Neutronenabsorbtion wird gegeben. Geeignete Elemente wie z.B. Gadolinium zönnen zur Bestimmung von nichtabsorbierenden Elementen z.B. Fluor herangezogen werden, indem die Absorbtion eines Niederschlages (im Beispielsfalle Gadoliniumfluorid) gemessen wird. Die Indirekte Bestimmung durch Neutronenabsorbtion gibt rasch reproduzierbare Resultate. Weitere Anwedungsmöglichkeiten der Methode werden studiert.

Résumé—L'auteur donne un compte-rendu préliminaire sur l'utilisation de l'absorption des neutrons par des éléments convenables (tels que le gadolinium) pour le dosage d'éléments non absorbants (tels

que le fluor) par la mesure de l'absorption d'un précipité convenable (dans le cas cité, fluorure de gadolinium). Le dosage indirect par absorption de neutrons donne rapidement des résultats reproductibles et n'altère pas l'échantillon. Les applications de cette méthode sont étudiées actuellement.

REFERENCES

[1] I. H. Ford and E. E. Picciotto, *Nuovo cimento*, 1952, **2** (9), 141.
[2] R. P. Hamlen and W. S. Koski, *Analyt. Chem.*, 1956, **28**, 1631.
[3] V. K. Khristianov and G. I. Panov, *Zhur. Anal. Khim.*, 1957, **12**, 362.
[4] V. K. Khristianov, G. I. Panov and A. A. Chernova, *Geokhimiya*, 1957, **2**, 95.
[5] D. D. DeFord and R. S. Braman, *Analyt. Chem.*, 1958, **30**, 1765.
[6] Y. Kusaka, *Bull. Chem. Soc. Japan*, 1958, **31**, 917.
[7] W. H. Sullivan, *Trilinear Chart of Nuclides*, 2nd Edition. U.S. Government Printing Office, Washington 25, D.C., 1957.
[8] *Chem. Eng. News*, 1957, **35**, No. 23, 52.
[9] Mine Safety Appliances Co. Bulletin, *M-S-A Boron Analyzer*, 210 North Braddock Ave., Pittsburgh 8, Pennsylvania.

Talanta, 1960, Vol. 5, pp. 267 to 287. Pergamon Press Ltd. Printed in Northern Ireland

SHORT COMMUNICATIONS

The application of the cathode ray polarograph to the analysis of explosives—III

Simultaneous determination of nitroglycerine and dinitroglycol

(*Received* 1 *February* 1960)

In a previous paper[1], details are given of the determination of nitroglycerine (NG) in various explosive mixtures without explanation of the electrode process involved in its reduction. In the present paper, a polarographic technique is described for the determination of NG and dinitroglycol(EGDN) in mixtures containing both explosives. The mechanism of the reduction process for NG is discussed. The simplicity of the determination of NG described in the previous paper provided the basis for investigating a method for the determination of EGDN in presence of NG.

It has been found that in a base electrolyte consisting of aqueous KCl and NH_4Cl, EGDN is reduced with the formation of two waves. NG is also reducible, forming 3 waves, the first of which closely precedes both waves of EGDN and cannot be separated using direct current. The second and third waves of NG coincide with the waves of EGDN. Applying derivative current, the three waves are well separated, allowing the possibility of the determination of both compounds.

EXPERIMENTAL

0·1, 0·2, 0·3 and 0·4 Ml of a standard solution of EGDN in methanol (2 mg/ml) were introduced into 10-ml flasks, made up to the mark with a base electrolyte consisting of 10 ml of *N* KCl, 50 ml of 2*N* NH_4Cl, and 40 ml of water (pH 6) and shaken well. For measurement, 5 ml of solution was transferred to a polarographic cell. The polarograms were recorded with a starting potential of −0·2 V, after de-aerating with nitrogen. The diffusion currents of EGDN were observed at peak potentials −0·44 V and −0·62 V. Both waves are quantitative. Applying direct current, the total height of both waves can be used to estimate the concentration of EGDN (Fig. 1) and applying derivative current, either of the wave heights can be used (Fig. 2), measuring the left-hand side of the first wave and the right-hand side of the second. The results are tabulated below.

TABLE I.—WAVE HEIGHTS OF DINITROGLYCOL

Dinitroglycol, μg	Wave heights, *divisions*		
	Direct current	Derivative current	
	Total wave height	First wave	Second wave
100	12	7·5	3·5
200	22·5	15·5	7
300	33·5	22	9
400	44	29	13

The wave heights are measured in divisions of the graticule, where 9 cm are divided into 50 divisions. The scale factor on direct current was 6·0 and on derivative current 0·06. The mercury pool was used as the reference electrode throughout at a constant temperature of 25°.

The effect of the presence of NG on the reduction of EGDN was investigated. The addition of 100 μg of NG to the above samples (100–400 μg EGDN) increases the second EGDN wave by approximately 1 % and depresses the first (Fig. 3).

Working with calibration graphs prepared from synthetic samples, with a selected range of concentration of both explosives, a simple and accurate determination of NG and EGDN can be achieved. In exceptional cases, where the determination of NG is required in a large excess of EGDN, it is only necessary to modify the method by the addition of pyridine to the base electrolyte. It has been found that EGDN is not reducible in the presence of pyridine, although the reduction of NG results in the formation of a single wave. Such a phenomenon is of great interest in the analysis of both compounds, since it allows the possibility of determining NG in the presence of a large excess of EGDN.

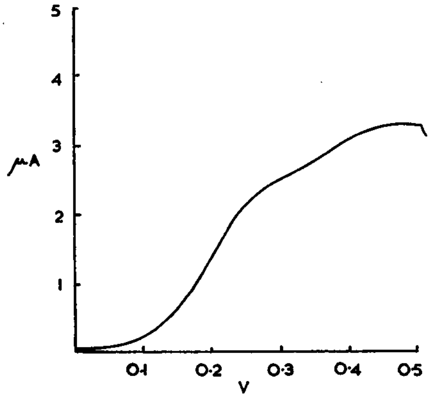


FIG. 1.—300 μg dinitroglycol. Direct current

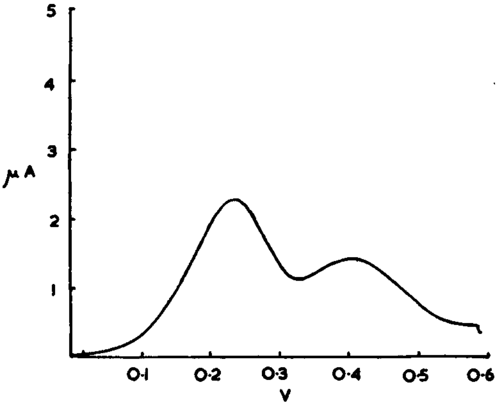


FIG. 2.—300 μg dinitroglycol. Derivative current

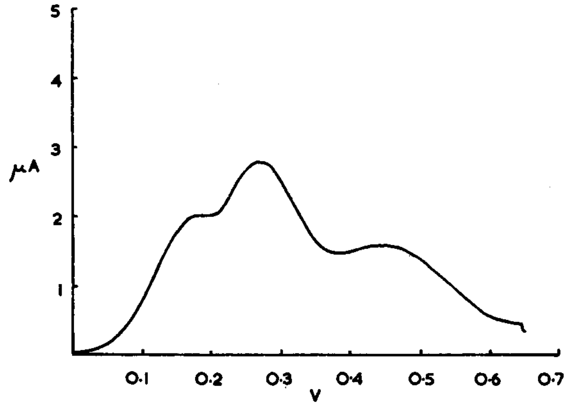


FIG. 3.—300 μg nitroglycerine, 300 μg dinitroglycol

Procedure

The main components of blasting explosives are ammonium nitrate (30–70%) and sodium chloride (10–40%). Introduce 0·5 g of sample into a 50-ml flask, shake with 25 ml of methanol, and make up to the mark with water. Transfer 1 ml to a 10-ml flask, make up to the mark with base electrolyte, and record the polarogram on a 5-ml aliquot, after de-aerating with nitrogen for 5 min. Record the NG wave and the first EGDN wave with a starting potential of —0·15 V, and the two EGDN waves with a starting potential of —0·3 V, using a scale factor of 0·06.

The concentrations of NG and EGDN given in Table II were obtained by comparison with a standard sample prepared in the following way. 300 mg of ammonium nitrate and 140 mg of sodium chloride were introduced into a 50-ml flask, 25 ml of a standard solution of NG in methanol (2 mg/ml) and 6·25 ml of the standard solution of EGDN were added, and made up to the mark with water, thus making the concentrations of NG and EGDN, 10% and 2·5% respectively; 1 ml was transferred into a 10-ml flask, made up to the mark with base electrolyte and the polarograms recorded as before.

TABLE II. NITROGLYCERINE AND DINITROGLYCOL IN BLASTING EXPLOSIVES.

	% in sample I		% in sample II	
	Actual*	By comparison	Actual*	By comparison
Nitroglycerine	9·4	9·6	11·3	11·6
Dinitroglycol	2·3	2·4	2·8	2·7

* Percentages as found at I.C.I. Laboratories, Nobel Division.

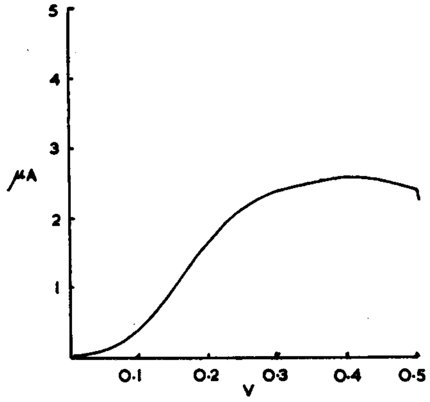


FIG. 4.—200 μg nitroglycerine. Direct current

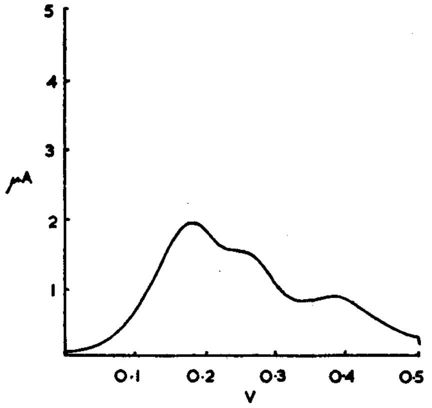


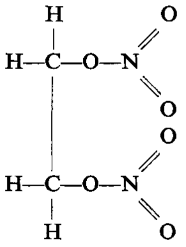
FIG. 5.—200 μg nitroglycerine. Derivative current

DISCUSSION

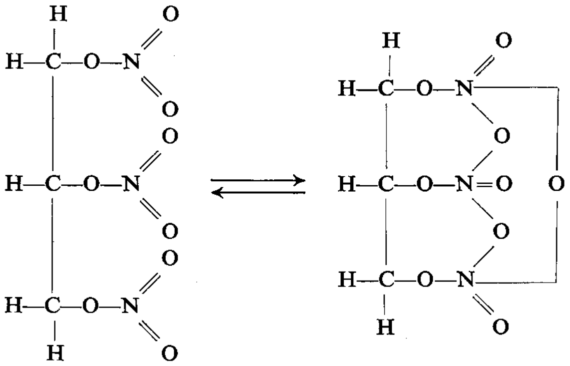
The mechanism of reduction of polynitrate esters has been investigated by Whitnack *et al*[2]. They show that the reduction is independent of pH, and that the number of electrons involved in the reduction is two for each O—NO_2 group in the molecule. In the base electrolyte used above, the reduction of EGDN results in the formation of two waves, as is expected, due to the presence of two O—NO_2 groups. The reduction of NG produces three clearly marked waves at peak potentials −0·35 V, −0·44 V, and −0·62 V (Figs. 4 and 5).

