An International Journal of Analytical Chemistry

ταλαντα

talanta

PERGAMON PRESS

OXFORD · LONDON · NEW YORK · PARIS

1963 VOLUME 10 OCTOBER

WHAT'S NEW FROM B.D.H?

BORON TRIFLUORIDE METHANOL COMPLEX—for preparing methyl esters of fatty acids

For the routine analysis of fatty acids by gas chromatography their methyl esters may be prepared by boiling the sample with the complex for 2 minutes followed by a simple purification. The whole procedure requires only about 10 minutes for each sample[1]. The complex is also used catalytically in determining alcoholic hydroxyl groups and aliphatic carboxylic acids[2].

1. Metcalfe, L. D. and Schmitz, A. A., *Anal. Chem.*, **1961, 33, 363-4.**
2. Mitchell, J., Jnr., Smith, D. M. and Bryant, M. W. D., *J. Amer. Chem. Soc.*, **1940, 62, 4-6.**

TOLUENE-*p*-SULPHON-HYDRAZIDE—a versatile reagent for carbonyl groups

The reagent can be used for characterising, separating and determining certain sugars, which usually yield crystalline, sparingly soluble hydrazones[1,2]. Toluene-*p*-sulphon-hydrazones of aromatic aldehydes and ketones react with sodium in ethane-diol to yield aryl diazo-methanes, while aliphatic carbonyl compounds usually give olefins[3].

1. Hough, L. and Jones, J. K. N., *J. Chem. Soc.*, **1951 1122-6.**
2. Easterby, D. G., Hough, L. and Jones, J. K. N., *J. Chem. Soc.*, **1951, 3426-8.**
3. Bamford, W. R. and Stevens, T. S., *J. Chem. Soc.*, **1952, 4735-40.**

NEW CAESIUM SALTS

Three more items, caesium bromate, chlorate and iodate, have been added to the list of B.D.H. caesium salts. B.D.H. have for years produced caesium salts on a large scale and welcome enquiries for laboratory or bulk quantities of both listed and unlisted caesium compounds. A list of those available from stock may be obtained on request.

'FLASH POINTS'

A new B.D.H. publication to assist those concerned with the handling and storage of liquid chemicals gives flash points for nearly a thousand liquids, listed alphabetically and generously cross-referenced. The information available from chemical literature, where however it is widely scattered, has been supplemented by a large number of determinations carried out in the B.D.H. Laboratories at Poole on standard grade materials.

NICKEL PEROXIDE—a powerful oxidising agent

The black higher oxides of nickel, conveniently termed 'nickel peroxide', have a large surface area for a given weight. The available oxygen can be used effectively for oxidising alcohols to the corresponding carboxylic acids; in organic solvents aromatic alcohols are oxidised to the aldehydes in good yield[1]. These oxidations are reported to proceed more quickly and with a smaller excess of oxidising agent than is the case when manganese dioxide is employed.

1. Nagakawa, K., Konaka, R. and Nakata, T., *J. Org. Chem.*, **1962, 27, 1597-1601.**

BDH
THE BRITISH DRUG HOUSES LTD.
B.D.H. LABORATORY CHEMICALS DIVISION · POOLE · ENGLAND

G.7

SUMMARIES FOR CARD INDEXES

***p*-Thiocresol as a new reagent for technetium and rhenium:** M. AL-KAYSSI and R. J. MAGEE: *Talanta*, 1963, **10**, 1047 (The Queen's University, Belfast, Northern Ireland.)

Summary—*p*-Thiocresol has been developed as a new reagent for technetium and rhenium. By means of it technetium is reduced from the heptavalent state, and is determined spectrophotometrically by the colour produced between the reduced technetium and the reagent. Rhenium is not reduced, so that a separation of the two elements is facilitated. The influence of other elements has been investigated, and a procedure for the determination of technetium and rhenium is presented.

The direct polarography of aluminium: I. TALESNICK and JOHN A. PAGE, *Talanta*, 1963, **10**, 1055 (Department of Chemistry, University of Toronto, Toronto, 5. Canada.

Summary—The direct polarography of aluminium has been investigated in a 0·10M tetrabutylammonium chloride (tbNH$_4$Cl) electrolyte. Adjustment of pH prior to polarography is accomplished by a constant current electrolysis of the acid solution using a platinum cathode and a silver anode. The pH can be adjusted precisely and the aluminium waves are highly reproducible. For analytical determinations a pH of 3·70 has been arbitrarily chosen for concentrations of aluminium up to 2mM. The method is applied to the analysis of a zinc-base alloy, using both controlled potential electrolysis and amalgamometry to separate interfering elements.

The application of some hydroxamic acids in analytical chemistry—III: A spectrophotometric examination and analytical application of the reaction between vanadium^{V} and thiophene-2-hydroxamic acid: JERZY MINCZEWSKI and ZOFIA SKORKO-TRYBUŁA, *Talanta*, 1963, **10**, 1063. (Katedra Chemii Analitycznej, Politechniki Warszawskiej, Warszawa, Poland.)

Summary—Thiophene-2-hydroxamic acid has not previously been used as an organic reagent for inorganic analysis. Its ultraviolet absorption spectra have been studied in acid and alkaline solutions, and its dissociation constant has been established as about $1{\cdot}7 \times 10^{-8}$. The acid reacts with many metallic ions, *e.g.*, Fe^{III}, Co^{II}, Mn^{II}, Mo^{VI} and Nb^{V}, giving precipitates or soluble compounds. It forms violet complexes with V^{V}. The composition of these complexes has been studied in relation to the pH of the solution. The complex formed at pH 3.5 has the composition V:R = 1:3, and the maximum of the absorption band is at $\lambda = 590$ mμ. The corresponding values for the complex formed at pH 7·7 are 1.3μ and 550 mμ. The extractability of the complex formed in moderately acid solution has been used in devising a method for the determination of low concentrations (1·5–0·05%) of vanadium in various materials.

Anion-exchange separation of rare earth elements and thorium from uranium with carbonate solutions: TOMITSUGU TAKETATSU, *Talanta*, 1963, **10**, 1077. (General Education Department, Kyushu University, Fukuoka, Japan.)

Summary—Quantitative separation of some rare earth elements and thorium from uranium^{VI} is carried out using Dowex 1, X–8 with 0·7*M* potassium carbonate or 0·4*M* ammonium carbonate* solution as eluant.

Determination of nitrogen in organic compounds using ion-exchange resins: R. A. Shah and A. A. Qadri, *Talanta*, 1963, **10**, 1083. (Central Laboratories, Pakistan Council of Scientific and Industrial Research, 34–37 P.N.H. Lines, Karachi-Cantt., Pakistan.)

Summary—Nitrogen in an organic compound is determined by decomposing the sample in a sealed tube with sulphuric acid and passing the digest through two columns of anion-exchange resin, placed one above the other. The upper column contains the resin in the hydroxide form and the lower column in the iodide form. Hence, the ammonium sulphate in the digest is converted to ammonium iodide, which is determined by the Leipert amplification procedure.

A solvatochromic chelating agent: A. MUELLER, J. TRAVIS LEACH and J. P. PHILLIPS, *Talanta*, 1963, **10**, 1087. (Department of Chemistry, University of Louisville, Louisville 8, Kentucky U.S.A.)

Summary—1-Methyl-2-[2-(8-hydroxy-5-quinolyl)vinyl]-8-hydroxyquinolinium chloride has been prepared as an example of a chelating agent for metals that changes colour with solvent polarity. As a chelating agent it has some selectivity, precipitating only the copper^{II} ion in an acidic solution and forming a distinctively coloured product with zinc in neutral solutions. In ammoniacal methanol it gives a red solution with magnesium and several other ions. A number of related solvatochromic compounds have also been prepared.

Non-destructive activation analysis of arsenic and antimony in lead: F. ADAMS and J. HOSTE, *Talanta*, 1963, **10**, 1093. (Institute for Analytical Chemistry, Ghent University, Belgium.)

Summary—A neutron-activation analysis has been devised for the non-destructive simultaneous determination of arsenic and antimony in lead. The ^{122}Sb and ^{76}As activities are computed by gamma counting at two discrete energies. The method has been tested with synthetic samples in the antimony and arsenic concentration range of 1 to 10^{-4}%. The reproducibility is generally better than 10%.

Systematic titration errors in titrimetric analysis: U. A. TH. BRINKMAN, *Talanta*, 1963, **10**, 1103. (Chemical Laboratory, Free University, Amsterdam, The Netherlands.)

Summary—A brief summary is given of the formulae that can be derived for the systematic titration error for different types of titration using visual end-point detection. The methods by which these formulae can be elaborated to make them suitable for calculations are indicated. Mention is made of the introduction of the indicator-compound into the formula used for precipitation titrations.

The dissolution of alunite employing hot concentrated perchloric acid: Determination of silica and aluminium: G. FREDERICK SMITH and W. H. TAYLOR, *Talanta*, 1963, **10**, 1107. (Noyes Chemical Laboratories, University of Illinois, Urbana, Illinois, U.S.A.)

Summary—Finely ground alunite (hydrated potassium aluminium sulphate) can be dissolved in hot 72·5% perchloric acid. Determinations of silica and R_2O_3 metals in samples of alunite so dissolved agree closely with similar determinations following a sodium carbonate fusion procedure.

The determination of thiomalic acid: V. CHROMÝ and V. SVOBODA, *Talanta*, 1963, **10**, 1109. (Spolana N.C., Research Centre of the Lachema Plant, Brno, Czechoslovakia.)

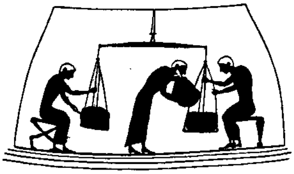
Summary—A titrimetric method for the determination of thiomalic acid is described. It is based on the titration of the —SH group of thiomalic acid with a solution of sodium *o*-hydroxymercuribenzoate in the presence of thiofluorescein as indicator. The method is simple and rapid, and it allows the determination of thiomalic acid with an accuracy of ±0·1%.

Spot tests for pyridine aldehydes, pyridine-2-aldehyde, phenylhydrazine, phenylhydrazones and osazones: F. FEIGL and L. BEN-DOR, *Talanta*, 1963, **10**, 1111. (Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel.)

Summary—Spot tests for the detection of the three isomeric pyridine aldehydes and for pyridine-2-aldehyde are described. The tests are based on colour reactions with phenylhydrazine and with iron^{II} sulphate and hydroxylamine respectively. The chemical basis of the colour reactions is discussed and the pertinent procedures are outlined. The colour reaction between pyridine-2-aldehyde and phenylhydrazine makes possible the detection of the latter as well as of phenylhydrazones and osazones after their acidic hydrolytic cleavage.

TALANTA

An International Journal of Analytical Chemistry



PERGAMON PRESS LTD.

4 & 5 FITZROY SQUARE, LONDON W.1 122 EAST 55TH STREET, NEW YORK 22, N.Y.

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

Published monthly - 1 Volume *per annum*

Annual subscription (including postage): (A) for Libraries, Government Establishments and Research Institutions—£21 ($60). (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).

(C) for *bona fide* students—£3.10. ($10).

Payments must be made in advance

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

PRINTED IN NORTHERN IRELAND AT THE UNIVERSITIES PRESS, BELFAST

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, preliminary and short communications, reviews and letters will be published.

Because TALANTA is an international journal, contributions are expected to be of a very high standard. They should make a definite contribution to the subject. Papers submitted for publication should be new publications. The submission of a paper is held to imply that it has not previously been published in any major language (English, French, German, Russian), that it is not under consideration for publication elsewhere, and that, if accepted for publication, it will not be published elsewhere without the written consent of the Editor-in-Chief. 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, **but should be critical.** The Editor-in-Chief will welcome correspondence on matters of interest to analytical chemists.

Original papers, short communications and reviews will be refereed (see *Talanta*, 1962, **9**, 89). 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-in-Chief, 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.

Preliminary communications will be refereed urgently, and will be accorded priority in publication. Letters to the Editor will not be refereed, but will be published at the discretion of the Editor-in-Chief. If accepted, they will also be given priority.

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

General

Contributions should be submitted to the Editor-in-Chief, **or to the appropriate Regional Editor,** and may be written in English, German or French.

Preliminary communications should be limited to less than 1000 words in length and should not contain diagrams. If they do not fulfill these conditions they will be treated as short communications.

Scripts should be submitted in duplicate. They must be typewritten and the lines double-spaced. Where possible, papers should follow the pattern: *Introduction, Discussion, Conclusion, Experimental* (or such of these headings as apply).

Because all material will be set directly in page proof, every attempt should be made to ensure that before being submitted, manuscripts are essentially in the final form desired by the authors, and that no alterations of moment will be required at the proof stage. Alterations suggested by the referee will be agreed with the authors at the manuscript stage. Authors whose native language is not English are advised that in submitting papers in English they should endeavour to have the paper thoroughly corrected before submitting for publication. If the manuscript requires considerable editing, it may have to be returned to the authors for retyping, resulting in a serious delay in publication.

Summaries

The essential contents of each paper should be briefly recapitulated in a summary placed at the beginning of a paper, or at the end of a preliminary or short communication. 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.

Illustrations

Illustrations should be separate 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; this will ensure more rapid publication. It is**

not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The following standard symbols should be used on line drawings, because they are easily available to the printers:

▲ △ ⊡ □ ● ○ ◬ ⊙ ⊕ ⊖ ⏻ ⊗

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 produced in both tables and figures.

The preferred positions for all figures and tables should be indicated in the manuscript by the authors.

References

References should be indicated in the text by consecutive superior numbers; and the full reference 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.

Proofs

Proofs will be sent out to authors in page form for correction. **It is emphasised that at this stage extensive alterations to the text or failure to return the corrected proofs promptly may result in serious delay in publication.**

Authors are particularly requested to check the correctness of their references, which should, at some stage, also be checked against the original papers.

Miscellaneous

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. In editing papers for publication the conventions used, on the whole, will be English spelling for all matter in the English language, and the general usages described in *Handbook for Chemical Society Authors* (The Chemical Society, London, Special Publication No. 14, 1960). It would be helpful if authors would consult this for guidance in the preparation of their manuscripts. Authors who wish to retain American spelling, or to adhere to other generally accepted usages, should indicate this clearly at the time of submission of the manuscript.

Where several authors are involved in a paper, an indication of the author to whom requests for reprints should be addressed may be given by placing the symbol ® after the name of that author.

By following the Script Requirements carefully, authors will assist greatly in ensuring rapid publication.

ADVISORY BOARD

Chairman:	Professor R. Belcher	University of Birmingham, England
	Professor G. Ackermann	School of Mines, Freiberg, German Democratic Republic
	Dr. D. M. W. Anderson	University of Edinburgh, Scotland
	Professor F. E. Beamish	University of Toronto, Ontario, Canada
	Mr. E. Bishop	University of Exeter, England
	Dr. C. E. Crouthamel	Argonne National Laboratory, Illinois, U.S.A.
	Dr. E. A. M. F. Dahmen	Koninklijke/Shell Lab., Amsterdam, Netherlands
	Professor L. Erdey	Technical University, Budapest, Hungary
	Professor Fritz Feigl	Ministry of Agriculture, Rio de Janeiro, Brazil
	Professor H. Flaschka	Georgia Institute of Technology, Atlanta, Georgia, U.S.A.
	Mr. J. K. Foreman	U.K.A.E.A., Windscale Works, Cumberland, England
	Professor H. Freiser	University of Arizona, Tucson, Arizona, U.S.A.
	Professor R. B. Hahn	Wayne State University, Detroit, Michigan, U.S.A.
	Mr. J. O. Hibbits	General Electric Company, Cincinnati, Ohio, U.S.A.
	Professor K. J. Karrman	University of Lund, Sweden
	Professor W. Kemula	University of Warsaw, Poland
	Professor G. Kortüm	University of Tübingen, German Federal Republic
	Dr. R. J. Magee	The Queen's University, Belfast, Northern Ireland
	Professor H. Malissa	Technical University, Vienna, Austria
	Professor J. Minczewski	Politechnika Warsaw, Poland
	Mr. John Mitchell, Jr.	E. I. duPont de Nemours, Wilmington, Delaware, U.S.A.
	Dr. D. F. C. Morris	Brunel College, London, England
	Dr. Maurice Pesez	Roussel-Uclaf, Paris, France
	Dr. G. A. Rechnitz	University of Pennsylvania, Philadelphia, U.S.A.
	Professor W. Rieman III	Rutgers University, New Brunswick, U.S.A.
	Professor Shu-Chuan Liang	Academia Sinica, Peking, China
	Professor E. Schulek	L. Eötvös University, Budapest, Hungary
	Professor G. Frederick Smith	University of Illinois, Urbana, Illinois, U.S.A.
	Dr. M. Steinberg	The Hebrew University of Jerusalem, Israel
	Professor E. H. Swift	California Institute of Technology, Pasadena, California, U.S.A.
	Dr. E. Wänninen	Åbo Academy, Finland
	Dr. T. S. West	Imperial College of Science and Technology, London, England
	Dr. James C. White	Oak Ridge National Laboratory, Tennessee, U.S.A.
	Dr. D. H. Wilkins	General Electric Company, Schenectady, U.S.A.
	Professor Hobart H. Willard	University of Michigan, Ann Arbor, Michigan, U.S.A.
	Mr. A. F. Williams	I.C.I., Ltd., Nobel Division, Stevenston, Scotland
	Dr. P. Zuman	Polarographic Institute, Czechoslovak Academy of Science, Prague, Czechoslovakia

Talanta, 1963, Vol. 10, pp. 1047 to 1053. Pergamon Press Ltd. Printed in Northern Ireland

-THIOCRESOL AS A REAGENT FOR TECHNETIUM AND RHENIUM

M. AL-KAYSSI* and R. J. MAGEE
Department of Chemistry, The Queen's University, Belfast, Northern Ireland

(*Received* 17 *July* 1962. *Accepted* 4 *March* 1963)

Summary—*p*-Thiocresol has been developed as a new reagent for technetium and rhenium. By means of it technetium is reduced from the heptavalent state, and is determined spectrophotometrically by the colour produced between the reduced technetium and the reagent. Rhenium is not reduced, so that a separation of the two elements is facilitated. The influence of other elements has been investigated, and a procedure for the determination of technetium and rhenium is presented.

FOR rhenium a large number of reagents are known,[1,2] but few are available for the detection and determination of technetium.[3-5] In recent papers the authors have suggested new colorimetric reagents for the determination of technetium and rhenium[6] which were successful within the limits imposed. However, in work of which the present results are a part, attention was drawn to the potentialities of sulphur compounds, in particular, the mercaptans, as analytical reagents for these elements.

Mercaptans are not new as analytical reagents. Toluene-3,4-dithiol has been used for the detection and determination of tin[7] and bismuth.[8] Molybdenum, tungsten and rhenium also form with this reagent coloured compounds which are soluble in chloroform and carbon tetrachloride.[9-11]

Miller and Thomason[12] used dithiol as a colorimetric reagent for technetium. But because technetium and rhenium are often associated with molybdenum and tungsten, dithiol cannot be used in the presence of these elements unless a prior separation has been carried out.

In the present work mercaptans as reagents were investigated, and a simpler mercaptan was sought which would be suitable for the detection and determination of technetium and rhenium.

Simple aliphatic and aromatic mercaptans may be considered as analogues of the alcohols, with the —SH groups corresponding to the —OH group in alcohols. The —SH group is more acidic and the hydrogen is easily replaced by metallic ions to form mercaptides.

Heavy metals which have a marked affinity for sulphur-containing compounds, such as mercury, silver, gold, copper, lead, cadmium, tin, antimony, platinum metals, *etc.*, form insoluble mercaptides with mono-thiols.[13] The mercaptides of tin, bismuth, antimony and platinum metals are soluble in chloroform; those of copper, silver and mercury are insoluble in this solvent.

In the case of the coloured compounds formed by toluene-3,4-dithiol with molybdenum, tungsten, rhenium and technetium, the metal is directly bound to the sulphur atoms of both mercapto-groups, to one by a principal valence, to the other by an

---

* Present address: Baghdad University, The Republic of Iraq.

auxiliary valence, so that anionic chelates result. With molybdenum, for example, a five-membered ring chelate compound with two anionic basic groups is formed. The presence of two adjacent mercapto-groups in a benzene ring therefore appears to cause such compounds to form complex compounds with a large number of metal ions. For this reason, the investigation was directed towards simple mercaptans in order to study their behaviour towards technetium and rhenium under different conditions.

Particular attention was given to thiophenol, *o*-thiocresol and *p*-thiocresol. The last was preferred, because it is solid under normal conditions (m.p. 43°). *p*-Thiocresol (PTC) does not react with technetium^{VII} or rhenium^{VII}; but it forms, with the lower valence states of these two elements, yellowish-brown complexes which are soluble in chloroform, carbon tetrachloride, benzene and ether. The reaction is carried out in acetic acid medium. Technetium^{VII} is reduced by the reagent in glacial acetic acid; rhenium^{VII} is reduced by stannous chloride. Molybdenum^{VI} and tungsten^{VI}, on the other hand, apparently do not react with PTC to form complexes, but on the addition of stannous chloride, light blue and dark brown precipitates, respectively, are formed. These precipitates are not soluble in non-polar solvents. *p*-Thiocresol also forms insoluble mercaptides with tin, cadmium, bismuth, antimony, copper, silver, mercury, lead, *etc.*

p-Thiocresol is a powerful reducing agent in acid solution. This property was utilised to separate technetium and rhenium. Technetium was reduced by addition of a controlled amount of PTC in glacial acetic acid medium, presumably to the quinquevalent state. Under these conditions, rhenium^{VII} is not reduced, and does not therefore form a mercaptide. Glacial acetic acid as a medium has, also, the advantage of preventing precipitation of tin, antimony, lead, cadmium and bismuth mercaptides and in eliminating their interference in the technetium determination.

After the determination of technetium, rhenium is determined by the thiocyanate method,[15] being first separated as the mercaptide; in this way interference from the stannous chloride used as a reducing agent is avoided.

EXPERIMENTAL

Apparatus

Spectrophotometric measurements were made with the Unicam SP 600 instrument.

Reagents

p-*Thiocresol:* Supplied by British Drug Houses; recrystallised twice from glacial acetic acid. A 5% solution in glacial acetic acid was prepared. The solution keeps indefinitely.

Caesium pertechnetate: Spectrographically pure: supplied by the U.K. Atomic Energy Authority, Windscale. An aqueous solution containing 49 μg/ml was used.

Ammonium perrhenate: "Specpure," supplied by Johnson, Matthey and Co. Ltd. An aqueous solution containing 100 μg/ml. was used.

All other reagents used were of "AnalaR" grade.

Procedure

Place 2 ml of the neutral test solution in a 100-ml separatory funnel which has been coated with a water repellent; follow this by 10 ml of glacial acetic acid and 0·2 ml of 5% PTC solution. Mix the contents for 1 min and allow to stand for 30 min. Add 10 ml of chloroform and 5 ml of water, and shake the mixture gently for 2 min. Drain the yellowish-brown extract through a filter paper holding approximately 5 g of anhydrous sodium sulphate. Collect the extract in a 25-ml volumetric flask. To the original solution in the separatory funnel add 5 ml of glacial acetic acid and 0·2 ml of PTC solution. Mix, and extract with another 10 ml of chloroform after 10 min. Wash the filter paper with chloroform until the extract is diluted to the mark. A "blank" solution is carried through the whole procedure at the same time as the test solution. Measure the absorbance of the solution against the "blank" solution in a 1-cm cell at 410 mμ and determine the concentration of technetium from a calibration curve (Fig. 1).

To the original solution in the separatory funnel, add 5 ml of glacial acetic acid, 2 ml of PTC solution and 0·5 ml of 10% stannous chloride solution. Mix the contents of the funnel for 1 min, and allow to stand for 5 min. Add 10 ml of chloroform and shake gently for 2 min. If there is no phase separation, add a few ml of water and shake again. Drain the yellowish-brown extract into a 250-ml boiling flask. To the original solution in the separatory funnel, add 5 ml of glacial acetic acid and 1 ml of PTC solution, followed by 0·5 ml of stannous chloride solution. After 5 min, extract with another 10 ml of chloroform.

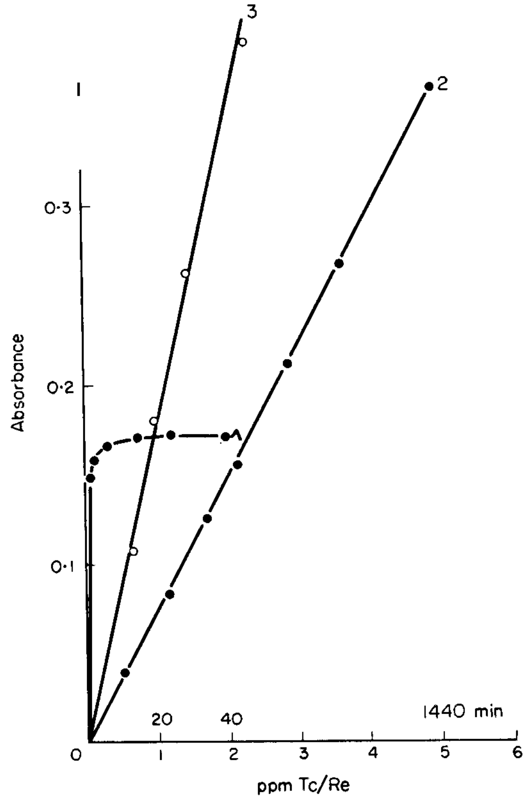


FIG. 1.—Calibration curves.
1—Absorbance-time curve for Tc-TPC.
2—Calibration curve for Tc-TPC.
3—Calibration curve for Re (thiocyanate method).

Combine the chloroform extracts in a 250-ml boiling flask. If molybdenum was present in large amount, shake the extract with 20 ml of 20% acetic acid to which has been added 1 ml of PTC solution. Attach the boiling flask to a distillation apparatus and distil the chloroform under a slight vacuum to incipient dryness. Remove the last traces of chloroform and acetic acid by swirling the flask. Add 20 ml of 2*M* sodium hydroxide solution and 5 ml of 30% hydrogen peroxide. Boil gently, add another 5 ml of hydrogen peroxide, and continue boiling for about 20 min until the solution becomes almost clear, when complete decomposition of rhenium complex and oxidation of rhenium to the heptavalent state has taken place.

Add 1 ml of 0·5% nickel sulphate solution and continue boiling to decompose excess hydrogen peroxide. Neutralise the solution with concentrated hydrochloric acid and add a slight excess to dissolve nickel hydroxide. If less than 100 μg of rhenium was present, transfer the cold solution to a 250-ml separatory funnel; otherwise, transfer an aliquot to the separatory funnel, dilute to 40 ml with water, and add 10 ml of concentrated hydrochloric acid followed by 2 ml of 20% ammonium thiocyanate solution and 3 ml of 35% stannous chloride solution. Mix the contents, and after a period of 5–7 min extract the orange colour with 2 × 20-ml portions of ether. Combine the extracts in a 50-ml volumetric flask, and dilute to the mark with ether. Measure the absorbance at 432 mμ, using a 1-cm cell, against a "blank" solution carried through the entire procedure. Determine the amount of rhenium from a calibration curve (Fig. 1, curve 3). Results obtained using this procedure are shown in Table I.

TABLE I

Rhenium^{VII}		Technetium^{VII}		Other elements present	Amount, *mg*
Taken, *μg*	Found, *μg*	Taken, *μg*	Found, *μg*		
100·0	99·6	24·0	25·0	Mo^{VI}	5·0
100·0	98·0	24·0	24·0	W^{VI}	7·3
—	—	24·0	24·6	Re^{VII}	3·7
100·0	98·2	—	—	UO$_2^{II}$	5·0
100·0	98·0	—	—	Th^{IV}	4·6
100·0	98·8	—	—	Mn^{II}	5·4
100·0	97·2	—	—	Fe^{III}	5·6
100·0	98·0	—	—	Pb^{II}	6·6
100·0	99·1	—	—	Co^{II}	6·0
100·0	98·8	—	—	Ni^{II}	6·0
100·0	97·9	—	—	V^{V}	5·1

RESULTS AND DISCUSSION

The reaction between technetium^{VII} and *p*-thiocresol is relatively slow, because two successive reactions occur; reduction, presumably, to the quinquevalent state, and then complexing of technetium^{V} with PTC. Full development of the yellowish-brown colour occurs after 30 min as shown in Fig. 1, curve 1. Stannous chloride gives more rapid reduction, and the complex is formed almost immediately. Rhenium^{VII} is not affected by PTC in neutral solution; but in strong acetic acid, and when the concentration of the reagent exceeds 0·1% in the final solution, rhenium^{VII} is slowly reduced, and is complexed by PTC. If the concentration of PTC is kept below this limit, no reduction of rhenium occurs. The concentration of acetic acid is not critical so long as the precipitation of certain metallic mercaptides is prevented, *e.g.*, lead, tin, antimony and bismuth. In chloroform solution *p*-thiocresol shows an absorption maximum at 300–305 mμ. The technetium complex, on the other hand, shows two absorption maxima, at 320–325 mμ and 410 mμ, as shown in Fig. 2. The latter maximum, which is used to determine technetium, is weaker but less subject to interference from the reagent, as can be seen from Fig. 2 curve. At 410 mμ technetium has a molar absorbancy index of about 7350.

Solubility in organic solvents

Technetium and rhenium *p*-thiocresol complexes may be extracted from acetic acid solution into chloroform, carbon tetrachloride, ether, benzene or toluene. In all these solutions the complexes maintain their original colour.

In order to study the extractibility of the technetium complex into chloroform, the extraction was carried out according to the standard procedure described above; it was found that about 0·2% of the β-activity (emitted by technetium-99) was not extracted into chloroform. The extractibility of the rhenium complex was determined, using the thiocyanate method to determine the amount of rhenium unextracted. Under the same conditions 0·5–1% of rhenium was left in the aqueous phase.

Effect of mineral acids

The effect of hydrochloric acid on the formation and the extraction of the rhenium complex was studied in detail. The presence of hydrochloric acid greatly reduces the extractibility of the rhenium complex into chloroform. At higher hydrochloric acid concentrations the extraction becomes almost negligible, and a new, red complex with an absorption maximum at 455 m*μ* is formed. This red species is extracted into amyl alcohol from approximately $8N$ acid solution, but not into chloroform. From the solubility in the two latter solvents it is suggested that the red species is presumably a chlorinated product with slight anionic character. Under these conditions, the yellowish-brown technetium complex is not formed.

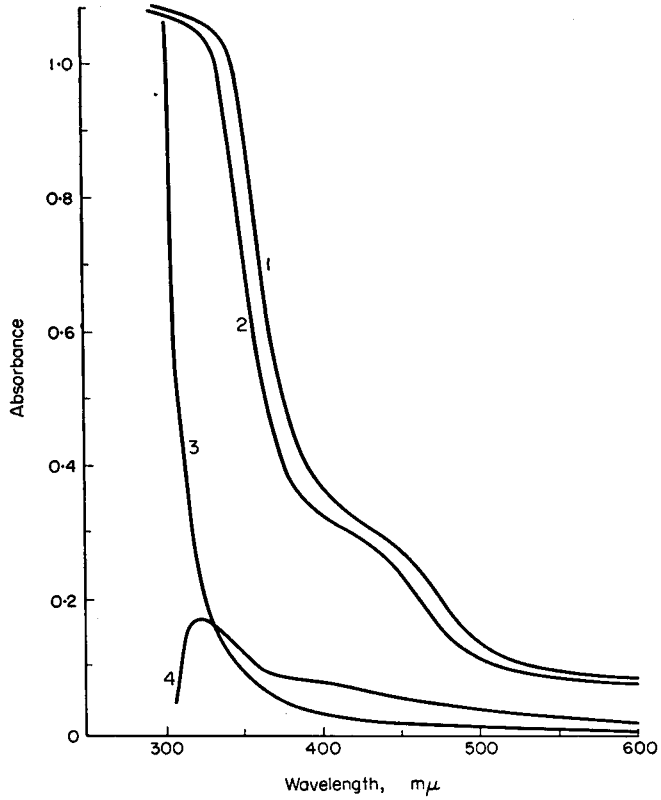


FIG. 2.—Absorption spectra.
1—3·8 ppm of Tc-PTC *vs.* $CHCl_3$ as blank.
2—3·8 ppm of Tc-TPC *vs.* PTC as blank.
3—PTC *vs.* $CHCl_3$ as blank.
4—0·7 ppm of Tc-PTC *vs.* PTC as blank.

Action of alkali and hydrogen peroxide mixture

When the technetium complex, in chloroform, is shaken with $2N$ sodium hydroxide solution, no appreciable change in the absorbance of the solution is noticed. On the addition of hydrogen peroxide a partial decomposition of the complex occurs, and decomposition is complete on boiling with a mixture of sodium hydroxide and hydrogen peroxide. It is essential, as described in the *Procedure*, to decompose unused hydrogen peroxide by means of nickel salts.[14]

Interfering ions

The behaviour of a large number of ions with the reagent and the extractibility of any products into chloroform was investigated.