The addition of 0·5 ml of pyridine to 5 ml of base electrolyte containing NG changes the reaction mechanism, resulting in the formation of a single wave at peak potential −0·27 V. The addition of the same amount of pyridine to a solution containing EGDN completely removes both waves, indicating the irreducibility of EGDN under these conditions.

The addition of pyridine increases the pH of the solution from 6 to 7·3. Originally it was believed that the change in reaction mechanism was due to the change in pH. The effect of pH was further investigated. A water solution of 0·4M trihydroxymethyl-aminomethane was prepared and 0·1, 0·2 and 0·3 ml were added to 5 ml of base electrolyte containing both NG and EGDN, the resulting pH values were 7·4, 7·8, 8·0. No alteration of the reduction waves was observed, confirming the investigation of Whitnack. This behaviour may be explained by a consideration of the structures:



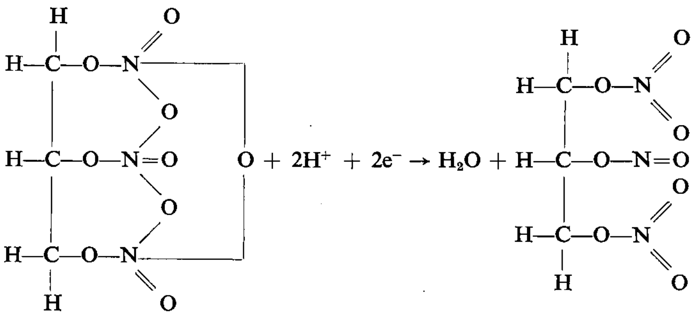
Dinitroglycol



(I) Stable (II) Labile

Nitroglycerine.

Assuming that the second tautomeric form[3,6] is stable in pyridine, it is possible that the oxygen link between the two external nitrogen atoms is more exposed to chemical reaction, involving a two-electron reduction, at the cost of the secondary O—NO_2 group



For EGDN, no configuration similar to that of NG is possible, and this could explain the irreducibility in the presence of pyridine. Work on the mechanism of the reaction, including the determination of the number of electrons taking place in the reduction of EGDN, is in progress and will be published in a future paper.

J. S. Hetman

Southern Instruments Limited
Camberley, Surrey, England

Summary—A polarographic method for the determination of nitroglycerine and dinitroglycol in mixtures containing both of these substances is described. The nature of the reductions involved is discussed.

Zusammenfassung—Eine polarographische Methode zur Bestimmung von Nitroglyzerin und Dinitroglycol in Mischungen beider wird beschrieben. Die Reduktionsreaktionen werden diskutiert.

Résumé—Une méthode polarographique de dosage de la nitroglycérine et du dinitroglycol dan des mélanges contenant ces deux substances est décrite. La nature des réductions mises en jeu est discutée.

REFERENCES

[1] J. S. Hetman, *The Application of the Cathode Ray Polarograph to the Analysis of Explosives. Part I., Determination of Nitroglycerine.* International Congress of Polarography, Cambridge, 1959.
[2] G. C. Whitnack, J. M. Nielsen and E. St. C. Gantz, *J. Amer. Chem. Soc.* **76,** 4711, 1954.
[3] Ph. Naoúm and A. Berthmann, *Explosivstoffe.* Carl Hanser Verlag. München. 1954, p. 26.
[4] A. Stettbacher, *Spreng-und Schiesstoffe.* Rascher-Verlag, Zürich, 1948.
[5] T. L. Davis, *The Chemistry of Powder and Explosives.* John Wiley and Sons Inc., New York, 1956 p. 207.
[6] W. Taylor, *Modern Explosives.* Royal Inst. Chem. Monog, 1959, No. 5, 19.

Analytical applications of 3-acetyl-4-hydroxycoumarin—II*

Spectrophotometric determination of iron$^{\text{II}}$

(*Received* 18 *March* 1960)

Bhat and Jain[1] have recently used 3-acetyl-4-hydroxycoumarin for the determination of uranium and thorium and for their separation from each other as well as from rare earths. We have now found that this reagent may also be used successfully for the spectrophotometric determination of iron$^{\text{II}}$. Iron$^{\text{III}}$ gives, with this reagent, a yellowish tinge which is too faint for spectrophotometric investigations. When an alcoholic solution of the coumarin is added to an aqueous solution of an iron$^{\text{II}}$ salt, a deep orange-red complex, soluble in 50% (v/v) ethanol is obtained. The colour of the complex is stable for several days and is not affected by temperature variations between 5° and 40°. The complex obeys the Lambert-Beer law at 400 mμ in the concentration range 1·5–5·3 ppm of iron. The intensity of the colour does not vary between pH 2·8 and 4·3.

EXPERIMENTAL

Reagents

3-*Acetyl*-4-*hydroxycoumarin:* 3-Acetyl-4-hydroxycoumarin, prepared as outlined previously,[1] was purified to a colourless crystalline product by sublimation at 75–85° under reduced pressure. 204·2 Mg of this material were dissolved in about 200 ml of ethanol, then diluted to 500 ml. The strength of the solution so obtained was 2×10^{-3} g mole/litre.

Standard solution of iron$^{\text{II}}$: Prepared by dissolving 784·3 mg of iron$^{\text{II}}$ ammonium sulphate (Pro Analysi E. Merck) in about 50 ml of 1% aqueous hydroquinone solution, then finally making

---

* For Part I see reference 1.

the volume to 1 litre with further hydroquinone solution of the same strength. The solution contained 2×10^{-3} g mole per litre of the iron$^{\text{II}}$ salt.

All other metal salts used were of either of A. R. quality or E. Merck Pro Analysi.

Apparatus

A Hilger U.V. spectrophotometer was employed for taking the absorption spectra of 3-acetyl-4-hydroxycoumarin and its iron$^{\text{II}}$ complex. The other spectrophotometric measurements were made with a Unicam Spectrophotometer S.P. 600.

The absorption cells had a light path of 10 mm. These cells could not be thermostated but all solutions were brought to a constant temperature of $30 \pm 0{\cdot}05°$ in a thermostat before measuring the optical density.

A Beckmann pH Meter Model H2 was used for measuring pH.

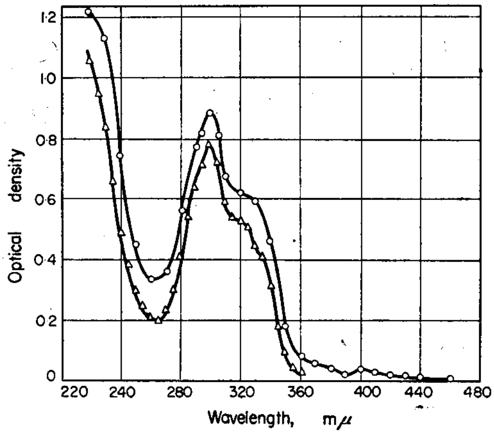


FIG. 1.—Δ-absorption spectrum of 3-acetyl-4-hydroxycoumarin. O-absorption spectrum of iron$^{\text{II}}$ 3-acetyl-4-hydroxycoumarin complex.

Absorption spectra

The absorption spectrum of 3-acetyl-4-hydroxycoumarin was taken in the ultraviolet region of the spectrum and the maximum absorption occurred at 300 mμ (Fig. 1). There was no absorption observed in the visible region.

The absorption spectrum of iron$^{\text{II}}$ 3-acetyl-4-hydroxycoumarin was taken in the ultraviolet as well as in the visible region of the spectrum. A maximum observed in the ultraviolet region at 300 mμ was obviously due to the reagent itself. At 400 mμ another maximum, though of low intensity, was also recorded (Fig. 1) even when the strength of the complex was extremely low as normally required for ultraviolet absorption studies. In the later part of the present investigations a strong absorption at 400 mμ was observed when adequate concentrations were employed, and thus the wavelength of 400 mμ was chosen for all spectrophotometric studies of the complex throughout this investigation.

Minimum amount of 3-acetyl-4-hydroxycoumarin necessary for determination of iron$^{\text{II}}$

The optical densities at 400 mμ of a series of solutions containing the coumarin and iron$^{\text{II}}$ in the mole ratio of 0·5:1 to 9:1 are plotted in Fig. 2; it is seen that the portion AB of the curve is a straight line up to the molar ratio of 5. For the determination of iron$^{\text{II}}$, however, the molar ratio of the coumarin to iron$^{\text{II}}$ was maintained at 8 in the subsequent studies. An excess of the reagent had no effect on the optical density of the complex.

Effect of pH on iron$^{\text{III}}$ *3-acetyl-4-hydroxycoumarin complex*

The effect of pH on the complex was studied and it was found that the absorption by the complex remained the same in the pH range 2·8–4·3 (Fig. 3). The pH of the iron$^{\text{II}}$ solution was adjusted by the addition of 0·1N sodium hydroxide or 0·1N hydrochloric acid. The pH of each solution was determined with the Beckmann pH meter using a suitable glass electrode.

Stability of the colour

The formation of the complex was instantaneous and its colour was stable for more than 1 week. The effect of temperature on the colour of the complex was studied by placing the coloured complex in a thermostat for 0·5 hr at various temperatures between 15° and 40°. The effect of low temperature was studied by keeping the complex in a refrigerator. No change in the optical density of the complex could be observed in the temperature range 5–40°.

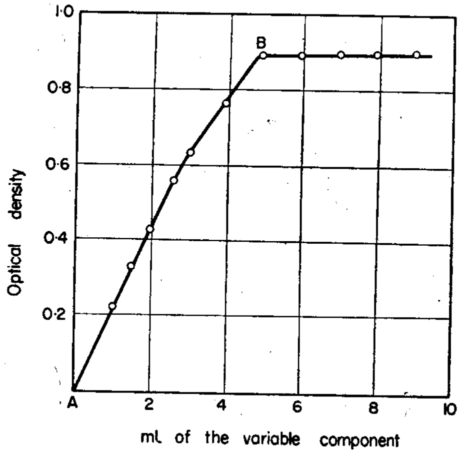


FIG. 2.—Minimum amount of 3-acetyl-4-hydroxycoumarin necessary for the determination of iron^{II}.