Molybdenum^{VI} is reduced by PTC in acetic acid medium yielding a blue precipitate which is not extracted into chloroform; this element therefore does not interfere in the determination of technetium. When stannous chloride is added to the solution in order to reduce and complex rhenium^{VII}, molybdenum^{VI}, if present in mg-quantities, is reduced to a dark brown precipitate, which is also not extracted into chloroform. Sometimes, however, it was found that a few μg of molybdenum diffused through the chloroform phase during the shaking of the mixture. However, this source of interference may be eliminated by shaking the chloroform extract of the rhenium complex with 20 ml of 20% acetic acid containing PTC. Tungsten^{VI}, cobalt^{II}, iron^{III}, thorium^{IV}, uranium^{VI}, lead^{II}, nickel^{II}, copper^{II}, chromium^{III}, silver, vanadium^{V}, titanium^{III}, manganese^{II} and mercury^{II} do not interfere in the determination of technetium and rhenium. About 3 mg of tin^{II}, antimony^{III}, bismuth^{III} or cadmium, when treated with PTC and extracted with chloroform, show an absorbance at 410 mμ of 0·150, 0·014, 0·060 or 0·075, respectively. To eliminate this source of interference, the extraction stage is omitted and the absorbance of the technetium complex solution is measured directly in the acetic acid solution, provided that no other metallic ions which impart an interfering colour are present.

The elements which were not found to interfere with the determination of these elements are included in Table I. Ruthenium, palladium, platinum and rhodium form coloured complexes with PTC which are extracted into chloroform and their initial separation is, therefore, essential.

Acknowledgement—The authors wish to thank the United Kingdom Atomic Energy Authority (Production Group), Windscale, Cumberland, for the supply of technetium-99 which made this work possible.

Zusammenfassung—*p*-Thiocresol wurde als neues Reagens für Technetium und Rhenium eingesetzt. Technetium wird vom siebenwertigen Zustand reduziert und mittels der hierbei entwickelten Färbung photometrisch bestimmt. Rhenium wird nicht reduziert, sodass eine Trennung der beiden Elemente erleichtert ist. Der Einfluss anderer Elemente wurde untersucht und eine Methode zur Bestimmung von Technetium und Rhenium wird mitgeteilt.

Résumé—Le *p*-Thiocresol est un nouveau réactif du technétium et du rhénium. Après réduction du technétium VIII, celui-ci est dosé par spectrophotométrie en utilisant le complexe coloré formé entre le technétium réduit et le *p*-thiocrésol. Le rhénium n'est pas réduit de sorte que la séparation des deux éléments est rendue plus facile. L'influence d'autres éléments a été étudiée et une méthode de dosage du technétium et du rhénium est décrite.

REFERENCES

[1] L. C. Hurd, *Ind. Eng. Chem., Analyt.*, 1936, **8**, 11.

[2] D. I. Ryabchikov and A. I. Lazareve, *Zhur. Analyt. Khim.*, 1955, **10**, 228.

[3] C. E. Crouthamel, *Analyt. Chem.*, 1957, **29**, 1756.

[4] J. R. Embleton and J. K. Foreman, United Kingdom Atomic Energy Authority, Production Group Report 93 (W), March, 1960.
[5] F. Jasim, R. J. Magee and C. L. Wilson, *Talanta*, 1960, **4,** 17; 1959, **2,** 93.
[6] M. Al-Kayssi, R. J. Magee and C. L. Wilson, *ibid.*, 1962, **9,** 125; R. J. Magee and M. Al-Kayssi, *ibid.*, 1962, **9,** 667; *Analyt. Chim. Acta*, in press.
[7] R. E. D. Clark, *Analyst*, 1937, **62,** 661.
[8] C. C. Miller and A. J. Lowe, *J. Chem. Soc.*, 1940, 1258.
[9] J. H. Hamence, *Analyst*, 1940, **65,** 152.
[10] C. C. Miller, *J. Chem. Soc.*, 1941, 792.
[11] *Idem*, *ibid.*, 1943, 72.
[12] F. J. Miller and P. F. Thomason, *Analyt. Chem.*, 1961, **33,** 404.
[13] E. E. Reid, *Organic Chemistry of Bivalent Sulphur*. Chemical Publishing Co. Inc., New York, 1958, p. 142.
[14] F. Feigl, *Chemistry of Specific, Selective and Sensitive Reactions*. Academic Press, New York, 1949, p. 143.
[15] W. Geilmann, F. W. Wrigge and F. Weibke, *Z. anorg. Chem.*, 1932, **208,** 217.

Talanta, 1963, Vol. 10, pp. 1055 to 1062. Pergamon Press Ltd. Printed in Northern Ireland

THE DIRECT POLAROGRAPHY OF ALUMINIUM

I. TALESNICK and JOHN A. PAGE
Department of Chemistry, University of Toronto, Toronto 5, Canada

(*Received* 8 *March* 1963. *Accepted* 7 *May* 1963)

Summary—The direct polarography of aluminium has been investigated in a 0·10*M* tetrabutylammonium chloride (tbNH$_4$Cl) electrolyte. Adjustment of pH prior to polarography is accomplished by a constant current electrolysis of the acid solution using a platinum cathode and a silver anode. The pH can be adjusted precisely and the aluminium waves are highly reproducible. For analytical determinations a pH of 3·70 has been arbitrarily chosen for concentrations of aluminium up to 2*mM*. The method is applied to the analysis of a zinc-base alloy, using both controlled potential electrolysis and amalgamometry to separate interfering elements.

INTRODUCTION

THE direct polarography of aluminium has been reviewed by Kolthoff and Lingane,[1] Milner,[2] Perkins and Reynolds,[3] and most recently by Heyrovský.[4] At the dropping mercury electrode in acid solution aluminium gives a reduction wave in the same potential region as the wave from hydrogen ion discharge, and a careful control of the acidity of the solution is necessary.

Von Stackelberg[5] has suggested that the polarography should be carried out in a lithium chloride electrolyte of pH 2 to 3. He found that the half-wave potential of the aluminium shifted to more negative values with decreasing pH, and at this acidity there was a clear separation between the aluminium wave and the preceding hydrogen wave. The procedure could only be recommended for relatively concentrated aluminium solutions (10^{-2}"*N*") because of the magnitude of the wave from hydrogen ion reduction. In addition, the current plateau for the aluminium wave is irregular because the large current forms discrete gas bubbles at the dropping mercury electrode.

A second technique, originated by Gull,[6] carries out the polarography at the minimum acidity necessary to prevent the formation of colloidal aluminium hydroxide. Under these conditions there is no separate hydrogen wave, but it is merged into the foot of the aluminium wave (Fig. 1). The pH of the solution is adjusted to some fixed value so that the hydrogen ion contribution to the total wave is constant. The wave height, in some cases measured from a rather arbitrary graphical construction, is related to the aluminium concentration by a calibration curve.

Kolthoff and Lingane[1] have recommended that the pH be less than the natural pH resulting from the hydrolysis of the aluminium or precipitation will occur. Semerano and Ronchi[7] state that the pH of a pure solution of aluminium chloride depends on the molar concentration (C) according to the relation:

$$\text{pH} = 2{\cdot}65 - 0{\cdot}54 \log \text{C}$$

which gives a value of 4·27 for the pH of a 1*mM* pure aluminium chloride solution. In practice, this pH value may be exceeded, for the complexing action in a chloride supporting electrolyte will inhibit precipitation.

The pH of the solution must be adjusted to the final exact value without the benefit of buffers, for the un-ionised weak acid (HA) will result in a larger hydrogen wave at a given pH:

$$i_d = k_{H_{aq}^+} C_{H_{aq}^+} + K_{HA}C_{HA}$$

and any appreciable concentration of buffer constituents will obscure the aluminium wave. However, Reynolds and Webber[8] have found that a trace (0·8–1·0*mM*) of potassium acid phthalate was necessary to give satisfactory results in the single sweep polarography of aluminium at the dropping mercury electrode at pH 4·0 in a 0·1*M* calcium chloride electrolyte. The method of analysis gave a peaked wave with no discernable separate hydrogen wave, but even here higher than trace concentrations of the buffer caused a prewave that affected the aluminium peak. The trace of buffer was evidently necessary to withstand the very large local changes of pH which occurred at the surface of the mercury drop during the potential sweep.

In most cases of direct polarography the pH adjustment is made using mixed indicators and additions of base, and there is a danger of formation of collodial aluminium hydroxide from local excess of the reagent. Most of the procedures recommend several hours standing after pH adjustment to allow any such precipitate to redissolve. If there is a significant amount of this reaction, the pH will drift to a more acid value and there will be need for further adjustment. There are subsequent pH drifts on dilution to volume and de-aeration prior to polarography.

A variety of supporting electrolytes have been used. In many cases, such as the analysis of light metal alloys, the nature of the supporting electrolyte is dictated by the composition of the sample, but with a complete freedom of choice there has been no agreement on the best electrolyte or the most appropriate pH. Lithium chloride, lithium sulphate, potassium chloride, magnesium chloride, calcium chloride and barium chloride have all been employed and the recommended acidities have ranged from pH 3·25 to 4·5. Tetra-alkylammonium salts have been suggested,[1,4] but no actual investigations of these supporting electrolytes have been reported in the literature.

There exists a relatively simple electrolysis procedure for the adjustment of the pH of these solutions before polarography.[9] Hydrogen ion can be reduced at a platinum cathode:

$$2H_{aq}^+ + 2e \rightarrow H_2$$

and if the anode is chosen so that the oxidation is non-protolytic, *e.g.*,

$$Ag + Cl^- \rightarrow AgCl + e$$

then electrolysis will serve to decrease the acidity of the solution. Alternatively, the anode may be completely isolated from the solution by employing a diaphragm cell. The electrolysis can be carried out with a small cathode current density and good stirring to eliminate the danger of the local excesses of base that form colloidal aluminium hydroxide. The electrolysis is not accompanied by any significant change in volume so that the aluminium solution can be made up to final volume and deaerated before pH adjustment. The solution can then be polarographed directly.

The technique of direct polarography requires that the aluminium be separate from more easily reducible species and also present in a dilute solution of a strong acid containing no buffer constituents or complexing agents. One method that can be

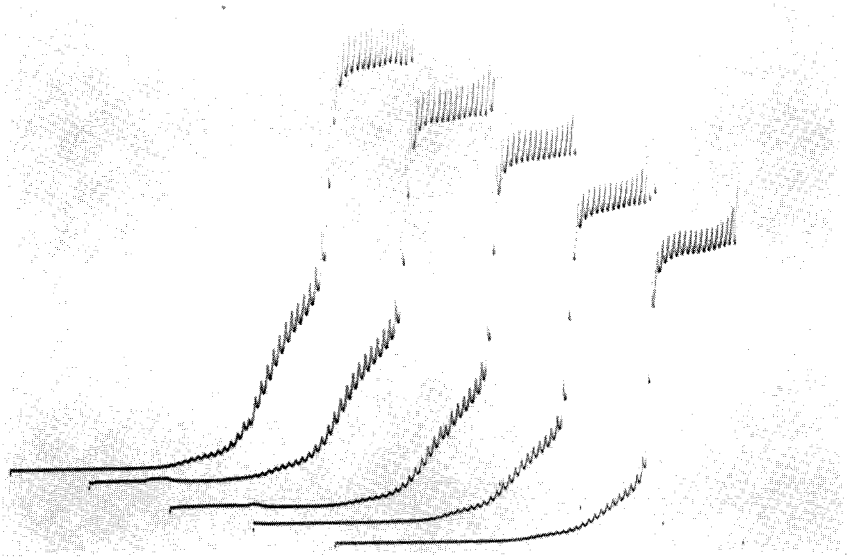


FIG. 1.—Polarographic aluminium curves in 0·10*M* tbNH$_4$Cl electrolyte containing 0·002% Triton X-100 (pH increasing from left to right: 3·38, 3·48, 3·54, 3·73, 3·90).
Waves extend from −1·00 to −2·00 V *vs*. Ag/AgCl reference electrode.

applied to the separation is mercury cathode electrolysis.[10] The sample can be dissolved in acid, then electrolysed, either at a constant current or at a controlled cathode potential. Aluminium is not deposited at a mercury cathode from acid solution, and is thus left in a solution free from the more easily reducible species. A controlled cathode potential electrolysis is preferable, for this uses the minimum of electricity and introduces a minimum of anode oxidation products in the electrolysis. A diaphragm cell with an isolated anode is not suitable because significant amounts of anionic aluminium may migrate to the anode compartment; an internal platinum anode can be used.

A second technique that can be applied to the separation is that of amalgamometry.[10] If the sample could be reacted directly with mercury to form an amalgam, it is conceivable that conditions could be established that would allow only the aluminium to be stripped from the amalgam into an acid solution; the more easily reducible elements would remain in the amalgam. The technique would be restricted to those samples which amalgamated readily.

In the case of a zinc-base alloy it was found that the sample was readily wet by the mercury, but the system was heterogeneous. Cathodic polarisation at a small current density with a hydrochloric acid electrolyte resulted in a rapid decomposition of the sample phase. The reaction was such that only traces of zinc appeared in the electrolyte solution and continued electrolysis resulted in a quantitative separation of the aluminium from the zinc. The net electrolysis current results in reduction of hydrogen ion at the cathode. If the electrolysis is carried out with an internal silver anode depolarised by the chloride ion, the acidity of the solution will be decreased. The concentration of the hydrochloric acid electrolyte was chosen to give a pH between 2 and 3 at the end of the electrolysis, and an aliquot of the aluminium solution was then taken for the final pH adjustment prior to polarography.

EXPERIMENTAL

Apparatus and reagents

Polarograms were recorded on a Leeds and Northrup Type E Electrochemograph with the damping set in the No. 1 position. The dropping mercury electrode was used with a 38·1-cm head of mercury. It had a flow rate (m) of 0·730 mg. sec^{-1} and a drop time (t) of 5·41 sec at $-1·90$ V *vs.* the silver-silver chloride reference electrode in the supporting electrolyte. The capillary constant had a value of 1·07 mg$^{2/3}$.sec$^{-1/2}$ under these conditions.

The pH measurements were made using a Beckman Model G meter and external electrodes. The glass electrode was of the General Purpose (GP) type. The meter was standardised against a 0·05*M* solution of potassium hydrogen phthalate prepared according to the directions of the National Bureau of Standards from their sample 185c. The pH of the standard was taken as 4·01 at 25·0°. Concentrations of hydrogen ion were calculated via the relation $\text{pH} = -\log C_{\text{H}^+}$.

The electrolysis currents for the pH adjustment and amalgamometry were obtained from a low voltage d.c. power supply with a series resistance to regulate the current. The cell for pH adjustment (Fig. 2) consisted of a 200-ml electrolysis beaker, a 40 × 40-mm cylindrical platinum gauze cathode, and an anode wound from a 50-cm length of 3-mm diameter hard (99·98%) silver wire. Stirring was carried out by a magnetic stirring bar. The cell temperature was regulated at 25·0° by circulation of water through the jacket. The same cell was used for polarography, the silver electrode coated with silver chloride acting as a reference electrode. The silver chloride was stripped from the electrode between electrolyses by immersion in 6*M* aqueous ammonia.

The electrolytic separation of interfering elements was carried out at a mercury cathode. The cell consisted of a 200-ml electrolysis beaker and the electrode consisted of 20 ml of mercury with a surface area of 28 cm^2. Stirring was carried out by a magnetic stirring bar. For controlled potential electrolyses an internal platinum anode was used and a silver-silver chloride reference electrode. The potentiostat was of the servo type described by Lamphere.[11] For amalgamometry an internal silver anode similar to that for pH adjustment was used.

Prepurified nitrogen (less than 20 ppm of oxygen) was used to displace the oxygen from the electrolysis solutions in each case. All volumetric dilutions and the final polarography were carried out with the solutions at 25·0°.

The standard aluminium solution was prepared from "H.S." metal supplied by Johnson, Matthey and Company, London, England. A known weight was dissolved in a slight excess of hydrochloric acid, then diluted to volume. The final solution was 9·190 × $10^{-3}M$ in dissolved aluminium and had a pH of 0·7.

A stock 0·50*M* supporting electrolyte solution was prepared from aqueous 1·0*M* polarographic grade tetra-n-butylammonium hydroxide ($tbNH_4Cl$) supplied by Southwestern Analytical Chemicals, Austin, Texas, U.S.A. The hydroxide was neutralised to pH 4·0 with hydrochloric acid before dilution.

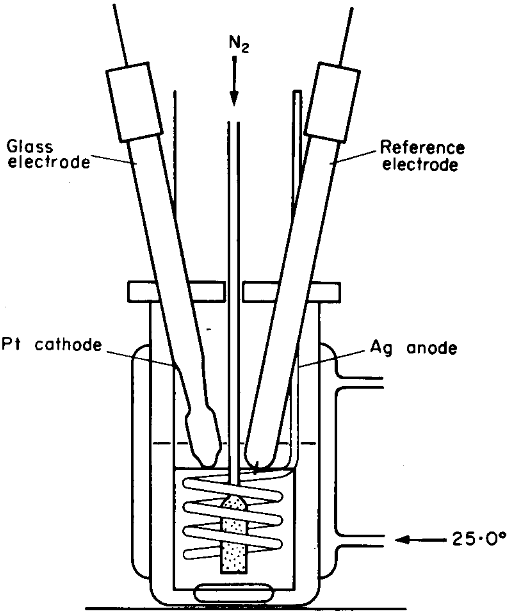


FIG. 2.—Electrolysis cell for pH adjustment and polarography.

Polarography of aluminium

A series of solutions of known concentration was prepared by dilution of the standard aluminium solution. Sufficient $tbNH_4Cl$ was added to each solution before dilution to provide a final 0·10*M* supporting electrolyte concentration. Triton X-100 was similarly added to provide a final 0·002% concentration of the maximum suppressor. Portions of each solution were then transferred to the electrolysis cell and de-aerated. The pH was then adjusted, the current being decreased in steps as the desired pH was approached, *e.g.*,

pH 1·5 → 3.0,	70 mA,
pH 3·0 → 3·4,	20 mA,
pH 3·4 → desired value,	5 mA.

When the desired pH was reached, the electrolysis was discontinued, the dropping mercury electrode was inserted into the solution and the polarogram obtained.

The pH adjustment could be made to 0·01 unit on the pH meter scale. In each case, the polarographic wave from hydrogen ion discharge preceded but was not separate from the wave from the aluminium. The total diffusion current, corrected for the residual by extrapolation of the base line, was measured at −1·90 V. The half-wave potential for the aluminium wave itself was estimated to be −1·76 V. Insignificant changes in pH (±0·02 unit) and in the character of the polarographic wave were obtained on standing for 24 hr under nitrogen of the pH adjusted solutions. The calibration results have been plotted in Fig. 3. Each point represents the mean results of duplicate polarograms on a sequence of two or three separate aluminium solutions of the same concentration adjusted to the same pH. The mean deviation of the 86 experimental values from the mean of each of the 17 sets was 0·06 μA. The horizontal bars represent a spread of ±0·01 pH unit at each hydrogen ion concentration, the vertical bars represent a spread of ±0·15 μA or 1% of full scale deflection at the recorder sensitivity used. Straight lines have been fitted to the experimental data by the method of least squares. The data of Table I shows that the intercept ($i_d°$) is a function of the aluminium concentration and that the diffusion current constant corresponding to zero hydrogen ion concentration ($i_d°/C_{Al}$) changes significantly and continuously with aluminium concentration.

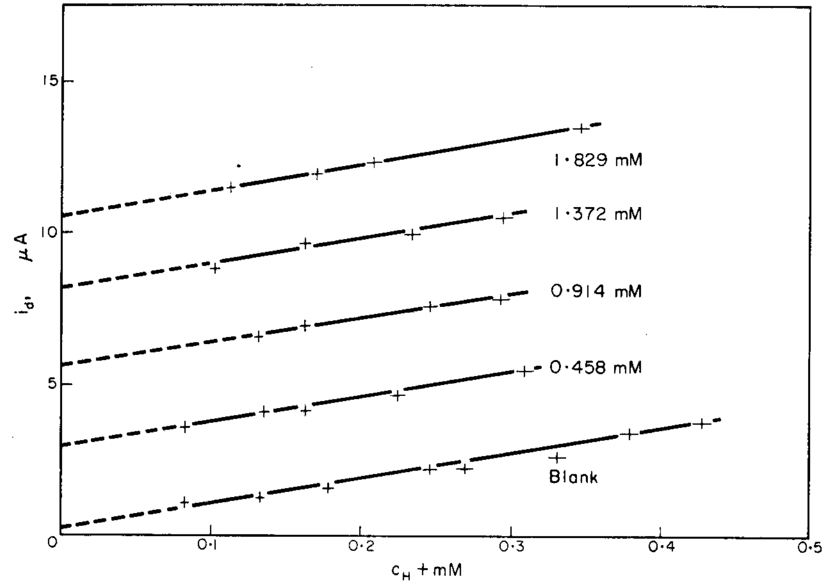


FIG. 3.—Calibration curves: diffusion current *vs.* hydrogen ion concentration at fixed aluminium concentrations.

TABLE I

C_{Al}, *mM*		Slope i_d^*/C_{H^+}, *μA/mM*	$i_d°$, *μA*	$i_d°/C_{Al}$, *μA/mM*
1·829		8·66	10·52	5·75
1·372		8·13	8·13	5·93
0·914		8·00	5·60	6·13
0·458		8·12	2·92	6·38
	Mean	8·20		
Blank		8·19		

* i_d measured at −1·90 V *vs.* Ag/AgCl reference electrode; 25·0°.

For actual analyses, a calibration curve was prepared at a fixed and arbitrarily chosen pH (3·70), and the unknown samples were adjusted to this pH.

Analysis of standard samples

The polarographic method was applied to the analysis of standard samples of zinc-base die-casting alloys. In one or another of these alloys, the concentration of the copper was as high as 2·8%, of lead 0·03% and of magnesium 0·11%; the concentrations of the other elements were within specification limits for A.S.T.M. Alloy AG40A or AC41A. The more easily reducible elements were separated from the aluminium by a preliminary electrolysis.

(a) *Controlled potential mercury cathode electrolysis.* A 0·16 to 0·18-g sample of the alloy was dissolved in 30 ml of 1*M* hydrochloric acid with warming. The solution was evaporated to 1-2 ml to remove most of the excess acid, cooled and diluted to 60 ml. The solution was transferred to the mercury cathode electrolysis cell, deaerated, and the zinc deposited at −1·20 V. When the zinc removal was complete the electrolyte was transferred to a 100-ml volumetric flask and made to volume. A 50-ml aliquot of this solution was mixed with 20 ml of 0·50*M* $tbNH_4Cl$ solution, and 10 ml of 0·02% Triton X-100 solution were added. The solution was then diluted to 100 ml and a portion transferred to the electrolysis cell for adjustment to pH 3·70 and polarography. The concentration of aluminium was read from a calibration curve prepared at this pH. The results of a number of alloy analyses are given in Table II.

(b) *Amalgamometry*. Exactly 100 ml of a 0·01*M* hydrochloric acid solution were pipetted into the mercury cathode electrolysis cell, de-aerated, and pre-electrolysed with a current of 5 mA for 10 min. A 0·16 to 0·18-g sample of the alloy was added to the cell and the electrolysis was continued at 5 mA for 90 min. The decomposition of the sample takes place at the interface and is accompanied by the evolution of hydrogen. The solution becomes black and turbid at the start of the decomposition but clears as the electrolysis proceeds. At the end of the electrolysis a portion of solution was withdrawn from the cell, brought to 25·0°, and a 50-ml aliquot was mixed with 20 ml of 0·50*M* $tbNH_4Cl$ solution, and 10 ml of 0·02% Triton X-100 solution. The solution was then diluted to 100 ml and a portion taken for adjustment to pH 3·70 and polarography. The results of a number of alloy analyses are included in Table II.

TABLE II

Alloy	Certified value, %Al[a]	Polarographic value, %Al[b]
National Bureau of Standards Sample 94b	4·07	4·13 ± 0·07[c] 4·09 ± 0·05[d]
Apex Smelting Company Sample D 2080C2	4·68	4·84 ± 0·04[c]
Sample D 2080G	3·20	3·13 ± 0·05[c]

[a] Weighed as Al_2O_3 after precipitation with aqueous ammonia or 8-hydroxyquinoline.

[b] Results of triplicate analyses.

[c] Mercury cathode electrolysis.

[d] Amalgamometry.

DISCUSSION

The adjustment of pH by electrolysis is convenient and precise. It permits a rapid and accurate determination of aluminium by direct polarography. The aluminium wave in the tbNCl electrolyte has a well-defined diffusion current plateau in the presence of a maximum suppressor. The calibration results indicate a high degree of internal self consistency, but errors in pH calibration apparently cause a disparity in correlation of results. The polarographic wave evidently consists of a contribution from both hydrogen reduction and aluminium reduction. The similar slopes of the calibration curves indicate that the hydrogen ion contribution is relatively constant over the series of aluminium concentrations. The diffusion current constant for the aluminium reduction corrected for the hydrogen ion contribution is found, however, to decrease with increasing aluminium concentration. The reduction of the aluminium is a complex reaction but nevertheless the direct polarography is feasible. The results contrast with the complex phenomena obtained in the absence of a maximum suppressor.[4]

It was found necessary to exclude oxygen rigorously from the solutions during the electrolysis for pH adjustment. The potentials used in the adjustment are such that hydrogen peroxide can form and accumulate in the solution:

$$O_2 + 2H_{aq}^+ + 2e \rightarrow H_2O_2.$$

The peroxide has been found to give a polarographic reduction wave with a half-wave potential of −1·45 V in the $tbNH_4Cl$ electrolyte. This wave not only precedes the aluminium wave but the presence of peroxide was found to decrease the height of the hydrogen-aluminium wave. Such a decrease is to be expected, for peroxide reduction at the dropping mercury electrode will require the diffusion of hydrogen ion to the electrode surface;

$$H_2O_2 + 2H_{aq}^+ + 2e \rightarrow 2H_2O.$$

This will affect the subsequent aluminium wave which contains at least one component dependent on hydrogen ion diffusion. Polarography of blank acid solutions of the tbNCl electrolyte with added hydrogen peroxide shows that the peroxide wave grows at the expense of the hydrogen wave, the diffusion current at −1·90 V remaining constant until the peroxide is present in excess.

The direct polarography requires that the aluminium be separate from more easily reducible species and also present in a dilute solution of a strong acid containing no buffer constituents or complexing agents. It was found possible to separate aluminium from zinc by both electrolytic deposition of the zinc from an acid sample solution and also by stripping the aluminium from a two phase sample amalgam into an acid electrolyte. The zinc separation must be quantitative because the zinc gives a polarographic reduction step with a half-wave potential of −1·75 V in the $tbNH_4Cl$ electrolyte. The zinc removal can be checked by polarography in a buffered ammonia-ammonium chloride electrolyte where the zinc gives a wave with a half-wave potential of −1·33 V. While the technique of amalgamometry is potentially useful in isolating the aluminium for polarography, it is severely restricted in that it may be used only with samples which amalgamate readily. The method has been found to give a clean simple separation of aluminium from a zinc-base alloy sample.

Acknowledgements—The authors are indebted to the National Research Council of Canada and the Advisory Committee of the University of Toronto for financial support. We are also indebted to Dr. R. P. Graham, McMaster University, who provided standard samples from the Apex Smelting Company, Chicago, U.S.A.

Zusammenfassung—Die direkte Polarographie von Aluminium mit 0,1 m Tetabutylammoniumchlorid als Leitsalz wurde untersucht. Der p_H wurde vor der Polarographie durch Elektrolyse der sauren Lösung bei konstanter Stromstärke mit Platinkathode und Silberanode eingestellt. Er ließ sich auf diese weise genau festlegen und die Aluminiumstufen waren sehr gut reproduzierbar. Für analytische Bestimmungen wurde ein p_H von 3,70 für Aluminium-konzentrationen bis zu 2 mMol/l willkürlich gewählt. Die Methode wurde auf die Analyse einer Legierung mit Zink als Hauptbestandteil angewandt, wobei störende Elemente durch Elektrolyse bei kontrolliertem Potential und durch Amalgampolarographie abgetrennt wurden.

Résumé—Ici une étude de la polarographie directe de l'aluminium en utilisant comme électrolyte une solution à 0,10 M de chlorure de tétrabutyl-ammonium. La mise au point des conditions de pH préalablement à la polarographie a été faite par électrolyse à courant constant de la soluion acide avec une cathode de platine et une anode d'argent. Le pH peut être défini d'une manière très précise et les courbes de l'aluminium sont hautement reproductibles. Pour des déterminations analytiques la valeur du pH a été arbitrairement fixée à 3,70 pour des concentrations d'aluminium supérieures à 2 mM. Cette méthode a été appliquée à l'analyse des alliages à base de zinc, en utilisant à la fois l'électrolyse à potentiel contrôlé et l'amalgammométrie pour séparer les éléments gênants.

REFERENCES

[1] I. M. Kolthoff and J. J. Lingane, *Polarography.* Interscience Publishers, Inc., New York, 2nd Edition, 1952.

[2] G. W. C. Milner, *The Principles and Applications of Polarography.* Longmans, Green and Co., Ltd., London, 1957.

[3] M. Perkins and G. F. Reynolds, *Analyt. Chim. Acta*, 1958, **18**, 616.

[4] M. Heyrovský, *Coll. Czech. Chem. Comm.*, 1960, **25**, 3120.

[5] M. von Stackelberg, *Polarographische Arbeitsmethoden.* Walter de Gruyter, Berlin, 1950. pp. 116.

[6] H. C. Gull, *J. Soc. Chem. Ind.*, 1937, **56**, 177.

[7] G. Semerano and I. Ronchi, *Atti reale ist. Veneto sci.*, 1942, **100**, 401.

[8] G. F. Reynolds and Webber, *Analyt, Chim. Acta*, 1958, **19**, 293, 406.

[9] J. J. Lingane, *Electroanalytical Chemistry.* Interscience Publishers, Inc., New York, 2nd Edition, 1958.

[10] J. A. Page, J. A. Maxwell and R. P. Graham, *Analyst*, 1962, **87**, 245.

[11] R. W. Lamphere, *Analyt. Chem.*, 1951, **23**, 258.

Talanta, 1963, Vol. 10, pp. 1063 to 1076. Pergamon Press Ltd. Printed in Northern Ireland

APPLICATION DE CERTAINES ACIDES HYDROXAMIQUES DANS LA CHIMIE ANALYTIQUE—III

ANALYSE SPECTROPHOTOMÈTRIQUE ET APPLICATION ANALYTIQUE DE LA RÉACTION DE VANADIUM(V) AVEC L'ACIDE THIOPHÈNE-2-HYDROXAMIQUE

JERZY MINCZEWSKI et ZOFIA SKORKO-TRYBUŁA
Département de chimie analytique de l'école polytechnique, Varsovie

(Reçu le 19 Mars 1963. Accepté le 29 Mars 1963)

Résumé—L'acide thiophène-2-hydroxamique n'a pas été jusqu'alors utilisé comme réactif organique dans l'analyse minérale. On a donc examiné le parcours de son spectre d'absorption dans l'ultraviolet, dans le milieu alcalique et dans le milieu acide. On a déterminé sa constante de dissociation qui s'exprime par la valeur, $1{,}7 \times 10^{-8}$. Cet acide réagit avec une suite d'ions de métaux comme Fe(III) Co(II), Mn(II), Mo(VI) et Nb(V) formant des composés solubles où bien des précipités. Il réagit aussi avec le vanadium(V) dans le milieu aqueux formant des complexes colorés aux diverses nuances de violet. On a éxaminé ensuite la composition de ces complexes en fonction de pH de la solution À $pH = 3{,}5$ éxiste un complexe bleu-violet qui atteint son maximum d'absorption pour $\lambda = 590$ mμ. On obtient la relation moléculaire de réactifs $V:R = 1:3$. À $pH = 7{,}7$ éxiste un autre complexe de la même relation moléculaire mais de la couleur violette qui atteint son maximum d'absorption pour $\lambda = 550$ mμ. On a élaboré la méthode de la détermination de faibles quantités de vanadium de l'ordre de 1,5–0,05% dans les corps divers en se servant de la propriété permettant d'extraire le complexe stable dans le milieu peu acide avec l'acide thiophène-2-hydroxamique.

PROCÉDANT à l'étude des possibilités de l'application de certains acides hydroxamiques dans l'analyse, on s'est intéressé aux acides, aux substituants héterocycliques, analogues de l'acide benzohydroxamique, à savoir: nicotine-[1,2] isonicotine- et thiophène-hydroxamiques. Ce dernier n'est pas mentionné dans la littérature scientifique, il paraît, tout de même, être intéressant par son substituant de thiophène. Il n'est rencontré que dans quelques réactifs organiques comme 2-thiophène-aldoxime[3] et 2-thiénoyle-trifluoracétone;[4] et il témoigne d'intéressantes propriétés analytiques.