The complex was found to obey the Lambert-Beer law at 400 mμ for the concentration range of 1·3–5·5 ppm of iron.

Molar composition of the complex

The molar composition of the complex was determined by Job's[2] method of continuous variations as modified by Vosburgh and Cooper.[3] The optical densities at 400 mμ of the following two solutions, prepared by mixing (a) x ml of 2·0 × $10^{-3}M$ 3-acetyl-4-hydroxycoumarin solution with (10 − x) ml of 2·0 × $10^{-3}M$ iron^{II} solution and (b) x ml of 1·0 × $10^{-3}M$ coumarin solution with (10 − x) ml of iron^{II} solution (where x varied from 1 to 10), were determined employing alcohol as a reference solution. The absorption due to the iron^{II} solution and 3-acetyl-4-hydroxycoumarin solution is negligible at 400 mμ. Hence the function Y, defined as the difference between the optical density observed for a given mixture of the constituents and the corresponding optical densities of the respective components for no reaction, was taken in the present case as the observed optical density of the complex solution. The values of Y are plotted against x in each case in Fig. 4, in which the peaks occur when the molar ratio of the coumarin to iron^{II} ions is 7·5:2·5, *i.e.* 3:1 in each case. The complex, therefore, has the molar composition FeL_3 where L is an ion of the coumarin ligand.

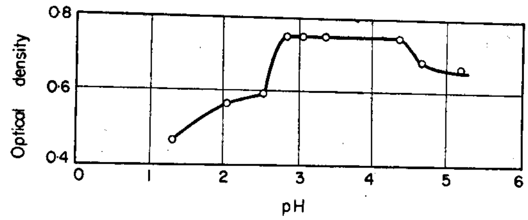


FIG. 3.—Effect of pH on the optical density of the iron^{II} complex.

The molar composition of the iron complex was also verified by the slope ratio method of Harvey and Manning.[4] For this purpose two series of solutions were prepared employing $2{\cdot}0 \times 10^{-3}M$ solutions of the coumarin and of iron^{II}. In one series the iron^{II} concentration was varied, maintaining the concentration of the coumarin constant and in a sufficient excess. In the other, the coumarin concentration was varied maintaining the iron^{II} concentration constant and in a sufficient excess. The optical densities of the solutions of both these series were determined at 400 mμ with alcohol as reference. The obtained values are plotted as the curves P and Q of Fig. 5. In the curves P and Q, only the straight line portions AB and CD, respectively, were taken into account to find out the slopes:

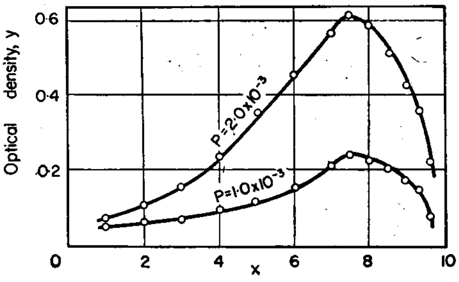


FIG. 4.—Determination of the molar composition of the iron^{II} complex by Job's method of continuous variations.
x ml of P-molar 3-acetyl-4-hydroxycoumarin solution added to (10 — x) ml of P-molar iron^{II} solution, and total volume made to 20 ml with alcohol.

$$\tan \theta_1 = \text{slope of the curve P(AB)} = 0{\cdot}59$$
$$\tan \theta_2 = \text{slope of the curve Q(CD)} = 0{\cdot}19$$
$$\text{Molar ratio of the complex} = \frac{0{\cdot}59}{0{\cdot}19} \simeq 3$$

Thus the slope ratio of the two curves indicates that the molar ratio of the coumarin to iron^{II} in the complex is 3, which confirms the results obtained by using Job's method.

Studies relating to the elucidation of the structure of the above complex are in progress.

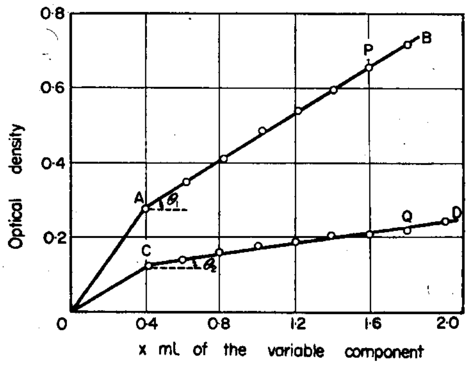


FIG. 5.—Determination of the molar composition of the iron^{II} complex by the slope ratio method.
Curve P: x ml of $2 \times 10^{-3}M$ iron^{II} solution added to 12 ml of $2 \times 10^{-3}M$ coumarin solution and the final volume made to 14 ml with alcohol.
Curve Q: x ml of $2 \times 10^{-3}M$ coumarin solution added to 5 ml of iron^{II} solution and the final volume made to 14 ml with alcohol.

Interference due to foreign ions

The interference due to various cations and anions in the determination of iron^{II} with the reagent was studied and it was found that copper^{II}, molybdate, tungstate and citrate interfered even when present in extremely small quantities. The limits of interference due to the following ions were determined: tartrate (200 ppm), oxalate (10 ppm), nickel^{II} (5·8 ppm), lead^{II} (115 ppm), manganese^{II} (15 ppm), magnesium (125 ppm) and beryllium (4·5 ppm). No interference was observed in the case of chloride, bromide, iodide, thiocyanate, sodium or potassium, even when these ions were present at 200 ppm per 2 ppm of iron.

Acknowledgement—Our sincere thanks are due to Professor T. R. Seshadri F.R.S. for his keen interest and helpful discussions. Our thanks are also due to the Atomic Energy Commission, Government of India, for sponsoring a research scheme under which this investigation was carried out.

A. N. Bhat
B. D. Jain

Department of Chemistry
University of Delhi
Delhi 8, *India*

Summary—3-Acetyl-4-hydroxycoumarin has been used for the spectrophotometric determination of iron^{II}. With iron^{II} this reagent forms an orange-red complex soluble in 50% (v/v) ethanol. The characteristics of the complex have been studied spectrophotometrically, and its molar composition determined. The complex obeys the Lambert-Beer law at 400 mμ within the concentration range 1·5–5·3 ppm of iron in the reaction mixture. The molar composition of iron^{II}-3-acetyl-4-hydroxycoumarin shows that it contains iron and the coumarin in the molar ratio of 1:3. The limits of interference due to various cations and anions in the determination have been defined.

Zusammenfassung—3-Acetyl-4-oxycumarin wurde zur spectrophotometrischen Bestimmung von Eisen (II) verwendet. Der entstehende orangeröte complex ist in 50% igem (volum) Äthanol löslich. Die Eigenschaften des Komplexes wurden studiert und seine Zusammensetzung spektrophotometrisch ermittelt. Bei 400 mμ ist Beer's Gesetz in einem Konzentrationsbereich von 1·5–5·3 milligramm per Liter erfüllt. Die Zusammensetzung des Komplexes ist Fe:Cumarin 1:3. Störungen durch verschiedene Ionen wurden untersucht.

Résumé—La 3-acétyl-4-hydroxycoumarine a été utilisée pour le dosage spectrophotométrique du fer(II). Le réactif forme avec le fer(II) un complexe rouge orangé soluble dans l'éthanol à 50% (en volume).

Les caractéristiques du complexe ont été étudiées par spectrophotométrie, et sa composition molaire déterminée. Le complexe obéit à la loi de Beer à 400 mμ dans le domaine de concentration 1,5–5,3 p.p.m. de fer dans le mélange réactionnel. Il contient le fer et la coumarine dans le rapport molaire 1/3. Les limites d'interférence de divers cations et anions ont été déterminées.

REFERENCES

[1] A. N. Bhat and B. D. Jain, *Talanta*, 1960, **4**, 13.
[2] P. Job, *Ann. Chim.*, 1928, **9** (10), 113.
[3] W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437.
[4] A. E. Harvey and D. L. Manning, *ibid.*, 1950, **72**, 4488.

Determination of reducing sugars with 3:6-dinitrophthalic acid*

(*Received* 15 *March* 1960)

Several nitro compounds are now available with which reducing sugars can be determined spectrophotometrically in an alkaline medium. In the authors' laboratory, 3:6-dinitrophthalic acid proved to give the most sensitive and stable colour reaction.[1] This new reagent was successfully used in the

---

* Organic Analysis—XXVI. For part XXV see *Chem. Pharm. Bull.* (*Tokyo*), 1960, in press.

determination of glucose in blood and urine by a simple procedure,[2] and also in the estimation of the sugar in the same sample with the naked eye.[3] This communication extends the use of the reagent to the determination of other reducing sugars.

EXPERIMENTAL

Sugars

These were recrystallised from dilute alcohol and dried at 100°, except for maltose and rhamnose which were weighed in the form of the monohydrate. The purity of the sugars was checked by means of melting point determinations.

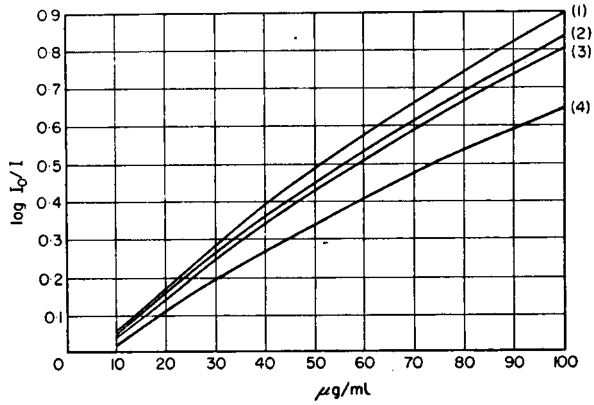


FIG. 1.—Calibration Curves: (1) Xylose and Arabinose, (2) Rhamnose, (3) Glucose, Fructose, and Galactose, and (4) Lactose and Maltose.

Inversion of sucrose

To 10 ml of a sucrose solution which contained 0·1 ~ 1 % of the sugar, 3 ml of 0·1N hydrochloric acid was added, and heated under reflux in a boiling water bath for 30 min. After cooling, the mixture was neutralised with 3 ml of 0·1N sodium hydroxide, then diluted with water to measure 1000 ml.

Colour developing agents and procedure

These were as detailed previously.[2] Two ml of the sample solution, containing 10 ~ 100 μg/ml of reducing sugar, should be used.