L'acide thiophène-2-hydroxamique (ATH) réagit avec une suite d'ions de métaux comme Fe(III), Co(II), Mn(II), Mo(VI) et Nb(V) formant des composés colorés stables ou bien des précipités. Il réagit aussi avec le vanadium (V) dans le milieu aqueux, formant des complexes colorés aux diverses nuances de violet. ATH n'a pas été jusqu'alors utilisé comme réactif. On a donc examiné le parcours de son spectre d'absorption dans l'ultraviolet, dans un milieu alcalin et dans un milieu acide. On a déterminé sa constante de dissociation. On a examiné ensuite la composition des complexes de ATH avec le vanadium en fonction de pH de la solution. On a élaboré la méthode de la détermination de faibles quantités de vanadium dans les corps divers en se servant de la propriété permettant d'extraire le complexe avec ATH, stable dans le milieu peu acide.

PARTIE EXPÉRIMENTALE

Réactifs et appareillage

On a préparé la solution de base de vanadium(V), en dissolvant dans l'eau, une adéquate quantité de métavanadium d'ammonium (NH_4VO_3). La concentration de vanadium determinée par le dosage titrimétrique se traduit par 1 mg V/ml. On a préparé d'autres solutions de vanadium par une dilution adéquate de la solution de base.

L'acide thiophène-2-hydroxamique a été préparé de thiophène par 2-acétylthiophène,[5] l'acide thiophène-2-carboxylique,[6] le convenable chlorure d'acide, préparé de la manière analogue au chlorure de benzoyle[7] et par l'action de la hydroxylamine*. La température de fondation est comprise entre 123°–124°C. On a préparé les solutions de ATH en dissolvant une quantité convenable dans l'eau à la température de 50°–60°. Ces solutions gardées dans les récipients sombres, sont stables pendant 5 jours.

Spectrophotomètres: Unicam SP 400, Unicam SP 500 et "Uvispec" des établissements "Hilger and Watts".

Pehamètre "Electromatyka" (précision du dispositif 0,1 de l'unité pH).

RÉSULTATS ET DISCUSSION

Acide thiophène-2-hydroxamique

Spectres d'absorption dans l'ultra-violet

On a préparé les solutions de ATH à la concentration $1\cdot10^{-4}M$ dans l'acide chlorhydrique $0,1M$ et dans la solution de la soude $0,005M$, ainsi, que les solutions analogues pour l'acide thiophène-2-carboxylique. On a mésuré l'absorption de ces solutions en fonction de la longueur de l'onde. On a présenté les spectres de l'absorption sur le fig. 1 et on a dressé un tableau présentant les maxima d'absorption des solutions diverses.

Se basant sur les expériences de Plapinger[8] prouvant que dans le milieu alcalin l'anion de l'acide hydroxamique de présente sous deux formes tautomères à savoir

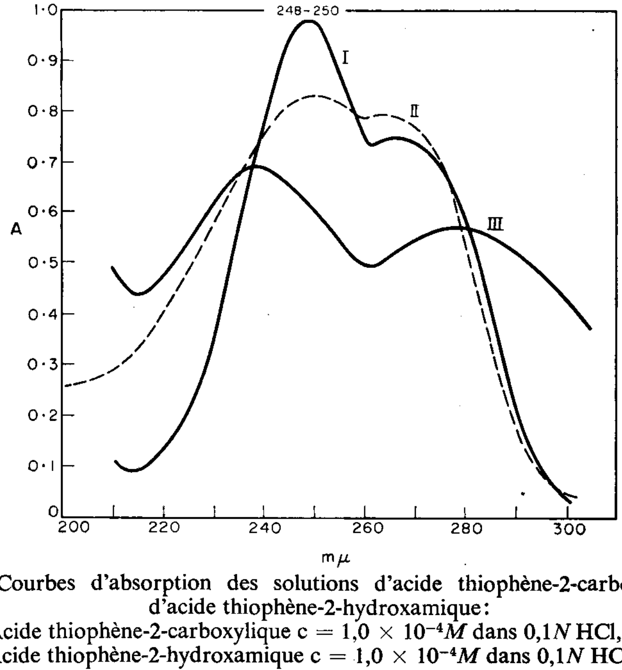


FIG. 1.—Courbes d'absorption des solutions d'acide thiophène-2-carboxylique et d'acide thiophène-2-hydroxamique:
I Acide thiophène-2-carboxylique c = 1,0 × $10^{-4}M$ dans 0,1N HCl,
II Acide thiophène-2-hydroxamique c = 1,0 × $10^{-4}M$ dans 0,1N HCl,
III Acide thiophène-2-hydroxamique c = 1,0 × $10^{-4}M$ dans 0,005N NaOH.

* Le docteur St. Goszczyński et le docteur N. Porowska ont préparé la synthése.

cétonique et énolique qui sont signalées par la présence de deux maximums de la courbe d'absorption. On peut constater que l'acide thiophène-2-hydroxamique se comporte de la manière analogue, atteignant deux points maximums dans la solution NaOH 0,005M pour λ = 240 mμ et pour λ = 280 mμ. Un déplacement hypsochromique en rapport au maximum, atteint dans un milieu acide, temoigne de la présence d'une cétoforme—tandis qu'un déplacement batochromique témoigne de la présence de la forme énolique. La coubre I sur le fig. 1 illustre le spectre de l'acide thiophène-2-carboxylique, atteignant son maximum pour la longueur d'onde de 240 mμ à 250 mμ. La coubre II a une forme pareille, tout de même le maximum pour ATH s'accentue d'une manière beaucoup plus faible. Sur la courbe III, illustrant le spectre d'anion ATH (le milieu alcalin) on aperçoit nettement un déplacement de maximum. La position de maximum est stable. On peut observer tout de même un déplacement hypsochromique de maximum de 250 mμ à 240 mμ—ce qui témoigne de la présence d'une forme cétonique—et un déplacement batochromique à 280 mμ—ce qui signale la présence de la forme énolique.

TABLEAU I.—LES MAXIMA D'ABSORPTION

Acide	Milieu	
	0,1M HCl mμ	0,005M NaOH mμ
Thiophène-2-hydroxamique	250	240 280
Thiophène-2-carboxylique	248–250	— —

Des données ci-mentionnées on peut déduire que l'anion de l'acide thiophène-2-hydroxamique se présente sous deux formes tautomères, tandis que l'acide non dissocié se présente, dans le milieu acide, sous la forme cétonique. La présence de cette forme cétonique est prouvée par des recherches sur d'autres acides hydroxamiques.[9,10]

Constante de la dissociation

La constante de la dissociation a été déterminé par la méthode potentiométrique.[11,12] On a titré la solution de ATH sans CO_2 avec la solution de soude libre de carbonates. Le titrage a été exécuté en présence de l'électrode de verre et de l'électrode de calomèle à l'aide du pehamètre. La constante de la dissociation a été calculée de la valeur pH dans le point de la mi-neutralisation. Elle s'exprime par $1{,}7 \times 10^{-8}$.

Analyse spectrophotomètrique des composes de vanadium(V) *avec l'acide thiophène-2-hydroxamique*

Coubres d'absorption

On a déterminé les courbes d'absorption pour les composés de vanadium(V) avec ATH en présence de l'excès du réactif, dans les solutions pour les différentes valeurs de pH, la force ionique restant constante.

Sur le fig. 2 on a présenté les courbes d'absorption. Leur pentes restant douces—les points maximums se traçant à peine.

La solution à pH = 7,6–7,8 présente la plus grande valeur d'absorption et elle atteint son maximum pour la longueur d'onde égale à λ = 550 mμ (courbe 1), tandis que, pour la solution à pH = 3,0, le maximum est atteint pour λ = 590 mμ (courbe 3).

Il est facile de remarquer que, la valeur de pH augmentant, le maximum d'absorption se déplace, en se dirigeant, vers les ondes plus courtes. La figure 3 présente le

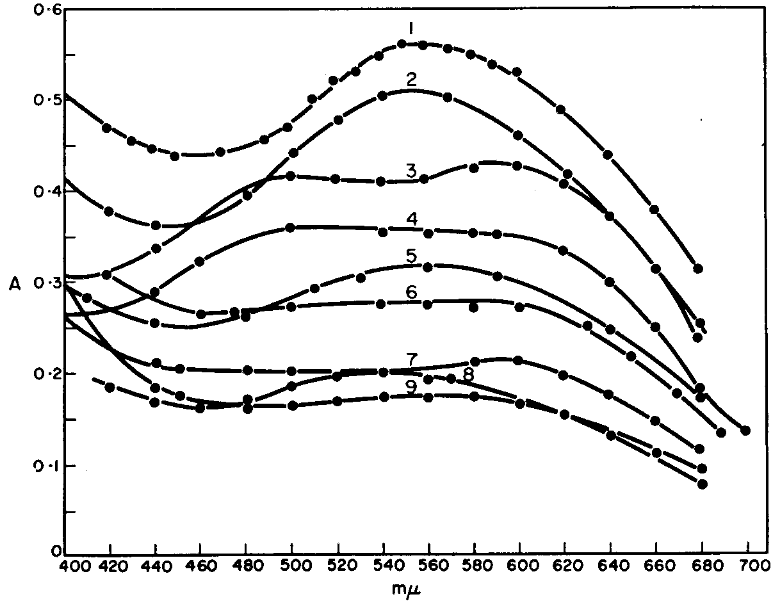


FIG. 2.—Courbes d'absorption de la solution de complexe de V(V) avec ATH en présence de KCl 0,2N:
([V] = 2,1 × $10^{-4}M$ [ATH] = 2,8 × $10^{-2}M$)
1. pH = 7,8 2. pH = 9,0 3. pH = 3,0 4. pH = 2,3
5. pH = 7,1 6. pH = 4,1 7. pH = 5,1 8. pH = 10,0
9. pH = 6,2

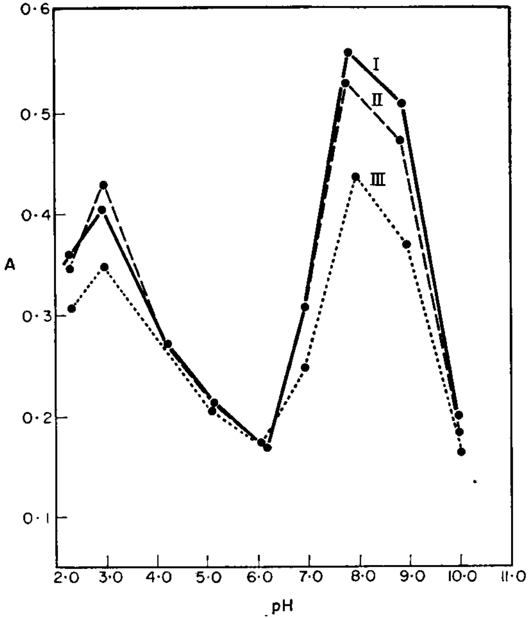


FIG. 3.—Courbes de dépendance de l'absorption et de la concentration d'ions d'hydrogène de la solution de complexe de V(V) avec ATH en présence de KCl 0,2N:
([V] = 2 × $10^{-4}M$ [ATH] = 2,8 × $10^{-2}M$)
I: 550 mμ. II: 590 mμ. III: 450 mμ.

graphique des dépendances des valeurs d'absorption à partir de pH de la solution aqueuse A = f(pH), pour une déterminée longueur d'onde. On voit ici le maximum, se traçant d'une manière distincte pour pH = 3,0 et pour pH = 7,7. Cela peut servir de preuve qu'existent deux différents complexes. Des résultats des recherches de plusieurs scientifiques (cités ci-dessus[1]) on voit que, pour les domaines dont nous nous intéressons de pH et pour des concentrations de vanadium(V)—dans un milieu peu acide—existe l'ion VO_2^+—et à pH = 8,0 l'ion $H_2VO_4^-$—susceptibles de réagir avec le ligand. Il est intéressant de signaler, pour les valeurs de pH dépassant 8,8 la capacité d'absorption baisse rapidement. Se basant sur les recherches d'Ingri et Brito[13], on peut déduire que dans le domaine de pH = 6–8, il existe l'anion $H_2VO_4^-$ qui à pH croissant, passe en HVO_4^{2-} ortovanadate susceptible de donner des anions condensés $HV_2O_7^{3-}$ et $V_3O_9^{3-}$ pour les concentrations de vanadium $2{,}5 \, . \, 10^{-3}M$.

Cette hypothèse est prouvée par le fait que les métavanadates cristalliques se produisent dans le domaine de pH = 6–8. Cela démontre que la forme méta, pour ces conditions, existe aussi dans la solution, L'anion métavanadate réagit donc avec ATH. Il en résulte que pour pH >8 le complexe se décompose. Dans les solutions plus alcalins les hydroxy-complexes de vanadium emportent sur les composés de ce dernier avec le ligand.

Détermination de la composition des complexes

On s'est servi de deux méthodes, basées sur les réactions des solutions équimoléculaires d'ion central avec un réactif à savoir: de méthode des variations continues de Job[14] et de celle de titrage spectrophotométrique.[15]

Le complexe de vanadium(V) *avec* ATH *stable à* pH = 3,0: Dans ces conditions se forme un complexe bleu-violet qui atteint son maximum d'absorption pour $\lambda = 590$ mμ. Pour les concentrations de vanadium dépassant $10^{-2}M$ on obtient un précipité noir-bleu soluble dans les alcools aliphatiques supérieurs.

L'acide 2-brome-thiophène-3-hydroxamique[16] forme, dans un milieu acide (pH = 2), avec le vanadium un précipité peu soluble, déjà pour les concentrations de vanadium de l'orde de $10^{-4}M$, bleu-noir, bien soluble tout de même, dans les solvants oxygénés.

Il paraît que la présence du noyau de thiophène diminue la solubilité des complexes de vanadium, puisque ni l'acide benzohydroxamique, ni nicotinehydroxamique ne cèdent les molécules de vanadium(V) sous forme d'un précipité.

On a tracé les coubres de Job (fig. 4). La position maximum indique la relation V: R = 1; 3 (R = ligand). Au bout de deux heures l'absorption diminue.

A la suite d'un titrage spectrophotométrique on obtient la courbe (1) de la fig. 5 qui devient une droite horizontale pour l'excès du réactif multiplié 15 fois. Cela est causé par une hydrolyse d'ion VO_2^+ sur les anions polynucléaires, ces derniers ne pouvant être éliminés que par un excès du ligand. Selon Babko[17] on a redressé la coubre en la transformant en droite logarithmique à l'aide de l'équation

$$\log \frac{[ML_n^{-(n-1)}]}{[M^+]} = f(\log [L^-])$$

dans laquelle $[ML_n^{-(n-1)}]$ désigne la concentration du complexe

$[M^+]$—concentration d'ion central libre

$[L^-]$—concentration du libre anion du ligand

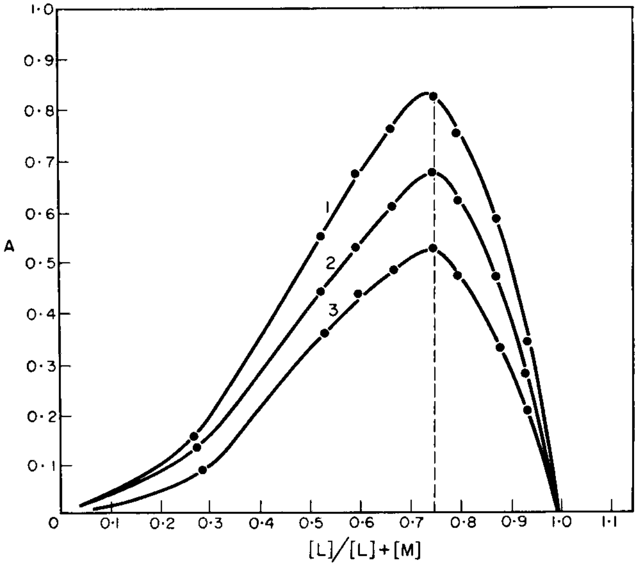


FIG. 4.—Courbes de Job pour les solutions equimoléculaires de V(V) et de ATH en présence de KCl 0,2*N*:

1. pH = 3,0 c = 5,65 × $10^{-3}M$ (590 mμ),
2. pH = 3,0 c = 5,65 × $10^{-3}M$ (590 mμ) absorption mésuré après 2 hrs,
3. pH = 7,7 c = 2,0 × $10^{-3}M$ (550 mμ).

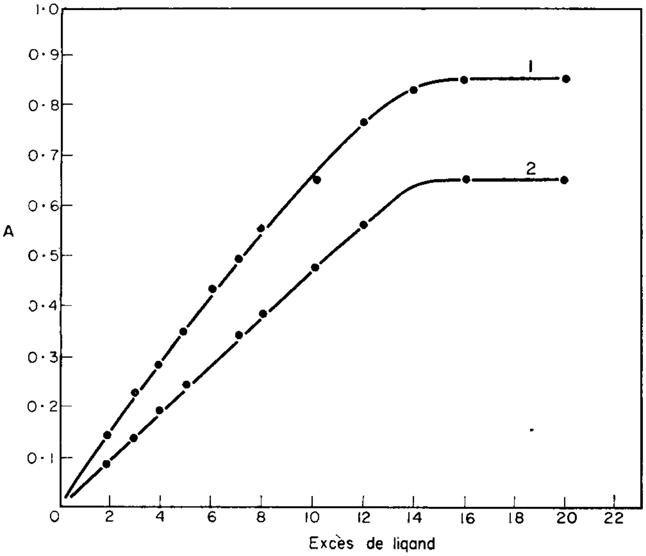


FIG. 5.—Courbes de titrage spectrophotométrique pour les solutions de V(V) et de ATH en présence de KCl 0,2*N*:

1. pH = 3,0 [V] = 4 × $10^{-4}M$ (590 mμ),
2. pH = 7,7 [V] = 5 × $10^{-4}M$ (550 mμ).

La tangente n de l'angle de l'inclination de la droite est égale au nombre des ligands liés en complexes. Dans le cas du complexe cité ci-dessus on obtient la valeur de la tangente $n = 3$ pour l'excès du ligand multiplié 10 fois (fig. 6).

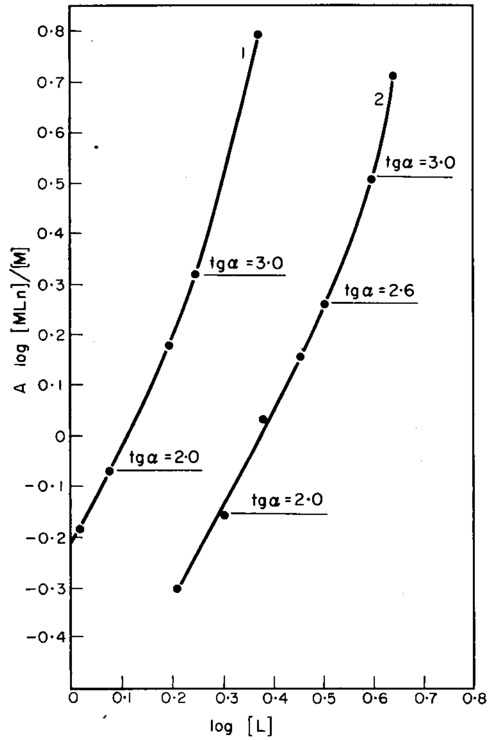


FIG. 6.—Droites logarithmiques pour les solutions de V(V) et de ATH:
1. pH = 3,0 (590 mμ). 2. pH = 7,7 (550 mμ).

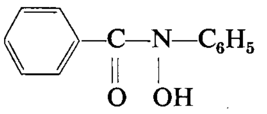
Dans le domaine 200–300 mμ la courbe d'absorption garde la forme de la courbe obtenue pour ATH. Dans le domaine 300–400 mμ la valeur d'absorption diminue rapidement. On peut déduire de la forme du spectre dans l'ultraviolet qu'il n'existe pas dans ces conditions, un autre individu, à coté du coloré complexe étudié.

Le complexe de vanadium(V) *avec* ATH *stable à* pH = 7,7: Dans un milieu alcalin, le vanadium(V) forme avec ATH un composé soluble de la couleur violette qui atteint son maximum d'absorption pour $\lambda = 550$ mμ. Des expériences faites par la méthode de Job (fig. 4, courbe 3), on obtient la relation V : R = 1 : 3. Sur la branche ascendante de la courbe se fait remarquer l'influence de l'hydrolyse de l'ion de vanadium en présence du déficit du ligand. Ce n'est que la forme du métavanadate, stable à pH = 6–8, qui est susceptible de lier ATH.

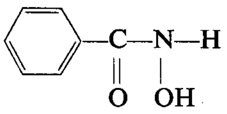
La courbe du titrage spectrophotométrique (fig. 5, coubre 2) ne fléchit que pour l'excès du ligand multiplié 15 fois. La droite logarithmique, obtenue de la courbe du titrage spectrophotométrique désigne, pour l'excès du ligand multiplié 8 fois (fig. 6, courbe 2), la valeur de la tangente n de l'angle de l'inclination de la droite égale à 3. Le spectre de l'absorption, dans le domaine 200–400 mμ ne démontre pas la présence d'un autre composé à coté du composé étudié.

Extraction des complexes à l'aide des solvants organiques

Les complexes au charactère d'un acide où d'une base forment des complexes susceptibles à l'extraction par les solvants oxygénés. On peut donc extraire le complexe de vanadium(V) avec ATH de la solution peu acide à l'aide des alcools aliphatiques en commençant par l'alcool butylique. Blair, Pantony et Minkoff[18] ont examiné les complexes de vanadium avec 8-oxyquinoléine. Les complexes se dissolvent dans les alcools et forment des solutions colorées de rouge. On a mis à profit cette réaction comme une preuve qualitative des alcools. La formation de cette conjonction est conditionnée par la présence de l'oxygène lié par coordination au vanadium, auquel, par une liaison à hydrogène se fixe une molécule d'alcool. Le vanadium(IV) ne donne pas de réaction pareille. Le complexe de vanadium(V) avec ATH s'extrait du milieu peu acide à l'aide des alcools en changeant de couleur, passant de violet en jaune-doré. Il serait intéressant de comparer les courbes d'absorption de l'extrait de l'alcool à celui de l'ester. Le complexe de vanadium(V) dans l'ester est coloré de bleu-sale: le maximum se maintenant dans le domaine de 450 $m\mu$ à 620 $m\mu$. Le défaut d'hydrogène actif, dans l'ester, susceptible de former une liaison directe, n'évoque que l'extraction. Le solvant n'entre pas dans le domaine de coordination de vanadium. On solvate seulement tout le complexe par la liaison de la molécule du solvant avec un hydrogène actif lié à l'azote du groupement hydroxamique. Cet hydrogène influence aussi sur la solubilité des complexes. Il est encore plus actif dans le cas où le groupement d'hydroxyle est bloqué. C'est pourquoi aussi les complexes de vanadium avec les réactifs, à l'hydrogène substitué, comme de benzoylphénylhydroxylamine et cupferron, ne se dissolvent pas dans l'eau.



Benzoylphényl-hydroxylamine



Acide benzohydroxamique

Le complexe de vanadium(V) avec ATH à pH = 3,0, s'extrait au même degré avec alcool butylique, isobutylique, isoamylique, hexylique et octylique. On atteint le maximum de l'absorption pour $\lambda = 485$ $m\mu$. On a examiné aussi la composition du complexe s'extrayant en procédant de la manière pareille à Specker et Jackwerth[19] qui ont examiné l'influence du solvant sur l'extraction des complexes minéraux.

D'après la méthode de Job on a préparé une suite de solutions mélangées aux différentes relations moléculaires au volume stable à la même force ionique. Au bout de 30 min., on a extrait la solution aqueuse, à pH = 3,5, à l'aide des mêmes doses d'alcool butylique. On a obtenu la composition V:R = 1:2. Une autre suite de solutions a été extraite deux heures après. On obtient le maximum sur la courbe de Job pour la relation V:R = 1:3 (fig. 7) La courbe du titrage spectrophotomètrique fléchit pour l'excès du ligand multiplié 8 fois (fig. 8) et sa droite logarithmique atteint la tangente de l'angle de l'inclinaison égalant 3 pour l'excès multiplié 3 fois (fig. 9).

Le milieu non aqueux diminue beaucoup la dissociation du complexe, éliminé l'influence d'hydrolyse de l'ion de vanadium. Des expériences citées ci-dessus, on peut déduire que, dans un milieu aqueux, l'équilibre s'établit lentement en faveur du complexe plus riche en ligand.

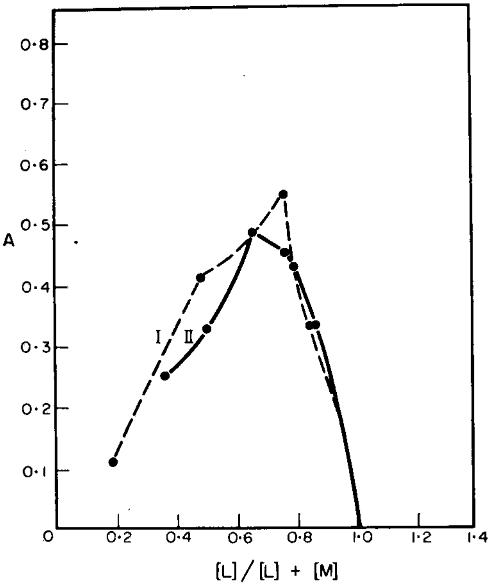


Fig. 7.—Courbes de Job pour les extraits d'alcool butylique de complexe de V(V) et de ATH:
I: Extraction au bout de 30 min.
II: Extraction au bout de 2 hr.

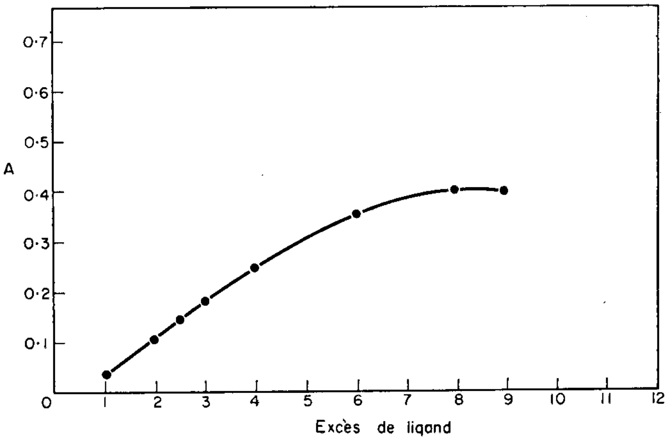


Fig. 8.—Courbes de titrage spectrophotométrique pour les extraits d'alcool butylique de complexe de V(V) et de ATH:
$[V] = 2,5 \times 10^{-4}M$ $\lambda = 490$ mμ

Dosage spectrophotomètrique de vanadium a l'aide de l'acide thiophène-2-hydroxamique

Le mieux approprié aux buts analytiques s'est montré le complexe de vanadium(V) avec ATH qui est stable en solution aqueuse, à pH = 3,0, et qui s'extrait facilement à l'aide des solvants oxygénés. Les réducteurs font obstacle à cette réaction, puisque le complexe de vanadium(IV) ne s'extrait pas. Les alcools aliphatiques se sont montrés les solvants les plus efficaces.

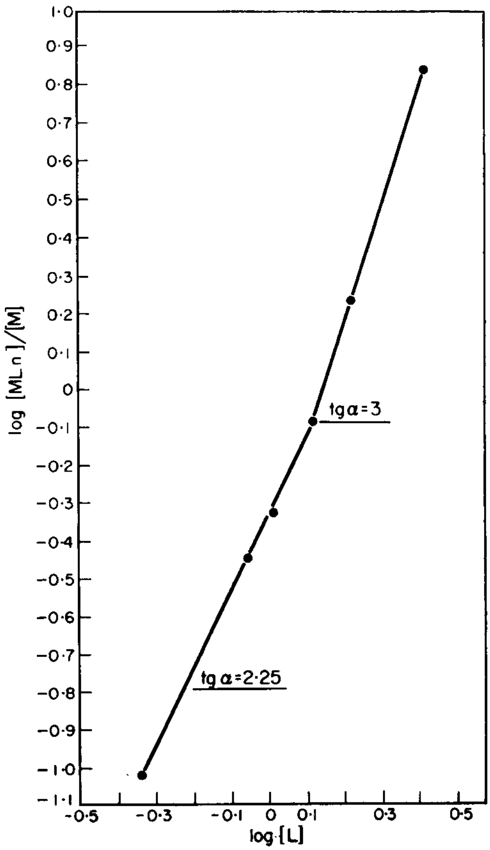


FIG. 9.—Droite logarithmique calculée à partir de la courbe de titrage spectrophotométrique des extraits d'alcool butylique

Indépendamment du genre d'alcool utilisé, les extraits atteignent le maximum d'absorption pour la longueur d'onde $\lambda = 485$ mμ. On a fait des expériences avec alcool hexylique, isobutylique, n-butylique et octylique. Le maximum de l'absorption est resté le même pour tous les solvants mentionnés ci-dessus. On s'est convaincu que la concentration du réactif utile pour le dosage quantitative de l'ion de vanadium $6 \,.\, 10^{-6}M$, s'exprime par $2 \,.\, 10^{-4}M$. Le pH optimum de la phase aqueuse est compris entre 3–4. Dans les experiences qui vont suivre on a utilisé pour l'extraction les solutions, à pH = 3,5 et à la force ionique I = 1, obtenue par l'addition de la chlorure de potassium. L'extraction dure 2 min. et le volume de la phase aqueuse peut varier de 20 ml. à 90 ml. sans exercer une influence sur le résultat de l'extraction. Dans l'étude présente on a gardé le volume égal à 50 ml.

La loie de Beer est valable pour les concentrations comprises entre $5 \times 10^{-7}M$–$6 \times 10^{-6}M$.

Mode opératoire

A la solution, dont le contenu de vanadium de dépasse pas $6 \times 10^{-6}M$, on a ajouté 25 ml. de KCl $2M$, 1 ml. de la solution du réactif (ATH) $0{,}14M$. Le tout a été dilué, le pH a été amené à la valeur 3,5 et le volume à 50 ml. Au bout de 30 min. on a extrait le complexe de vanadium avec 20 ml. de l'alcool butylique distillé fraîchement (l'alcool qui n'est pas distillé contient des hyperoxydes qui décomposent le complexe). On a fait disparaitre les restes de la phase organique à l'aide de quelques millilitres d'alcool butylique. Le tout a été mis dans une fiole jaugée jusqu'au volume de 25 ml. L'absorption a été mesuré pour $\lambda = 490$ mμ en se servant d'alcool butylique comme correspondant. La teneur de vanadium a été obtenue de la courbe d'étalonnage.

Influence des ions génants

On a examiné l'influence des ions génants en ajoutant l'ion examiné à la solution contenant 100 μg de vanadium. Ensuite on a ajouté des réactifs et on a amené le pH à la valeur 3,5. Au bout de 30 min. on a extrait la solution à l'aide de 25 ml. du solvant. Le tableau II nous montre que le tungstène, le nickel, le fer ainsi que les tartrates exercent une influence défavorable sur le rendement de l'extraction. Les tartrates ainsi que les citrates réduisent partiellement le vanadium(V) en le faisant passer en vanadium(IV) dont le complexe ne s'extrait pas. Cela diminue les résultats obtenus de l'extraction. S'il s'agit d'autres ions tels que U(VI), Mo(VI), Ti(IV), Zr(IV), Mn(II), Al(III), Cr(VI) bien qu'ils forment des complexes avec ATH, il est facile d'éliminer leur influence en utilisant un excès convenable du réactif. On a le plus de difficultés à éliminer le fer qui forme avec ATH un complexe coloré susceptible à l'extraction. On peut masquer des ions à l'aide de l'acétylacétone, des fluorures, des phosphates, mais cela s'est montré insuffisant. De même l'extraction du complexe de fer(III) à l'aide de l'acide salicylique, du sulfocyanure et du ATH s'est montré peu efficace puisque, imposant la nécessité de répéter plusieurs fois l'experience, elle faisait passer une partie de vanadium dans la phase organique. La solution de l'acide sulfosalicylique de 10% fixe 1 mg de fer (au plus) ce qui en même temps diminue le rendement de l'extraction des composés de vanadium. Wise et Brandt[20] donnent la méthode d'éliminer le fer sur l'électrode de mercure. Une trop forte concentration de sel évoquée par la neutralisation de l'électrolite en est tout de même inconvénient.