TABLE I.—ABSORPTION INTENSITY OF THE DEVELOPED COLOUR OF PENTOSES. MOLECULAR WEIGHT OF XYLOSE/MOLECULAR WEIGHT OF RHAMNOSE = 0·915

Concentration, *μg/ml*		30	50	70	90
Sugar	Rhamnose	0·264	0·448	0·612	0·767
	Xylose	0·285	0·490	0·662	0·821
Ratio of absorption intensities		0·926	0·915	0·925	0·934

RESULTS AND DISCUSSION

The calibration curves for the studied reducing sugars are shown in Fig. 1. Of the pentoses, xylose and arabinose give the same calibration curve, but rhamnose (methylpentose) gives a slightly different curve which is in inverse proportion to the molecular weight (Table I). The calibration curves for glucose fructose, and galactose coincide with each other. Therefore, the configuration of hydroxyl groups of the sugars has no effect on the reducing power to the reagent. This fact is also shown in the case of the disaccharides, lactose and maltose giving the same curve.

It is important to note that fructose gives exactly the same calibration curve as glucose. This fact indicates that sucrose can be determined in the presence of glucose or fructose. In the determination of a mixture of glucose and sucrose, one portion of the mixture is developed for glucose, and another portion is inverted and developed for total invert sugar. The sucrose is calculated from the equation:

$$(\text{Total invert sugar} - \text{Free glucose}) \times 0{\cdot}95 = \text{Sucrose}.$$

The results obtained by this method are shown in Table II. The found values of glucose and sucrose coincide with the calculated ones within a maximum error of ±3% over a wide range of the quantity of glucose and sucrose.

TABLE II.—DETERMINATION OF A MIXTURE OF GLUCOSE AND SUCROSE

Amount calculated, *μg/ml*		Amount found, *μg/ml*		Error, %	
Glucose	Sucrose	Glucose	Sucrose	Glucose	Sucrose
15	30	15·4	30·0	+2·7	0
15	40	14·8	38·8	−1·3	−3·0
15	50	15·0	48·8	0	−2·4
15	60	15·0	60·3	0	+0·5
15	70	15·3	69·7	+2·0	−0·4
15	80	15·1	81·5	+0·7	+1·9
20	50	20·5	49·1	+2·5	−1·8
30	50	30·8	49·6	+2·7	−0·8
40	50	39·9	50·2	−0·3	+0·4

The 3:6-dinitrophthalic acid solution and the alkaline solution are sufficiently stable for long use. This is proved by the absorption intensity of the blank solution which remains about 0·020 ~ 0·025 for several weeks. The calibration curves are reproducible within a maximum deviation of about ±0·01 in the absorption intensity. This value is equivalent to a maximum error of about ±2·5% for monosaccharides and of about ±3% for disaccharides at a concentration level of 50 μg/ml.

Pharmaceutical Institute, Medical Faculty
University of Kyushu, Fukuoka, Japan

TSUTOMU MOMOSE
YOSHIKO MUKAI
MITSUKO WATANABE

Summary—Reducing sugars are determined in the concentration range 10 ~ 100 μg/ml using 3:6-dinitrophthalic acid as a colour developing agent. Individual pentoses, hexoses, and disaccharides give the same calibration curves, respectively. Sucrose is also determined in the presence of glucose or fructose.

Zusammenfassung—Reduzierende Zucker können in Konzentrationen von 10–100 μg per ml bestimmt werden, wenn 3,6-dinitrophthalsäure als farbentwickelndes Reagens verwendet wird. Individuelle Pentosen, Hexosen und Disaccharide geben ähnliche Eichkurven. Sucrose kann in Gegenwart von Glucose und Fructose bestimmt werden.

Résumé—Les sucres réducteurs sont dosés à des concentrations de 10 à 100 μg/ml en utilisant l'acide 3-6 dinitrophtalique comme réactif coloré. Les pentoses, les hexoses et les disaccharides donnent individuellement des courbes d'étalonnage semblables. Le sucrose peut aussi être dosé en présence de glucose ou de fructose.

REFERENCES

[1] T. Momose and A. Inaba, *Chem. Pharm. Bull.* (Tokyo), 1959, **7**, 541.
[2] T. Momose, A. Inaba, Y. Mukai, and M. Watanabe, *Talanta*, 1960, **4**, 33.
[3] T. Momose, A. Inaba, Y. Mukai and T. Shinkai, *Chem. Pharm. Bull.* (Tokyo), 1960, **8**, 514.

Note on the titration of iodide by the Andrews method

(*Received* 28 *June* 1960)

INTRODUCTION

ANDREWS' method[1] for the determination of iodides involves two major stages:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \qquad (1)$$

$$IO_3^- + 2I_2 + 5Cl^- + 6H^+ \rightarrow 5ICl + 3H_2O \qquad (2)$$

The second of these is usually said to require the presence of relatively concentrated hydrochloric acid (at least $3N$). Most standard text-books of titrimetric analysis, however, do not make it clear whether hydrochloric acid is specific, nor why it must be so concentrated.

Andrews realised that it was necessary to prevent the hydrolysis of iodine monochloride and the subsequent disproportionation of the hypoiodous so formed. He represented the hydrolysis in terms of a molecular equation:

$$ICl + H_2O \rightarrow HOI + HCl \qquad (3)$$

It is now clear, however,[2] that the iodine monochloride is converted to the ion ICl_2^-. In the original form of the titration, it was necessary for this ion to be formed and retained in the aqueous layer so that the presence of iodine in the organic layer (chloroform or carbon tetrachloride) should not be masked by molecular iodine monochloride.

The position of the equilibrium:

$$ICl + Cl^- \rightleftharpoons ICl_2^- \qquad (4)$$

is, however, reported[3] to be substantially independent of the concentration of hydrochloric acid between $0{\cdot}2N$ and $10N$. Moreover, we have calculated from Faull's data[4] that in a titration of $0{\cdot}1N$ iodate against $0{\cdot}1N$ iodide, a final chloride ion concentration of only $0{\cdot}1N$ would reduce the concentration of free iodine monochloride below the level at which it could interfere with the end-point of the titration.

Once this minimum concentration of chloride ion has been reached, it is not clear why a much higher concentration of hydrochloric acid should be needed to achieve a satisfactory titration. Swift[5] has suggested that a high concentration of hydrogen ions is needed, not to suppress hydrolysis of iodine monochloride, but to increase the rate of reaction (2). The following results provide some experimental support for this suggestion, though the precise function of the hydrogen ion in this reaction is not yet clear.

EXPERIMENTAL

Titrations were carried out in which (a) the concentration of hydrochloric acid was varied, (b) the hydrochloric acid was replaced by combinations of other acids with potassium chloride to give varying concentrations of hydrogen and chloride ion. The results are shown in Table I.

The specific effects of hydrogen and chloride ion on reaction (2) were also investigated (Table II). The concentrations used were too low for satisfactory titration and the extent of oxidation of iodine was measured as a function of time. The effect of indifferent salts was also examined.

Reagents: The reagents used were of AnalaR grade, except for sulphuric acid and carbon tetrachloride. A sample of hydrochloric acid of "analytical reagent quality" liberated a small but significant quantity of iodine from potassium iodide. It probably contained free chlorine and was rejected as unsuitable for this work.

Table I. Oxidation of I^- to ICl_2^-

Series I	Concentration* of HCl, M		Nature of Reaction†
	4·68		A
	2·81		B
	0·93		C
	0·46		D
Series II	Concentration of KCl, M	Concentration of H_3PO_4, M	
	0·13	5·0	D
	0·63	5·0	D
	1·13	5·0	C
	3·00	5·0	A
Series III	Concentration of KCl, M	Concentration of HCl, M	
	3·0	0·0	no reaction
	3·0	0·2	D
	3·0	0·5	C
	3·0	1·0	B
	3·0	2·0	A-B
Series IV	Concentration of KCl, M	Concentration of H_2SO_4, M	
	0·2	2·5	D
	0·5	2·5	D-C
	1·0	2·5	C
	0·2	1·5	D
	0·5	1·5	D-C
	1·0	1·5	C
	0·2	0·5	D
	0·5	0·5	D
	1·0	0·5	D-C

* The concentrations are those obtaining at the end of each titration.

† A: the reaction proceeds at the optimum rate for titration,
B: the reaction is slower than in A, but fast enough for use in titrations,
C: the reaction is too slow for use in titration,
D: the reaction is slower than in C, taking up to 30 min for completion.

Procedure: The titrations (Table I) were carried out with standard solutions of approximately 0·1N potassium iodate (0·025M) and potassium iodide (0·05M). A standard volume, 5 ml, of carbon tetrachloride was used to indicate when the iodine liberated in the first stage had been completely removed. The volumes of solution used were arranged to give the quoted concentrations at the end of the titrations.

In the subsequent experiments (Table II), a standard solution of iodine in carbon tetrachloride was shaken with aqueous solutions of the remaining substances. For each point the carbon tetrachloride layer was separated from the aqueous layer at the stated time, washed quickly with a large volume of distilled water and separated again. The remaining iodine was then determined by titration with aqueous sodium thiosulphate.

The experiments were carried out at room temperature.

TABLE II. OXIDATION OF I_2 TO ICl_2^-

A. Effect of [Cl^-]

	Time, *min*	I_2, % oxidised
(i) 0·2*M* KCl 0·5*M* H_2SO_4	1	22
	2	32
	5	44
	10	50
(ii) 0·5*M* KCl 0·5*M* H_2SO_4	1	61
	2	71
	5	87
	10	89
(iii) 0·2*M* KCl 0·3*M* KNO_3 0·5*M* H_2SO_4	1	20
	2	28
	5	46
	10	52

B. Effect of [H^+]

(i) 0·5*M* H_2SO_4 0·2*M* NaCl	1	28
	2	32
	5	44
	10	52
(ii) 1·5*M* H_2SO_4 0·2*M* NaCl	1	47
	2	66
	5	77
	10	86
(iii) 0·5*M* H_2SO_4 1·0*M* Na_2SO_4 0·2*M* NaCl	1	10
	2	21
	5	24
	10	31

DISCUSSION

(*a*) *Concentration of hydrochloric acid*

From Table I it is clear that, for a satisfactory titration, the solution titrated should be no less than 3*N* in hydrochloric acid at the end of the reaction. Chloride ions must be present in a concentration greater than that required for substantially complete conversion of ICl to ICl_2^-.

Whereas some deficiency in hydrogen ions can be made up by excess of chloride ions (Series III), the reverse is not obviously the case (Series II*). Even in the former case, it appears that the ionic product, [H^+][Cl^-], must correspond to that in 3*M* hydrochloric acid.

(*b*) *Effect of indifferent ions*

From Table II it is clear that indifferent ions either do not seriously affect the rate of reaction (2), or reduce it, depending on the ionic strength of the solution.

This investigation clarifies the conditions needed for satisfactory titration of iodide by the Andrews

---

* For this purpose, phosphoric acid is regarded as being, to a first approximation, a monobasic acid.

method. It is not yet clear, however, whether the dependence of the rate of the slow reaction on the concentrations of hydrogen ion and chloride ion is due to their presence as reactants or as catalysts.