TABLEAU II.—INFLUENCE DES IONS GÉNANTS SUR L'EXTRACTION DE 100 μg DE VANADIUM AVEC L'ALCOOL BUTYLIQUE EN PRESENCE D'ACIDE SULFOSALICYLIQUE Á 10%

Ion	Quantité donnée, *mg*	Proportion V:Me	% d'extraction
U(VI)	0,5	1:5	100
Mo(VI)	10,0	1:100	100
Ti(IV)	2,0	1:20	100
W(VI)	0,5	1:5	70
Ni(II)	1,0	1:10	90
Ca(II)	1,0	1:10	100
Fe(III)	0,1	1:1	s'extrait avec V
Tartrate	10,0	1:100	50
Al(III)	10,0	1:100	100
NO_3	10,0	1:100	100
Cr(VI)	1,0	1:10	100
Zr(IV)	1,0	1:10	100
Mn(II)	1,0	1:10	100

Dans cette étude on s'est servi de la méthode plus simple et à la fois plus rapide d'éliminer le fer. Majumdar et De[21] ont proposé d'extraire le vanadium(V) quantitativement à l'aide de tributylphosphate (TBP) de la solution d'acide chlorhydrique

6*M* et de l'extraire ensuite à l'aide de l'eau. Il s'extrait à la fois Fe, Cu, U, Th et Mo. Mais le TBP n'extrait pas dans ces conditions le vanadium(IV), qui reste dans la solution aqueuse. On a réduit donc le vanadium à l'aide de fer bivalent et on a oxydé l'excès de fer à froid à l'aide d'iodate—iodate n'oxyde pas le vanadium(IV). On a extrait le fer(III) de la solution d'acide chlorhydrique 6*N* avec le TBP. Puis on a oxydé le vanadium resté dans la phase aqueuse à l'aide de persulfate en présence d'ions d'argent et on l'a dosé de la manière citée ci-dessus. On peut extraire 200 mg. de fer en utilisant pour l'extraction 15 ml. de TBP et, s'il s'agit de plus grandes quantités de fer, on les extrait à l'aide de convenablement plus grandes quantités de TBP. Avant d'extraire le complexe de vanadium il faut masquer quelques microgrammes de fer avec la solution de l'acide sulfosalicylique.

Dosage de vanadium dans les cendres de combustibles

La dose de 0,2 g environ a été traitée avec 2 ml. de l'acide perchlorate et de HF dans un creuset en platine. Puis elle a été évaporée à sec et de nouveau traitée avec HF. Après la seconde évaporation pour en éliminer HF, on y a ajouté une goutte de H_2SO_4. Le résidu a été dissous en HCl (1 + 19) et mis dans une fiole jaugée. On en a dosé un volume convenable à l'aide d'une pipette et on y a ajouté 0,4 ml. de solution de sel de Mohre 0,1*N*, ou de sulfate ferreux et, une minute après 1 ml de la solution de KJO_3 0,1*N*. Au bout de 5 min, on y a ajouté autant d'acide chlorhydrique concentré qu'il fallait pour obtenir 25 ml de solution de HCl 6*M*. On a mis tout cela dans une ampoule à robinet et on a extrait avec 10 ml de TBP de 100% pendant dix minutes.

Après avoir séparé la phase de TBP, on a évaporé la solution aqueuse jusqu'au volume de 5–10 ml, puis on l'a diluée avec de l'eau, on y a ajoute une goutte de solution de $AgNO_3$ 0,1*N* et un mililitre de solution de persulfate d'ammonium à 15%, préparée fraîchement. On a fait bouillir la solution pendant 5 min puis on l'a refroidie, neutralisée avec KOH solide jusqu'au pH ~ 3 et on y a ajouté 2 ml de la solution d'acide sulfosalicylique à 10%; ensuite on a amené le pH à 3,5, on a ajouté 2 ml de ATH 0,14*M* et on a laissé pour 30 min. Puis on a procéde de la même manière (citée cidessus) que pour le dosage de vanadium en absence d'ions génants. Les résultats obtenus pour le dosage de vanadium, dans deux échantillons de cendres de combustibles sont présentés sur le tableau III.

TABLEAU III.—RÉSULTATS D'ANALYSE DE CENDRES DE COMBUSTIBLES

Échantillon	V trouvé par autre méthode,* %	V trouvé, %	Moyenne standard de déviation
1	0,44	0,43	±0,03
2	0,50	0,48	±0,04

* On a dosé par la méthode phosphortungstènique.

Dosage de vanadium dans les aciers d'alliage

Dissoudre 1 g–0,2 g d'acier dans un mélange d'acides sulfurique et chlorhydrique. Après la dissolution, oxydez le fer avec l'acide nitrique et ensuite éliminez HNO_3 par évaporation. Puis réduire le vanadium à l'aide de fer bivalent. Oxydez l'excès de fer avec un mililitre de KJO_3 0,1*N*. Ajoutez l'acide chlorhydrique concentré en quantité utile pour obtenir la solution 6*N* de cet acide. L'extraire avec 20 ml de TBP pendant 10 min. Séparez la phase aqueuse et encore une fois extraire avec 5 ml de TBP Eliminez TBP, évaporez l'excès de l'acide chlorhydrique, oxydez le vanadium pour le faire passer en V(V) et après le refroidissement procédez au dosage d'après la méthode citée cidessus. Le tableau IV illustre les résultats du dosage de vanadium dans les aciers d'alliage.

L'erreur type estimée sur la moyenne citée dans les tableaux III et IV est calculée à partir de l'équation suivante

$$\bar{s} = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n(n-1)}}\, t_p(\phi)$$

TABLEAU IV.—RESULTATS D'ANALYSE DES ACIERS

Échantillon	Teneur de W, %	Teneur de V, %*	V trouvé, %	Moyenne standard de deviation
Cr-W-V	18,0	1,55	1,51	±0,03
Cr-W-Ni-V	8,33	1,87	1,84	±0,03
Cr-W-Ni-V	10,15	2,20	2,15	±0,05

* On a dosé par la méthode[22].

dans laquelle $t_p(\phi)$ désigne l'argument de la fonction de "Student" au degrée de croyance p = 90 et au degrée liberté égal à deux.

Remarque: Pour éviter l'influence défavorable de tungstène, il faut procéder de la manière suivante: dissoudre à chaud une dose convenable d'acier dans l'acide chlorhydrique. Après avoir refroidi la solution y ajoutez 5 ml de H_2O_2 et la faire bouillir jusqu'au moment d'obtenir le volume diminué 2 fois. Après avoir éliminé l'eau oxygénée, diluez la solution pour obtenir 100 ml, ajoutez 2 ml de cinchonine (125 g dans un litre de HCl, 1 + 1), chauffer au bain-marie pendant 30 min et laisser pour 24 heures. Filtrer le précipité, le dissoudre dans l'ammoniaque et de nouveau précipiter. Eliminer le précipité, ajouter le filtrate et doser le vanadium de la meme manière que dans les aciers.

CONCLUSIONS

Cette méthode simple et facile à exécuter permet de doser la teneur de vanadium de l'ordre de 1,5–0,05% Il est important de fixer la valeur de pH de la phase aqueuse avant l'extraction de vanadium sous la forme du complexe lié à ATH. La différence du volume de la phase aqueuse n'influe pas sur les résultats obtenus et il est avantageux de prendre la force ionique environ 1. Il suffit d'extraire une seule fois avec l'alcool butylique. On peut appliquer cette méthode pour doser le vanadium contenu dans les corps divers. Limite de sensibilité de la méthode—0,01 μg V × cm^{-2}; précision du dispositif—0,001 de l'unité d'absorption.

Summary—Thiophene-2-hydroxamic acid has not previously been used as an organic reagent for inorganic analysis. Its ultraviolet absorption spectra have been studied in acid and alkaline solutions, and its dissociation constant has been established as about $1{\cdot}7 \times 10^{-8}$. The acid reacts with many metallic ions, *e.g.*, Fe^{III}, Co^{II}, Mn^{VI}, Mo^{-} and Nb^{V}, giving precipitates or soluble compounds. It forms violet complexes with V^{V}. The composition of these complexes has been studied in relation to the pH of the solution. The complex formed at pH 3.5 has the composition V:R = 1:3, and the maximum of the absorption band is at $\lambda = 590$ mμ. The corresponding values for the complex formed at pH 7·7 are 1:3 and 550 mμ. The extractability of the complex formed in moderately acid solution has been used in devising a method for the determination of low concentrations (1·5–0·05%) of vanadium in various materials.

Zusammenfassung—Thiophen-2-hydroxamsäure wurde noch nicht als organisches Reagens in der anorganischen Analyse verwendet. Ihr UV-Absorptionsspektrum wurde in saurer und alkalischer Lösung gemessen und die Dissoziationskonstante zu etwa $1{,}7 \,.\, 10^{-8}$ bestimmt. Die Säure reagiert mit vielen Metallionen, z. B. Fe^{III}, Co^{II}, Mn^{II}, Mo^{VI} und Nb^{V} unter Bildung von Niederschlägen oder löslichen Verbindungen. Mit V^{V} werden violette Komplexe gebildet. Die p_H-Abhängigkeit der Zusammensetzung dieser Komplexe wurde untersucht. Der bei p_H 3,5 gebildete Komplex hat die Zusammensetzung V:R = 1:3 mit einem Absorptionsmaximum bei 590 mμ. Bei p_H 7,7 sind die Werte 1:3 und 550 mμ. Der in schwach saurer Lösung gebildete Komplex läßt sich extrahieren. Darauf wurde eine Methode zur Bestimmung kleiner Vanadinkonzentrationen aufgebaut.

BIBLIOGRAPHIE

[1] J. Minczewski et Z. Skorko-Trybula, *Chem. Analit.*, 1961, **6,** 377.
[2] Z. Skorko-Trybula et J. Minczewski, *ibid.*, 1961, **6,** 523.
[3] S. G. Tandon et S. C. Bhattacharya, *Analyt. Chem.*, 1960, **32,** 194.
[4] M. Calvin et K. W. Wilson, *J. Amer. Chem. Soc.*, 1945, **67,** 2003.
[5] *Organic Syntheses.* Coll. Vol. **3,** 14.
[6] *Organic Syntheses.* Coll. Vol. **2,** 428.
[7] A. Vogel, *A Textbook of Practical Organic Chemistry.* Longmans, London, 1948.
[8] R. E. Plapinger, *J. Org. Chem.*, 1959, **24,** 802.
[9] B. M. Usova et E. K. Voroszin, *Dokl. Akad. Nauk. SSSR*, 1957, **113,** 1505.
[10] F. Mathis, *Compt. rend.*, 1951, **232,** 505.
[11] J. Minczewski et Z. Lada, *Miareczkowanie potencjometryczne.* Warszawa, 1957.
[12] S. Kilpsi, *Z. physik. Chem.*, 1935, **A173,** 427.
[13] N. Ingri et F. Brito, *Acta Chem. Scand.*, 1959, **13,** 1971.
[14] P. Job, *Ann. Chim. (France)*, 1928, **9,** 113.
[15] J. H. Yoe et A. L. Jones, *Ind. Eng. Chem., Analyt.*, 1944, **16,** 111.
[16] J. Minczewski et Z. Skorko-Trybula, *Chem. Analit.*, 1960, **5,** 163.
[17] A. K. Babko, *Analiza fizykochemiczna zwiazków kompleksowych w roztworach Kijów*, 1956, Warszawa, 1959.
[18] A. J. Blair, D. A. Pantony et G. J. Minkoff, *J. Inorg. Nuclear Chem.*, 1958, **5,** 316.
[19] H. Specker et E. Jackwerth, *Z. analyt. Chem.*, 1959, **167,** 416.
[20] W. M. Wise et W. W. Brandt, *Analyt. Chem.*, 1955, **27,** 1392.
[21] S. K. Majumdar et A. K. De, *ibid.*, 1961, **33,** 297.
[22] D. E. Ryan, *Analyst*, 1960, **85,** 569.

Talanta, 1963, Vol. 10, pp. 1077 to 1082. Pergamon Press Ltd. Printed in Northern Ireland

ANION-EXCHANGE SEPARATION OF RARE EARTH ELEMENTS AND THORIUM FROM URANIUM WITH CARBONATE SOLUTIONS

TOMITSUGU TAKETATSU
General Education Department, Kyushu University, Fukuoka, Japan

(*Received* 30 *March* 1963. *Accepted* 16 *May* 1963)

Summary—Quantitative separation of some rare earth elements and thorium from uranium^{VI} is carried out using Dowex 1, X–8 with 0·7*M* potassium carbonate or 0·4*M* ammonium carbonate* solution as eluant.

IT is well known that uranium^{VI} and thorium can be easily dissolved in a carbonate solution and adsorbed on an anion-exchange resin from that solution.[1–4] Although the anion-exchange behaviour of trace amounts of several rare earth elements in a carbonate solution has been studied,[4–6] no anion-exchange separation of macro amounts of rare earth ions from other metal ions using a carbonate solution has yet been reported. The author has previously shown that the amounts of rare earth elements which can be dissolved in a solution of potassium or ammonium carbonate increases with an increase in the concentration of the carbonates and also with an increase in atomic number.[7] Moreover, it was found that scandium, yttrium and thorium were more soluble than the light lanthanons and that the rare earth ions as well as thorium ions dissolved in these carbonate solutions were adsorbed less firmly than uranyl ions on an anion-exchange resin.

In the present work, the separation of macro amounts of some rare earth elements and thorium from uranium^{VI} has been investigated using an anion-exchange resin with potassium and ammonium carbonate solutions as eluants.

EXPERIMENTAL

Reagents

Standard solutions of metal ions: Prepared by dissolving the reagent-grade oxides (praseodymium, neodymium, samarium, gadolinium, erbium, yttrium and scandium) or nitrates (cerium^{III}, thorium and uranium^{VI}) in dilute hydrochloric or nitric acid. The concentrations of rare earth and thorium ions were determined titrimetrically with EDTA using Xylenol Orange as indicator. The pH of the solutions to be titrated was adjusted to 4·5–6·0 for the rare earth ions[8] and to 1·5–2·5 for thorium ions.[9] The titration of uranyl ions with EDTA was made using PAN as indicator at pH 4·0.[10]

All other chemicals used were analytical reagent grade.

Apparatus

The anion-exchange resin Dowex 1,X–8 (carbonate form), 100 to 200-mesh, was used in a 12 cm × 0·6 cm^2 column.

Procedure

A slightly acidic solution, containing 1–10 mg of rare earth or thorium ions and 20–30 mg of uranyl ions, was transferred to a glass-stoppered conical flask, and the solution was evaporated to dryness on a water bath to remove any excess acid. Twenty ml of 0·5*M* potassium carbonate solution

---

* The molar concentration of ammonium carbonate is expressed on the basis of the molecular formula $NH_4CO_2NH_2{\cdot}NH_4HCO_3$, but the concentration is not accurate because of the volatility of the ammonia.

were added to the residue in the flask. A precipitate of basic rare earth or thorium and uranyl carbonates was thereby formed. The flask was vigorously shaken by a mechanical shaker to dissolve the precipitate. After the precipitate was completely dissolved, the solution was poured into the anion-exchange column at a flow rate of about 1 ml/min, then 100 ml of 0·7*M* potassium carbonate solution were passed through the column at a similar flow rate to elute the rare earth or thorium ions. During this operation the uranyl ions were strongly adsorbed on the resin, forming a yellowish adsorption band which moved only slowly down the column. The concentration of rare earth or thorium ions in the eluate was determined as described under *Reagents*. The uranyl ions remaining in the column were eluted with 40 ml of 1*M* potassium chloride solution and their concentration determined as described under *Reagents*.

The procedure in the case of elution with 0·4*M* ammonium carbonate solution was similar to that described above for potassium carbonate solution.

RESULTS AND DISCUSSION

Dissolution of rare earth elements[7]

A praseodymium solution of about 5×10^{-4} *M* concentration can be prepared by dissolving the chloride in 0·5*M* potassium carbonate or 0·4*M* ammonium carbonate solution. Other heavier rare earth elements, such as yttrium and scandium, are more soluble than praseodymium. Because a macro amount of lanthanum cannot be dissolved completely even in potassium carbonate solution more concentrated than 0·5*M* or in ammonium carbonate solution more concentrated than 0·4*M*, the separation procedure cannot be used for a macro amount of lanthanum. However, it may be applied for the separation of a trace amount of lanthanum. Cerium can exist as the stable orange-yellowish cerium^{4+} ion in the ammonium carbonate solution and it is more soluble than the light lanthanons. In the potassium carbonate solution it is dissolved completely at first, but a precipitate of the basic carbonate is formed on standing. Therefore, the cerium solution was prepared by dissolving the nitrate in ammonium carbonate solution.