The University J. J. Kipling
Hull, England G. Grimes

Summary—For a satisfactory determination of iodide by Andrews' method, the concentration of hydrochloric acid in the solution should not fall below $3N$. A high concentration of each ion is required; that of chloride ion is much greater than is needed for conversion of ICl to ICl_2^-. The effects of varying the concentrations of H^+, Cl^- and indifferent ions on the rate of the slow stage (oxidation of I_2 to ICl) are demonstrated.

Zusammenfassung—Für eine zuverlässige Bestimmung von Jodid nach der Andrews Methode soll die Salzsäurekonzentration in der Lösung nicht unter 3 n absinken. Eine hohe Konzentration für jedes Ion ist nötig. Die Chloridkonzentration ist viel grösser als an sich für die Überführung von JCl in JCl_2^- stöchiometrisch nötig. Der Einfluss wechselnder Konzentrationen von H^+, Cl^- und indifferenten Ionen auf die Geschwindigkeit des langsamen Reaktionschrittes (Oxydation von J_2 zu JCl) wird demonstriert.

Résumé—Pour une estimation satisfaisante de l'iodure par la méthode d'Andrews, la concentration de l'acide chlorhydrique dans la solution ne devrait pas être inférieure à 3 N. Une forte concentration de chaque ion est nécessaire; celle de l'ion chlorure est beaucoup plus grande que cela n'est nécessaire pour la transformation de ICl en ICl_2^-. Les influences des variations des concentrations de H^+, Cl^- et des indifférents sur la vitesse du stade lent (oxydation de I_2 enICl) sont démontrées.

REFERENCES

[1] L. W. Andrews, *J. Amer. Chem. Soc.*, 1903, **25**, 756.
[2] N. V. Sidgwick, *The Chemical Elements and their Compounds.* Clarendon Press, Oxford, 1950.
[3] A. C. Gillam and R. A. Morton, *Proc. Roy. Soc.*, 1931, **A132**, 152.
[4] J. H. Faull, *J. Amer. Chem. Soc.*, 1934, **56**, 522.
[5] E. H. Swift, *ibid.*, 1930, **52**, 894.

Contribution to the basic problems of complexometry—III

Some advantages of acetate buffer

(*Received* 2 *May* 1960)

It is well known, that some bivalent metals can be readily determined by EDTA titrations in a weak acid medium (pH 5–6). In addition, other indicators, Xylenol Orange[1] and Methyl Thymol Blue[2], have been recommended for these titrations because of their brilliant colour changes. Solutions are usually buffered with urotropine. Some cations having incomplete inner orbits, such as copper, nickel, cobalt etc. form substitution-stable complexes with these indicators, thus making direct complexometric titration impossible. It is not possible, for example, to titrate copper using Xylenol Orange or Methyl Thymol Blue, even at higher temperatures, but only copper solutions buffered with urotropine. We have found that by the use of acetate buffer it is possible to titrate copper directly at a temperature of about 70°, using either indicator, with the accuracy of the usual complexometric methods. Recently Přibil[3] discovered that in the direct titration of copper in the cold, after the addition of a small amount of *o*-phenanthroline, the colour change of Xylenol Orange was substantially improved. This phenomenon he explained on the basis of the formation of a substitution-labile copper complex with *o*-phenanthroline, which reacts with EDTA easily at the end-point.

In a detailed study it was found, that $\alpha{:}\alpha'$-bipyridyl*, cupferron, ethylendiamine, dicuprale,

---

* $\alpha{:}\alpha$-Bipyridyl at about pH 5·5 may be used like *o*-phenanthroline for masking most of bivalent metals.

o-phenylenediamine and glycine behave in the same manner as *o*-phenanthroline. Only milligram amount of these substances are required in the direct titration of copper using either indicator, if the solutions are buffered with sodium acetate. For the copper titration, the addition of 1 mg of dicuprale, 2 mg of cupferron, 20 mg of *o*-phenylenediamine, 25 mg of ethylenediamine or 300 mg of glycine are sufficient. When solutions are buffered with urotropine, it is necessary to use a higher concentration of these substances to produce the same effect (0·2 g of *o*-phenylenediamine, 0·3 g of ethylenediamine or 1 g of glycine). In this case, also, the success of the titration depends on the order in which the substances are added. The favourable effect of the additives is manifested only when their addition takes place before the buffer solution is added.

Even gram amounts of these substances do not affect the titration of copper favourably at room temperature. Only *o*-phenanthroline or α:α′-bipyridyl (0·1 mg) are effective, without regard to the order of addition.

It is advantageous, for routine analysis, to use sodium acetate buffer solution with addition of one of the above-mentioned complex-forming substances.

This phenomenon is not only important for the direct determination of copper, but its consequence is general. Traces of copper do not influence the consumption of EDTA solution but substantially obscure the colour change of Xylenol Orange or Methyl Thymol Blue. When the acetate buffer is used this disturbing effect is completely eliminated.

The proper buffer solutions, with the addition of complex-forming substance can also be used for the determination of copper in the presence of other compex-forming substances. For such titrations a back-titration with lead nitrate against Xylenol Orange was previously proposed.[4] Correct buffering permits direct titration of the copper. As before, *o*-phenanthroline or α:α′-bipyridyl was found to be the best additive.

The reason for the different behaviour of urotropine and acetate buffers has not yet been satisfactorily solved. Electrometric control has proved that the pH of the solution is not a decisive agent in influencing the phenomenon. One possible explanation is that sodium acetate functions here as an "auxiliary complex-forming agent" as well as the *o*-phenanthroline or other additive. It is effective only in higher concentrations. This is in agreement with the relative stabilities of the *o*-phenanthroline and acetate complexes of bivalent copper. Formation of the urotropine complex with copper, which has a disturbing effect on the mechanism of the indicating reaction, is a possible clue to the explanation. This opinion is supported by the fact that such substances as, for example, triethanolamine, which also form complexes with copper but are not capable of functioning as auxiliary complex-forming substances, according to Přibil, prevent the titration of copper, even where the solution is buffered with sodium acetate and is titrated at higher temperature. The behaviour of triethanolamine is thus similar to that of urotropine; it disturbs the indication of the end-point even in the presence of complex-forming substances. A more precise explanation may be possible after detailed study.

Acknowledgement—It is our pleasant duty to thank Dr. Rudolf Přibil, Analytical Laboratory, Czechoslovak Academy of Sciences, for his active interest in this work.

W. Berndt
J. Šára

Spolana n.p.
Neratovice, Czechoslovakia

Summary—Acetate buffer, in conjunction with additives such as *o*-phenanthroline or α:α′-bipyridyl, permits the titration of metallic cations such as copper with EDTA in weakly acid medium, using Xylenol Orange of Methyl Thymol Blue as indicators. In this it is superior as a buffer to the more generally used urotropine. The nature of its action is discussed.

Zusammenfassung—Die Verwendung eines Acetatpuffers in Verbindung mit Zusätzen wie o-Phenanthrolin oder α,α-Dipyridyl gestattet die Titration von Metallionen wie Kupfer mit EDTA in schwach saurem Medium unter Verwendung von Xylenolorange oder Thymolblau als Indicatoren. Die Pufferkombination ist der üblichen Verwendung von Urotropin überlegen. Der Mechanismus der Reaktion in der Puffermischung wird diskutiert.

Résumé—Le tampon acétate, en liaison avec des additifs tels que l'o-phénanthroline ou l'α-α′-bipyridyle permet le titrage de cations métalliques comme le cuivre par l'EDTA en milieu faiblement acide, le xylenol orange ou le bleu de méthyl thymol étant utilisés comme indicateurs.

Pour ce titrage, ce tampon est supérieur à l'urotropine plus généralement utilisée. La nature de son action est discutée.

REFERENCES

[1] J. Körbl, R. Přibil and A. Emer., *Coll. Czech. Chem. Comm.*, 1957, **22**, 961.
[2] J. Körbl and R. Přibil, *ibid.*, 1958, **23**, 873.
[3] R. Přibil, *Talanta*, 1959, **3**, 91.
[4] J. Šára and W. Berndt, *Svensk Pappers Tidning*, 1958, **11**, 353.

Determination of oxygen in zirconium by the platinum flux technique

(*Received* 28 *June* 1960)

OXYGEN in zirconium is often determined by the Walter method[1] at 2100° or, on a microscale, by the platinum bath method.[2] The practical difficulties involved in the Walter method, particularly the use of graphite chips in the crucible, were examined in an earlier paper.[3] Bennett and Covington[4] reported that zirconium, when present as an alloying constituent in titanium, did not interfere with the oxygen determination by the platinum bath method at 1900°. Smiley[5] suggested and Hansen, Mallett and Trzeciak[6] developed the platinum flux technique for the analysis of titanium and enumerated the advantages of this over the platinum bath method. The present paper deals with the application of the platinum flux technique to the analysis of zirconium for its oxygen content.

EXPERIMENTAL

Apparatus

The vacuum fusion apparatus was described earlier.[7]

Standard sample

A known amount of gaseous oxygen was added to a rod of iodide-zirconium in a Sieverts apparatus. Then the rod was heated at 1000° for 5 hr to diffuse and level the oxygen content. Further homogenisation was effected by arc melting the metal twice in an argon atmosphere.

Effect of temperature and flux-to-sample ratio

When a platinum flux was used with titanium, a brilliant flash was observed after each sample was dropped into the crucible. Smiley reported that, with a platinum bath, only the first sample dropped produced a flash. This is probably due to the exothermic formation of a compound between titanium and platinum. Since a similar reaction was anticipated for zirconium, the literature on the binary compounds with platinum was reviewed to arrive at a suitable ratio for the initial experiments. The compound which contains the highest amount of platinum is $ZrPt_3$.[8] The weight ratio of platinum to zirconium in this compound is approximately 6:1. Allowing an excess for quantitative reaction, a ratio of 10:1 was fixed for the initial experiments. An extraction temperature of 2100° was arrived at from a consideration of the operating temperature employed in the application of the Walter method to the analysis of zirconium. As the extraction of oxygen from the synthetic standard under these conditions was apparently quantitative, further experiments were carried out at each of several successively lower temperatures varying the flux-to-sample ratio. The results are given in Table I.

The extraction of oxygen was complete at temperatures of 1850°–2100°, with flux-to-sample ratios ranging from 10:1 to as low as 4:1. The extraction period was 20 min in most cases. Conditions under which the extraction had to be continued 5–10 min longer for completion, included flux ratios above 8:1 at 2100°, and sometimes at ratios of 4·2:1 and below at 2000° and lower. At 1800° and 1700°, the recovery of oxygen was only about 95%. Hence, the final experimental conditions, considered best for the extraction of oxygen from about 0·10-g samples, were 1900°–1950°, 20 min extraction, and a ratio of flux to sample of about 5:1.

Procedure

Samples weighing about 0·10 g were prepared in the normal way, cutting with a hacksaw, abrading the surfaces with a smooth flat file, degreasing with acetone (C.P.), and weighing. Approximately equal lengths of platinum wire of 1-mm diameter were cut, each length weighing about 0·5 ± 0·02 g. The samples were wrapped in the wire and loaded in the sample arm of the apparatus preceded by a 0·5-g sample of the platinum itself. The furnace assembly was prepared as described earlier.[3] The system was pumped down and degassed for 2 hr at about 2250°. By this time an outgassing rate lower than 0·05 ml STP for 5 min at 2250° was achieved. The temperature was then lowered to 1900°–1950° and maintained there throughout the run. The sample of platinum was dropped and gases were collected for 20 min. These gases constituted the blank for both the platinum flux and the furnace. The gases were passed over copper^{II} oxide at 325° and analysed by the fractional freezing method. The zirconium samples were dropped and analysed in the same manner as the flux. This procedure of analysing the flux gives the corrections due to the furnace blank and the gas content of the flux in a single step.

TABLE 1.—VARIATION OF PLATINUM FLUX-TO-SAMPLE RATIO AT DIFFERENT TEMPERATURES

Weight		Ratio of flux to sample	Extraction temperature, °*C*	Oxygen, *weight %*	
Sample, *g*	Platinum flux, *g*				
0·1635	1·675	10·3	2100	0·132*	
0·1580	1·616	10·2	2100	0·127*	
0·2040	2·021	9·9	2100	0·127*	
0·2960	2·963	10·0	2100	0·135*	
				Average	0·130
0·1166	0·342	8·1	2100	0·131	
0·1144	0·919	8·0	2100	0·132	
				Average	0·132
0·0895	0·532	6·0	2100	0·132	
0·1135	0·699	6·2	2100	0·130	
				Average	0·131
0·1077	0·649	6·0	2000	0·134	
0·1005	0·597	5·9	2000	0·132	
				Average	0·133
0·0995	0·422	4·2	2000	0·127	
0·1050	0·442	4·2	2000	0·138*	
				Average	0·133
0·0955	0·484	5·1	1900	0·133	
0·1090	0·457	4·2	1900	0·131*	
				Average	0·132
0·1010	0·505	5·0	1850	0·133	
0·1090	0·431	4·0	1850	0·138*	
				Average	0·136
0·0990	0·501	5·1	1800	0·124	
0·0343	0·418	4·4	1800	0·122	
				Average	0·123
0·0950	0·470	4·9	1700	0·122	
0·0870	0·391	4·5	1700	0·127	
				Average	0·125

* Extraction of gases required 5 to 10 min longer than the usual 20 min.

RESULTS

Table II contains the analytical results for iodide-zirconium (the base material) and a synthetic standard sample. Standard deviations of 0·0023 and 0·0038 weight %, and coefficients of variance of 10% and 2·9%, were obtained, respectively, at the 0·023- and 0·131-weight % oxygen levels. Because of the excellent results obtained with the 0·10-g samples, no attempt was made to analyse samples of greater weight. Also, no significant gain in precision was expected, since an increase in sample size would necessitate an increase in blank correction for the gas content of the flux. With 0·5 g of platinum, a total blank for 20 min at 1900° was of the order of 0·05 ml STP.

After a run of 8 samples, the furnace was allowed to cool to room temperature in vacuum overnight. The next day, the crucible and contents were reheated and degassed at 1900°, and two more samples were analysed. The results for these are the last two listed for the synthetic standard in Table II. They show no difference from the first-day values listed immediately above them.

The first two values listed for the standard were obtained in series with the base analysis.

TABLE II.—ANALYSIS OF ZIRCONIUM SAMPLES BY THE PLATINUM FLUX TECHNIQUE AT 1900°

Sample	Weight		Ratio of flux to sample	Oxygen, *weight %*
	Sample, *g*	Platinum flux, *g*		
Iodide-zirconium (base)	0·1080	0·499	4·6	0·022
	0·1075	0·504	4·7	0·024
	0·1088	0·519	4·8	0·022
	0·1063	0·501	4·7	0·022
	0·1045	0·498	4·8	0·021
	0·1030	0·509	4·9	0·020
	0·1065	0·483	4·5	0·023
	0·1080	0·493	4·6	0·028
	0·1015	0·505	5·0	0·022
	0·0995	0·486	4·9	0·021
				Average 0·023 ± 0·002
Synthetic* sample	0·0923	0·394	4·3	0·134
	0·0760	0·338	4·5	0·136
	0·0945	0·466	4·9	0·132
	0·1045	0·512	4·9	0·124
	0·0980	0·475	4·8	0·131
	0·1020	0·485	4·8	0·133
	0·0893	0·460	5·2	0·135
	0·1014	0·484	4·8	0·127
	0·1044	0·510	4·9	0·128
	0·1020	0·490	4·8	0·129
	0·1037	0·495	4·8	0·136
	0·0910	0·465	5·1	0·132
				Average 0·131 ± 0·003

* 0·023 base value + 0·102 added oxygen = 0·125 weight % of oxygen expected. The slightly higher average value is probably due to pick-up of a small amount of oxygen during arc melting.

DISCUSSION

It is normally considered that a higher operating temperature is required for the extraction of the oxygen from zirconium than from titanium. This is because of the difference in the free energies of formation of their oxides. The results of this study showed, however, that the extraction of oxygen from zirconium was quantitative at the same temperature of 1850° as reported in the case of titanium analysis,[6] using the same platinum flux method. Similarly Bennett and Covington[4] observed that, with a platinum bath method at 1900°, zirconium did not interfere in the analysis of titanium-base alloys for their oxygen contents. This apparent anomaly may be due to the exothermic reactions involved. Successful platinum flux analyses of both titanium and zirconium are initiated by a bright flash shortly after the sample enters the crucible. Although reactions with both metals start at the same temperature, the actual temperature of the flash may be different in the two cases. During the flash, conditions are established for the completion of the extraction reaction at the set temperature of the furnace.

It may be mentioned in this context that Booth, Bryant, and Parker[2] worked with the platinum bath method on a microscale and recommended an optimum temperature of 1880° ± 20° for titanium, which is slightly higher than the optimum temperature of 1860° ± 20° employed by them for the zirconium analysis. But they, also, stated that the extraction of oxygen from zirconium was complete in a temperature range of 1700° to 1950° without explaining how a fluid bath was obtained at 1700° with platinum (melting point, 1774°). In the present study, the extraction of oxygen from a homogeneous sample was only of the ordei of 95 % at 1700° and 1800°, as shown in Table I. Allowing a margin in the measurement and control of temperatures, 1900°–1950° was finally recommended.

The atomic ratio of zirconium to platinum, considered as optimum, corresponds approximately to 1:2. The atomic ratio of titanium to platinum employed[6] by Hansen *et al.*, also works out to be the same. This, again, points to the similarity in the nature of reactions taking place in both cases.

Acknowledgments—The authors are grateful to Mr. D. F. Kohler for his assistance in the preparation of the standard sample. One of the authors (Ch. V) gratefully acknowledges the Fellowship granted by the International Cooperation Administration, Washington, D.C., and the deputation by the Atomic Energy Establishment Trombay, Government of India, Bombay, India.

CH. VENKATESWARLU*
MANLEY W. MALLETT

Battelle Memorial Institute
Columbus 1,
Ohio, U.S.A.

Summary—The platinum flux technique, well established for the determination of oxygen in titanium, was successfully applied to the analysis of zirconium for its oxygen content after a systematic study of the optimum experimental conditions. The extraction of oxygen was complete in 20 min in the temperature range of 1850 to 2100° with a ratio of flux to sample of about 4·5:1 to 8:1. Statistical analysis of the results on a homogeneous sample gave a standard deviation of 0·0038 weight % and a coefficient of variance of 2·9 % at a level of 0·131 weight % of oxygen in zirconium. The recommended experimental conditions are a 0·1-g sample, a 5:1 flux-to-sample ratio, and 20 min extraction at 1900°–1950°.

Zusammenfassung—Die gut arbeitende Platin-Schmelz-Methode zur Bestimmung von Sauerstoff in Titan wurde nach eingehender Studie der experimentellen Bedingungen erfogreich auf die Bestimmung des Sauerstoffgehaltes von Zirkonmetall angewendet. Die Extraktion des Sauerstoffes war nach 20 Minuten vollständig bei einer Temperatur von 1850–2100° und einem Verhältniss Flussmittel: Probe von etwa 4,5:1 bis 8:1. Statistische Auswertung der Resultate an homogenen Proben ergab eine Standardabweichung von 0,0038 Gewichts % und einen Variationskoeffizienten von 2,9 % bei 0,131 % Sauerstoff in Zirkon. Die empfohlenen experimentellen Bedingungen sind: 0,1 g Probe, 5:1 Verhältnis von Flussmittel zu Probe und 20 Minuten Extraktion bei 1900–1950°.

Résumé—La technique du fondant au platine, bien connue pour le dosage de l'oxygène dans le titane, a été appliquée avec succès à l'analyse de la teneur en oxygène du zirconium après une étude systématique des conditions expérimentales les meilleures. L'extraction de l'oxygène était complète en 20 minutes dans le domaine de température 1850–2100° avec un rapport du fondant à l'échantillon d'environ 4,5/1 à 8/1. L'analyse statistique des résultats sur un échantillon homogène donnait un écart standard de 0,0038 pour cent en poids et un coefficient de variance de 2,9 pour cent pour une teneur en oxygène du zirconium de 0,131 pour cent en poids. Les conditions expérimentales recommandées sont: un échantillon de 0,1 g, un rapport du fondant à l'échantillon de 5/1 et 20 minutes d'extraction à 1900–1950°.

---

* Present address: Analytical Division, Atomic Energy Establishment Trombay, Government of India, 414-A Cadell Road, Bombay 28, India.

REFERENCES

[1] Dean I. Walter, *Analyt. Chem.*, 1950, **22**, 297.
[2] E. Booth, F. J. Bryant and A. Parker, *Analyst*, 1957, **82**, 50.
[3] Ch. Venkateswarlu and M. W. Mallett, submitted for publication to *Analyt. Chem.*
[4] S. J. Bennett and L. C. Covington, *Analyt. Chem.*, 1958, **30**, 363.
[5] W. G. Smiley, *ibid.*, 1955, **27**, 1098.
[6] W. R. Hansen, M. W. Mallett and M. J. Trzeciak, *ibid.*, 1959, **31**, 1237.
[7] M. W. Mallett and C. B. Griffith, *Trans. Amer. Soc. Metals*, 1954, **46**, 375.
[8] G. L. Miller, *Metallurgy of the Rarer Metals*-2 *Zirconium.* Butterworth's Scientific Publications, London, 1954, p. 269.

Talanta, 1960, Vol. 5, pp. 288 to 289. Pergamon Press Ltd. Printed in Northern Ireland

LETTERS TO THE EDITOR

SIR:

I read in the May issue of *Talanta* the letters of F. Solymosi[1] and of B. R. Sant and S. B. Sant[2] regarding their discussion on quantitative oxidations by potassium ferricyanide. I personally do not know any of the authors, and have never done similar investigations; therefore, I think that I can consider myself impartial.

I really do not know who is right in the discussion, whether B. R. Sant and S. B. Sant gave enough credit to F. Solymosi in their paper,[3] and I do not want to deal with this question. Unfortunately, however, each letter contained one remark which, I think, does not fit in a scientific communication. Please let me discuss this question very briefly.

F. Solymosi when dealing with the paper of S. B. Sant[4] raised the question in his letter[1] "whether slight changes in a procedure warrant a fresh scientific publication". In my opinion, the editor of a scientific journal and his editorial board have the exclusive right to decide whether a paper should or should not be published in that journal. Naturally everybody has the right to criticise the *contents* of the paper but not the fact whether its publication was justified or not.

B. R. Sant and S. B. Sant when answering[2] Solymosi's criticism, are not satisfied with a scientific answer ("In our opinion . . . any titration is . . . more convenient . . . if it can be performed at room temperature") but go further and mention, as a final thrust, that the "question arises . . . whether the same work by the same author need be published in two different journals".[5,6]

This statement raises the feeling that the authors were not sure that their scientific answer was strong enough, and wanted, therefore, to add a subjective remark to it. Besides the fact that there should be no place for such malicious remarks in a scientific communication, the statement by B. R. Sant and S. B. Sant demonstrates that they did not inform themselves.

It is well known that smaller countries, whose language is not understood in other countries, are accustomed to publishing scientific journals in the accepted international scientific languages (English, French, German) which contain, in addition to original publications, the text of some papers already published in a journal in the regional language. Such a journal, is, as you know, for example, the Collection of Czechoslovak Academy of Sciences.

In addition to this, it should not be forgotten that particularly in the Eastern-European countries, the Academy of Sciences is the highest scientific board and it is an honour for somebody who is not a member of the Academy to have the opportunity for a member to present his paper before a meeting of a section of the Academy. In practice, works are mostly presented "officially" which have already been published elsewhere. On the other hand, the papers which are presented in such a manner are then published automatically in one of the journals of the Academy. I think that this is the custom, for example, at the French Academy of Sciences (and the papers are then published in the Comptes Rendus des Scéances de l'Académie des Sciences); and the Hungarian Academy of Sciences works similarly, publishing the presented papers in one of its journals such as the Acta Chimica Academiae Scientiarum Hungaricae.

In Solymosi's case, it is quite natural that he should ask to present his work, which was already published in a Hungarian-language scientific journal (Magyar Kémiai Folyóirat, which is the journal of the Hungarian Chemical Society), before the chemical group of the Academy. This then resulted later (it is a two-year-difference in the two publications!) in the publication in the Acta Chimica.

I would like to repeat my statement at the beginning of my letter: I have no relation with any of the authors, and I am not working in their field. I felt, however, that for the case of scientific objectivity, the above mentioned facts should be mentioned.

L. S. ETTRE

Instrument Division
The Perkin-Elmer Corporation
Norwalk, Connecticut, U.S.A.
23 *August* 1960

REFERENCES

[1] F. Solymosi, *Talanta*, 1960, **4**, 211.
[2] B. R. Sant and S. B. Sant, *ibid.*, 212.
[3] *Idem*, *ibid.*, **3**, 261.
[4] S. B. Sant, *Z. analyt. Chem.*, 1959, **163**, 112.
[5] F. Solymosi, *Magyar Kém. Foly.*, 1956, **62**, 318.
[6] *Idem*, *Acta Chim. Hung.*, 1958, **16**, 267.

SIR:

The problem raised by Habashi[1], concerning the influence of phosphoric acid in the determination of uranium by the thiocyanate method has already been solved. The modification introduced by Crouthamel and Johnson[2] to the thiocyanate method, *i.e.* the use of an acetone medium, permits the accurate colorimetric determination of uranium with up to $0{\cdot}75M$ phosphoric acid present.[3] The success of the method is probably due to the fact that whereas phosphoric acid is not very much dissociated in the sulphuric acid-acetone medium employed, thiocyanic acid remains a strong electrolyte, and may compete successfully with the phosphate, forming the yellow uranium complex. In cases where the phosphoric acid concentrations are higher than $0{\cdot}75M$, the solutions may usually be diluted, since the method is sensitive down to $10^{-6}M$ uranium employing 10-cm light-path cells. The removal of the phosphoric acid before the colorimetric determination is thus unnecessary.

Israel Atomic Energy
Commission Laboratories, Rehovoth
21 September 1960.

Y. MARCUS

REFERENCES

[1] F. Habashi, *Talanta*, 1959, **2**, 380.
[2] C. E. Crouthamel and C. E. Johnson, *Analyt. Chem.*, 1952, **24**, 1780.
[3] Y. Marcus, Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, United Nations, Geneva, 1958, Vol. 3, Processing of Raw Materials, p. 465.

Talanta, 1960, Vol. 5, pp. 290 to 292. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Oxidation-Reduction Potentials of Organic Systems. W. Mansfield Clark. The Williams and Wilkins Company, Baltimore, 1960. pp. xi + 584. $13.50

The present reviewer has frequently had the opportunity to refer people studying the oxidation-reduction behaviour of organic compounds to the magnificent series of fundamental studies on that subject, which were made by W. Mansfield Clark and his co-workers during the period of 1923 to 1931, and which were published as Hygienic Laboratory Bulletins and Supplements to the Public Health Reports under the general title of "Studies of Oxidation-Reduction." Consequently, the reviewer welcomed with keen anticipation the appearance of the present volume by Dr. Clark, to whom contemporary chemists and biochemists, indeed all scientists and technologists, owe a great debt not only for his labours in the area indicated by the title of the volume, but also because of his pioneering work on pH. Those of us who started in chemistry during the nineteen twenties and thirties appreciate the impressive contribution to experimental and theoretical chemistry made by Dr. Clark's classic monograph, *The Determination of Hydrogen Ions* (first edition, 1920; third edition, 1928).

The present volume is an individualistically designed work which must be judged in its own terms. As one might expect, it is lucidly written; an added pleasure is the witty presentation (when will editors and authors again realise that scientific literature need not be necessarily poorly, or at least dully, written).

The first three chapters (106 pages) review the historical development of the general area of oxidation-reduction, relevant areas of thermodynamics, and the often confusing conventions and definitions which have accumulated in electrochemistry, including the omnipresent question of the signs to be used on potentials. Chapter 4 (42 pages) indicates how the relation between a cell reaction and the measured electromotive force of the cell has been formulated, the role of pH, and the reporting and interpretation of data. Chapter 5 (11 pages) deals with the rectification of experimental redox titration curves by the method of Reed and Berkson, which utilises the "ideal" portion of the curve. Chapters 6 to 8 (74 pages) consider some of the complications which are introduced by the nature of the chemical species involved in the cell reactions, specifically with the modifications which need to be made in the primary equations to account for the formation of dimers, semiquinones (intermediate free radicals), and co-ordination compounds.

Chapters 9 to 11 (87 pages) deal with experimental factors, including the effects of liquid junction potentials, the experimental standardisation of potential and pH scales, and the general techniques used in precise potentiometric measurement.

Chapter 12 (9 pages) on criteria for evaluating the reliability of oxidation-reduction potential data is followed by a chapter (26 pages) on miscellaneous topics (polarography, kinetics, oxidation-reduction in living cells). These serve to introduce Chapter 14 (162 pages) which is a massive and amazing compilation of data on what must be every reversible organic oxidation-reduction system for which adequate data are available, ranging from quinone-hydroquinone to systems that can be equilibrated with the DPN and TPN systems. The hundred tables of data in the latter chapter are supplemented by the text of the chapter, which lucidly and helpfully guides the reader in the evaluation and interpretation of the data given.

The text abounds in illustrative examples and critical analyses of perhaps overly complacently accepted scientific conceptions. The bibliography is delightfully convenient in including the titles of all of the papers listed.

The reviewer was much impressed by this synoptic picture of an area which is of such fundamental importance in the understanding not only of many chemical processes, but also in the elucidation of the oxidation-reduction processes which are so basic in biological systems. One might pick many things in the volume with which to disagree. One might argue about some of the specific interpretations made by the author in respect to thermodynamic and electrochemical conventions.

The reviewer would have liked a more extensive consideration of the problem of the deviation of organic oxidation-reduction systems from reversibility. However, the present volume should be judged not for what it is not, but for what it is; taken as a whole, the volume is a major contribution which can be strongly recommended to all concerned with the oxidation-reduction behaviour of organic systems both for a review of the fundamentals in the area and for stimulation in the furtherance of one's own specific research interests.

Dr. Clark has further put scientists in debt to him for this stimulating volume.

PHILIP J. ELVING

Électrochimie Theorique. EUGÈNE DARMOIS et GENÈVIEVE DARMOIS. Masson et Cie., Paris 1960. Pp. vi + 239.

THIS small book, in the French language, is concerned entirely with the fundamentals and basic theory of electrochemistry in a broad sense of the term. The treatment commences with a brief historical introduction, followed by a discussion of the ionic theory and Faraday's laws. This leads into a discussion of equivalent conductivity, transport numbers and the mobility of ions, together with the effects of hydration and viscosity. Throughout the book thermodynamic aspects are simply and clearly outlined and the more important equations are given.

A comparatively large space is devoted to the properties and anomalies of strong electrolytes and ionic interactions. The Debye-Hückel theory and more recent studies are adequately described. Galvanic cells of all types are given a comprehensive treatment with which is associated hydrogen ion concentration, pH, overvoltage and modern theories of acids and bases. The logical sequence of the book would have been improved if this large section had followed directly after the Chapter on E.M.F. and activity coefficient. Instead, these are separated by the Chapters on strong electrolytes and those dealing with the optical properties of electrolyte solutions and fused salt melts.

The wide coverage of the book is shown by the fact that it includes, in addition to the above, Chapters on colloidal electrolytes, polarisation and polarography, double-layer capacity phenomena and electrocapillarity, electro-osmosis and electrophoresis, electropolishing and solid electrolytes and semiconductors. The electrochemistry of gases is discussed in detail, including discharge phenomena and electrochemical reactions and products in the gas phases. Short Chapters at the end of the book give brief notes on various analytical applications and electrodeposition.

The inclusion of so great a volume of material on so many diverse topics in so small a book has been achieved by keeping the written text to an absolute minimum and relying on simple diagrams and equations. For this reason it is easy to read. It should prove attractive to the student and to those who require to make reference of the principles of the subject. Very little of a practical nature is included and the Chapter on analytical applications is too short and lacking in detail to be of real value.

The binding is flimsy and the type too small for comfort, but it is otherwise an excellent and up-to-date book which is welcomed and can be recommended.

G. F. REYNOLDS

Deutsche Einheitsverfahren zur Wasser Untersuchung. Fachgruppe Wasserchemie, Gesellschaft Deutscher Chemiker. Third Edition. Verlag Chemie, Weinheim, 1960. Pp. 88 in Ring Binder. DM 20.—.

THIS is the first part of the third edition of standard physical, chemical and bacteriological methods for the examination of water, sewage, sewage sludge and boiler water, prepared by a group of chemists of the German Chemical Society. It is well produced in loose-leaf form to enable improved methods of analysis to replace existing procedures without the need to await revision of the whole book.

In the physical section methods for measuring turbidity, temperature, reaction, β-radiation are described. Spectrographic, flame photometric and absorption spectroscopic methods are referred to briefly. Determinations of sulphite, sulphide, cyanide, thiosulphate and thiocyanate in water are described in adequate detail. The section on the determination in the ionic form of those heavy metals, zinc, nickel and copper found in water or polluted waters is the best in the collection of methods described, and is equalled only by the authoritative description of methods for determining phenols.

A useful feature of the book is the brief account of the theoretical basis of each method, with mention of interfering substances and an indication of the range of concentrations for which the method is suitable. References to the literature are either sparingly given or omitted altogether. The book is a collection of practical, well tried methods of analysis.

S. H. JENKINS

Talanta, 1960, Vol. 5, p. 293. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The B.S.I. News announces the following new British Standards:

B.S. 1748: *Methods for the analysis of copper alloys*: *Part* 6: 1960. *Tin* (*nickel coil reduction method*). This specifies reagents required, recommended methods of sampling, and test procedure for the determination of tin in alloys having a tin content between 1·0 and 14·0%. The method is applicable to phosphor bronze and gun metals. (Price 3s.)

Part 7: 1960. *Silicon* (*photometric method*). This specifies reagents required, recommended methods of sampling, and test procedure for the determination of silicon in alloys having a silicon content between 0·005 and 0·2%. The method is applicable to phosphor bronze and gun metals. (Price 3s.)

Part 8: 1960. *Phosphorus* (*photometric method*). This specifies reagents of phosphorus in alloys having a phosphorus content up to 1·20%. The method is applicable to all types of copper alloys provided a suitable compensating solution is used when elements are present which would otherwise interfere in the optical density determination. (Price 3s.)

B.S. 1121: *Methods for the analysis of iron and steel: Part* 41: 1960. *Lead in carbon and low alloy steel.* This specifies a gravimetric method applicable to carbon steels and low alloy steels containing chromium, copper, molybdenum and nickel and with lead contents up to 0·05%. Tin up to 0·25% and tungsten up to 2·0% do not interfere. (Price 3s.)

This method supersedes B.S. 1121: Part 1C.

The following amendment slips to British Standards are also given:

B.S. 604: 1952. *Graduated measuring cylinders. Amendment No.* 4: *PD* 3783. (Gratis).
B.S. 733: 1952. *Density bottles. Amendment No.* 2: *PD* 3763. (Gratis).
B.S. 1017: *Part* 1: 1960. *Sampling of coal. Amendment No.* 1: *PD* 3796. (Gratis).
B.S. 1797: 1952. *Tables for use in the calibration of volumetric glassware. Amendment No.* 2: *PD* 3766. (Gratis).

Talanta, 1960, Vol. 5, p. 294. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Spectrophotometric determination of manganese^{II} with benzohydroxamic acid: Dwight O. Miller and John H. Yoe. (15 *July* 1960).

The fluorometric determination of *o*-phthalic acid: Glen A. Thommes and Elmer Leininger. (15 *July* 1960).

Analytical applications of 3-acetyl-4-hydroxycoumarin—III: Gravimetric determination of zirconium and titanium; A. N. Bhat and B. D. Jain. (26 *July* 1960).

The rapid determination of water in magnesium perchlorate desiccant. G. Frederick Smith. (26 *July* 1960).

Effect of chloride ions on nitrate determinations by Leithe's method: Carla Heitner-Wirguin and Debora Friedman. (30 *July* 1960).

Deuterium analysis by infrared spectrophotometry. (Mrs) M. A. MacKenzie and R. Norman Jones. (1 *August* 1960).

The co-crystallisation of ultramicro quantities of molybdenum with α-benzoinoxime: Determination of molybdenum in sea water. Herbert V. Weiss and Ming Gon Lai. (3 *August* 1960).

Indirect neutron absorption. W. Wayne Meinke. (4 *August* 1960).

Tetracyanoethylene chemistry. Indirect photometric determination of anthracene in naphthalene. George H. Schenk and Mara Ozoline. (5 *August* 1960).

Applications of infrared spectroscopy, III: The simultaneous determination of methoxyl and ethoxyl groups. D. M. W. Anderson and J. L. Duncan. (10 *August* 1960).

Applications of complementary tri-stimulus colorimetry: II; A least squares method applicable to multicomponent systems. Hermann Flaschka. (12 *August* 1960).

Investigations with iridium-192 of separations of platinum and rhodium from iridium, I: K. W. Lloyd and D. F. C. Morris. (12 *August* 1960).

Investigations with iridium-192 of separations of platinum and rhodium from iridium, II: K. W. Lloyd and D. F. C. Morris. (12 *August* 1960).

TALANTA

An International Journal of Analytical Chemistry

VOLUME 5 1960

Editor-in-chief **CECIL L. WILSON** *Belfast, N. Ireland*

Regional Editors

L. GORDON *Cleveland*

R. PŘIBIL *Prague*

T. TAKAHASHI *Tokyo*

G. GOPALA RAO *Waltair*

Assistant Editor **M. WILLIAMS** *Birmingham*

Editorial Advisory Board

Professor F. E. Beamish—Toronto
Professor R. Belcher—Birmingham (*Chairman of the Board*)
Professor H. Bode—Hanover
Professor G. Charlot—Paris
Professor C. Cimerman—Haifa
Dr. C. E. Crouthamel—Argonne, Illinois
Professor P. Delahay—Baton Rouge, Louisiana
Professor H. Diehl—Ames, Iowa
Dr. C. Drǎgulescu—Timisoara
Professor L. Erdey—Budapest
Professor F. Feigl—Rio de Janeiro
Professor H. Flaschka—Atlanta, Georgia
Professor W. Geilmann—Mainz
Dr. J. Hoste—Ghent
Mr. H. W. Kirby—Miamisburg, Ohio
Professor J. J. Lingane—Cambridge, Massachusetts
Professor F. Lucena-Conde—Salamanca
Dr. S. J. Lyle—Durham
Dr. R. J. Magee—Belfast
Professor H. Malissa—Vienna
Professor W. Wayne Meinke—Ann Arbor Michigan
Professor J. Minczewski—Warsaw
Dr. A. D. Mitchell—London
Dr. G. H. Morrison—Bayside, New York
Professor F. Nydahl—Uppsala
Dr. M. Pesez—Paris
Dr. E. Rancke-Madsen—Copenhagen
Professor C. N. Reilley—Chapel Hill, N. Carolina
Dr. M. L. Salutsky—Clarksville, Maryland
Professor E. Schulek—Budapest
Professor G. Semerano—Padova
Professor G. Frederick Smith—Urbana, Illinois
Professor H. Specker—Dortmund-Aplerbeck
Professor E. H. Swift—Pasadena, California
Professor P. S. Tutundžić—Belgrade
Professor F. L. Warren—Pietermaritzburg
Professor H. Weisz—Freiburg-Breisgau
Dr. T. S. West—Birmingham
Dr. James C. White—Oak Ridge, Tennessee
Professor H. H. Willard—Ann Arbor, Michigan
Mr. F. J. Woodman—Sellafield

PERGAMON PRESS LONDON · NEW YORK · PARIS · LOS ANGELES

LIST OF CONTENTS

Volume 5

SUBJECT INDEX

AUTHOR INDEX

(*Names of authors of books reviewed are in italics*)

NOTES FOR CONTRIBUTORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable.

Original papers, short communications, preliminary communications and reviews will be published. Suitable books submitted to the Editor-in-Chief will be reviewed.

Since TALANTA is an international journal, contributions are expected to be of a very high standard. Research papers should make a definite contribution to the subject. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, and should be critical. The Editor will welcome correspondence on matters of interest to analytical chemists.

All papers and short communications submitted for consideration will be refereed in the normal way. Referees will be encouraged to present critical and unbiassed reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

It is hoped that research and review papers will be published within approximately three to four months of acceptance, and short communications within two months.

Twenty-five free reprints of each paper will be provided (with ten further free copies for each additional author) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

2. Script Requirements

1. Contributions should be submitted to the Editor-in-Chief, or to the appropriate Regional Editor, and may be written in English, German or French.

2. Scripts should be submitted in duplicate. They must be typewritten and the lines double-spaced. Where possible, research papers should follow the pattern: *Introduction, Discussion, Conclusion, Experimental* (or such of these headings as apply).

3. The essential contents of each paper should be briefly recapitulated in a summary at the beginning of the paper. This should be in the language of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

4. Illustrations should be separated from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require redrawing should include all relevant details and clear instructions for the draughtsman. If figures are already well drawn, it may be possible to reproduce them direct from the originals, or from good photoprints, if these can be provided; it is not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The lettering should be sufficiently large and bold to permit this reduction. The following standard symbols should be used on line drawings, since they are easily available to the printers:

△ △ ⊡ □ ● ○ ◬ ⊙ ⊕ ⊖ ⏻ ⊗

5. Tables should if possible be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarise results by an accepted method of expression, e.g., standard deviation. The same information should not be reproduced in both tables and figures.

6. References should be indicated in the text by consecutive superior numbers; and the full reference, including title of paper where desired, should be given in a list at the end of the paper in the following form:

[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.

[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds.* Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.

[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.

[4] W. Jones, *Brit. Pat.* 654321, 1959.

Footnotes, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, ¶, commencing anew on each page; they should not be included in the numbered reference system.

7. Except in the case of preliminary communications, proofs will be sent to authors for correction when their contribution is first set, but there is rarely time for page proofs also to be sent for checking. This will be done, however, when the amount of alteration makes it advisable.

8. Because of the international character of the Journal, no rigid rules concerning spelling, notation or abbreviation need be observed by authors, but each paper or series of papers should be self-consistent as to symbols and units.

TALANTA

SEPTEMBER–OCTOBER 1960 VOLUME 5 NUMBERS 3/4

CONTENTS

PERGAMON PRESS LTD.

4 & 5 FITZROY SQUARE, LONDON W.1 122 EAST 55TH STREET, NEW YORK 22, N.Y.

Printed in Northern Ireland at The Universities Press, Belfast