Equilibrium distribution coefficients

The distribution coefficient, Kd*, of the uranyl, thorium and some rare earth ions were measured (Table I) as follows:[7]

One g of air-dried resin (carbonate form) was added to 100 ml of the appropriate carbonate solution containing about $5 \times 10^{-4}M$/1. of the element under investigation. After the solution had been shaken mechanically for 3–4 hr, the resin was rapidly separated by suction from the solution with a glass filter and transformed into a column. The element adsorbed on the resin was subsequently eluted with dilute hydrochloric acid and titrated with EDTA. Although at the beginning of the elution the resin bed was disturbed by the release of carbon dioxide, this disturbance did not affect the elution because only the element under examination was adorbed on the resin.

From the distinct difference in the Kd value for uranyl ions and the other metal ions studied, it is considered that uranyl ions should be effectively separated from those ions by using column operation with the specified carbonate solutions as eluants.

Column elution

The quantities of metal ions used were 37·2 mg (UO_2^{2+}), 18·0 mg (Th^{4+}), 5·50 mg (Y^{3+}), 7·20 mg (Er^{3+}) and 10·60 mg (Ce^{4+}). The metal chlorides or nitrates were dissolved in 20 ml of 0·5*M* potassium carbonate or 0·4*M* ammonium carbonate solution and the same carbonate solution was used as influant. Based on the Kd

---

* $\mathrm{Kd} = \frac{(\mathrm{Mr})}{(\mathrm{Ms})}$ where Mr and Ms are the amounts of the element in 1 g of the resin and in 1 ml of the original solution, respectively.

TABLE I

Ion	Kd: 0·5*M* potassium carbonate	Kd: 0·4*M* ammonium carbonate
UO_2^{2+}	300	100
Th^{4+}	3	2
Sc^{3+}	8	—
Y^{3+}	40	5
Sm^{3+}	20	3
Nd^{3+}	6	2
Ce^{4+}	—	6

value of each metal ion, the effect of various concentrations of the eluants on the rate of column operation was examined. The data obtained are presented in Table II. Table II shows that all the carbonate solutions investigated may be used to separate uranyl ions from the other metal ions, but the use of 0·7*M* potassium carbonate or 0·4*M* ammonium carbonate solution is most effective. The elution graphs of individual metal ions eluted with these optimum concentrations of carbonate solution are given in Figs. 1 and 2.

These graphs were obtained by analysing 20 ml of each eluate fraction. The results show that a part of the thorium, cerium and yttrium has already broken through the column before the eluant passes through it, and the rare earth and

TABLE II.—ELUTION OF METAL IONS WITH POTASSIUM CARBONATE AND AMMONIUM CARBONATE SOLUTIONS OF VARIOUS CONCENTRATIONS.*

Ion	Potassium carbonate solution, *ml*					
	0·6*M*		0·7*M*		0·8*M*	
	Elution complete	Break-through	Elution complete	Break-through	Elution complete	Break-through
Th^{4+}	60	0	40	0	40	0
Sm^{3+}	100	0	80	0	60	0
Er^{3+}	140	0	80	0	80	0
UO_2^{2+}	—	140	—	180	—	100

Ion	Ammonium carbonate solution, *ml*			
	0·4*M*		0·5*M*	
	Elution complete	Break-through	Elution complete	Break-through
Th^{4+}	40	0	40	0
Y^{3+}	60	0	60	0
Ce^{4+}	60	0	40	0
UO_2^{2+}	—	100	—	80

* Results obtained by analysing 20 ml of each eluate fraction: "0" indicate that metal ions begin to flow out in the first fraction.

thorium ions are completely eluted with 40–80 ml of 0·7*M* potassium carbonate solution or 40–60 ml of 0·4*M* ammonium carbonate solution. The uranyl ions begin to be eluted with 180 ml of potassium carbonate solution or 120 ml of ammonium carbonate solution. Because tailing occurs in elution of the uranyl ions with these carbonate solutions and a large volume of the eluant is required, it is undesirable to elute the uranyl ions completely with these carbonate solutions. Therefore, when the rare earth and thorium ions had been eluted completely, 20–30 ml of 1*M* potassium chloride solution were passed through the column to elute the uranyl ions.

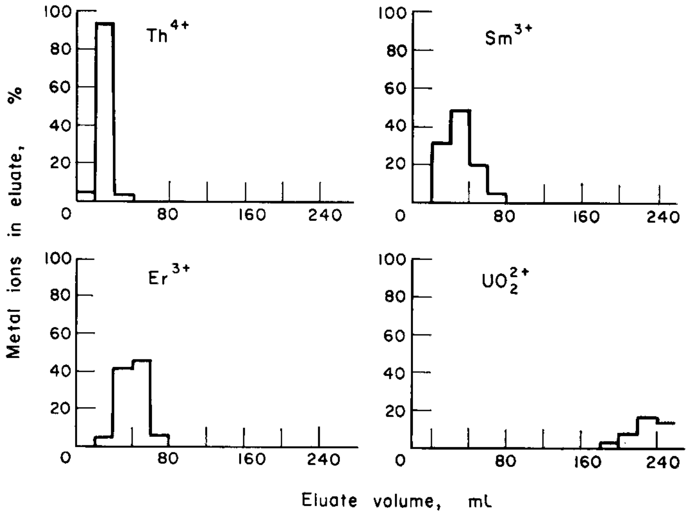


FIG. 1.—Elution of thorium, samarium, erbium and uranyl ions with 0·7*M* potassium carbonate solution.

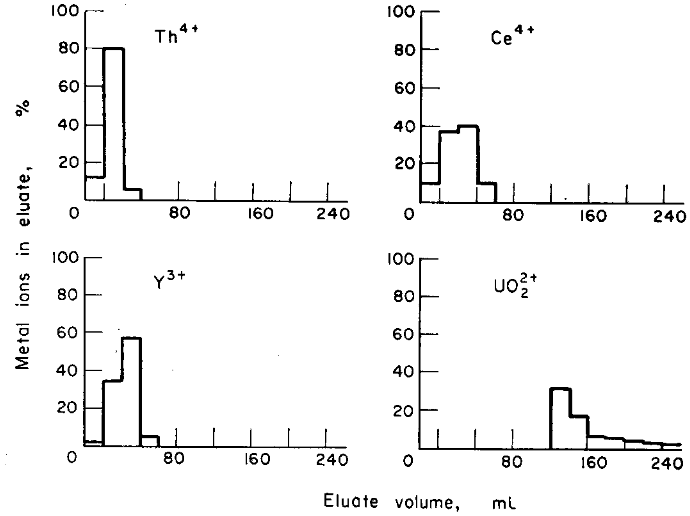


FIG. 2.—Elution of thorium, cerium, yttrium and uranyl ions with 0·4*M* ammonium carbonate solution.

Quantitative column separation

The results of some analyses for various quantities of uranium^{VI} and rare earth elements or thorium by this procedure are shown in Table III.

TABLE III.—RESULTS OF QUANTITATIVE SEPARATION OF URANIUM^{VI} FROM SOME RARE EARTH ELEMENTS AND THORIUM.

Ion	0·7*M* Potassium carbonate solution		
	Taken, *mg*	Found, *mg*	Error, *mg*
UO_2^{2+}	18·6	18·7	+0·1
Th^{4+}	18·0	18·2	+0·2
UO_2^{2+}	37·2	37·3	+0·1
Th^{4+}	7·2	7·1	−0·1
UO_2^{2+}	18·6	18·8	+0·2
Sc^{3+}	2·42	2·35	−0·07
UO_2^{2+}	18·6	18·6	±0·0
Sc^{3+}	1·21	1·23	+0·02
UO_2^{2+}	18·6	18·6	±0·0
Y^{3+}	5·50	5·46	−0·4
UO_2^{2+}	37·2	37·2	±0·0
Y^{3+}	2·19	2·20	+0·01
UO_2^{2+}	18·6	18·6	±0·0
Er^{3+}	7·23	7·26	+0·03
UO_2^{2+}	18·6	18·8	+0·2
Er^{3+}	3·61	3·68	+0·07
UO_2^{2+}	18·6	18·8	+0·2
Gd^{3+}	5·23	5·20	−0·03
UO_2^{2+}	18·6	18·7	+0·1
Sm^{3+}	4·90	4·87	−0·03
UO_2^{2+}	18·6	18·6	±0·0
Nd^{3+}	2·90	2·99	+0·09
UO_2^{2+}	18·6	18·6	±0·0
Pr^{3+}	1·46	1·42	−0·04

Ion	0·4*M* Ammonium carbonate solution		
	Taken, *mg*	Found, *mg*	Error, *mg*
UO_2^{2+}	37·2	37·2	±0·0
Th^{4+}	18·0	18·1	+0·1
UO_2^{2+}	18·6	18·8	+0·2
Y^{3+}	2·21	2·19	−0·02
UO_2^{2+}	18·6	18·6	±0·0
Er^{3+}	7·12	7·12	±0·00
UO_2^{2+}	18·6	18·7	+0·1
Sm^{3+}	4·80	4·84	+0·04
UO_2^{2+}	18·6	18·5	−0·1
Ce^{4+}	10·60	10·54	−0·06

Because the solubility of the light lanthanons (Pr or Nd) in 0·5*M* potassium carbonate and 0·4*M* ammonium carbonate solutions is about $5 \times 10^{-4}M$ at 20°, the quantities used here represent approximately the limiting solubility. However, it is supposed that a greater amount of heavy lanthanons than those specified can be separated from uranium, because the amount of lanthanon dissolved in the carbonate solution increases with increase in atomic number. The accurate measurement of the solubility of each lanthanon in the carbonate solution is now being carried out in this laboratory.

It is concluded that the separation of macro amounts of rare earth elements and thorium from uranium^{VI} can be carried out quantitatively.

The procedure may also be used to separate micro amounts, especially trace amounts of rare earth elements in the fission products from irradiated uranium.

Zusammenfassung—Seltene Erden und Thorium in einer Carbonatlösung werden an einem Anionenaustauscher weniger fest adsobiert als Uranylionen. Daher können seltene Erden und Thorium mit Dowex 1, X-8 mit 100 bis 200 mesh in einer Säule von 12 cm × 0,6 cm^2 quantitativ von Uran getrennt werden. Eluiert wird mit 0,7m K_2CO_3 oder 0,4m$(NH_4)_2CO_3$.

Résumé—Les ions des terres rares aussi bien que les ions thorium en solution carbonatée sont moins fermement retenus que les ions uranyl sur les résines échangeurs d'anions. Ainsi, des séparations quantitatives des éléments des terres rares et du thorium de l'uranium(V) peuvent être éffectuées sur Dowex 1,X-8 de 100 à 200 mesh, dans une colonne de 12 cm./0,6 cm^2, en utilisant des solutions de carbonate de potassium à 0,7 M ou de carbonate d'ammonium à 0,4 M comme éluant.

REFERENCES

[1] T. Ishimori and H. Okuno, *Bull. Chem. Soc. Japan*, 1956, **29**, 78.
[2] N. Saito and T. Sekine, *ibid.*, 1957, **30**, 561.
[3] S. M. Khopkar and A. K. De, *Analyt. Chim. Acta* ,1960, **23**, 147.
[4] S. Misumi and T. Taketatsu, *Bull. Chem. Soc. Japan*, 1959, **32**, 877.
[5] N. Saito and T. Sekine, *Nature*, 1957, **186**, 753.
[6] S. Misumi and T. Taketatsu, *J. Inorg. Nuclear Chem.*, 1961, **20**, 127.
[7] T. Taketatsu, *Bull. Chem. Soc. Japan*, 1962, **35**, 1573.
[8] J. Kinnunen and B. Wennerstrand, *Chemist-Analyst*, 1957, **46**, 92.
[9] J. Körbl, R. Přibil and A. Emr, *Chem. Listy*, 1956, **50**, 1440.
[10] E. Lassner and R. Scharf, *Z. analyt. Chem.*, 1958, **164**, 398.

Talanta, 1963, Vol. 10, pp. 1083 to 1086. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF NITROGEN IN ORGANIC COMPOUNDS USING ION-EXCHANGE RESINS

R. A. SHAH and A. A. QADRI
Central Laboratories, Pakistan Council of Scientific and Industrial Research
34–37 P.N.H. Lines, Karachi-Cantt., Pakistan

(*Received* 3 *May* 1963. *Accepted* 25 *June* 1963)

Summary—Nitrogen in an organic compound is determined by decomposing the sample in a sealed tube with sulphuric acid and passing the digest through two columns of anion-exchange resin, placed one above the other. The upper column contains the resin in the hydroxide form and the lower column in the iodide form. Hence, the ammonium sulphate in the digest is converted to ammonium iodide, which is determined by the Leipert amplification procedure.

THE decomposition of the organic nitrogen-containing compound is effected with concentrated sulphuric acid in a sealed tube in order to avoid the addition of potassium sulphate, catalysts, *etc.* (metals forming soluble sulphates interfere in the ion-exchange technique used to complete the determination). Moreover, the sealed-tube method has many advantages over the conventional Kjeldahl digestion procedure.[1–6] Subsequently, the digest containing ammonium sulphate and sulphuric acid is passed through two columns of anion-exchange resin, placed one above the other. The upper column contains the resin in the hydroxide form, which removes the sulphuric acid from the digest and converts the ammonium sulphate into ammonium hydroxide. The latter, on passing through the second column which is in the iodide form, is converted into ammonium iodide. The iodide is then oxidised to iodate with bromine. After removing the excess of bromine with formic acid, potassium iodide and sulphuric acid are added. The liberated iodine is titrated with standard sodium thiosulphate solution, thus giving a six-fold amplification.

EXPERIMENTAL

Reagents

Ion-exchange resin: Treat about 70 g* of analytical-grade strong-base anion-exchange resin Amberlite IRA-400 (chloride form) (Rohm and Haas company, Philadelphia, U.S.A.) with 500 ml of 2*N* sulphuric acid, then wash thoroughly with water. Convert the resin to the hydroxide form by treating with 1 litre of 2*N* sodium hydroxide solution; remove excess of the alkali by repeated water washing in a sintered glass funnel. Convert some of the hydroxide-form resin to the iodide form with 250 ml of 2*N* potassium iodide solution, then wash with water until free from potassium iodide and potassium hydroxide.

Concentrated sulphuric acid: Merck guaranteed reagent.

Bromine solution: Dissolve 100 g of potassium acetate in 1 litre of glacial acetic acid, then add 4 ml of bromine.

98–100% *Formic acid*
4*N Sulphuric acid*
10% *Potassium iodide solution:* Prepare freshly each day.
Standard 0·05*N sodium thiosulphate solution*
Starch indicator solution

---

* This quantity of resin is sufficient to fill two sets of ion-exchange columns.

Apparatus

Digestion tubes: Pyrex thick-walled test tubes, 10 × 100 mm.

1-ml Graduated pipette: Accurate to ±0·005 ml.

Heating block: An electrically heated (to 500°) thermostatically controlled (±5°) Dural block with 8 holes to accommodate digestion tubes.

Centrifuge: An electric centrifuge capable of 400 rpm and fitted with buckets to accommodate sealed digestion tubes.

Capillary teat pipette: Containing a 2-ml glass bulb in the stem.

Ion-exchange column: Fit together as shown in Fig. 1 two air condensers with B19 ground-glass joints (Quickfit and Quartz Ltd., Stone, Staffs., England). Add hydroxide-form resin to give a 19-cm bed in the upper condenser and iodide-form resin to the same length in the lower condenser. Wash the ion-exchange column with 100 ml of water. A 50-ml pear-shape funnel with B19 ground-glass joint may be used as a water reservoir on top of the columns.

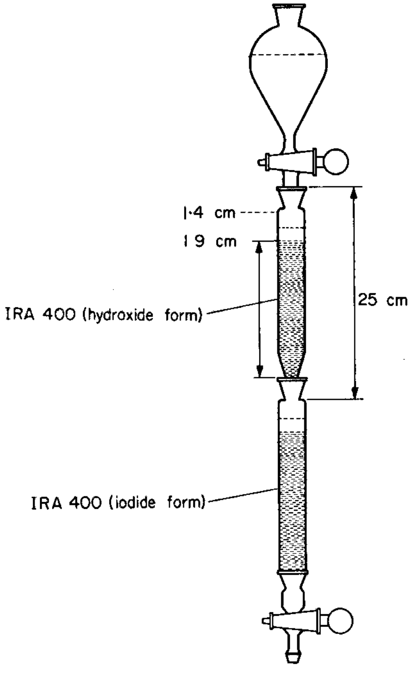


FIG. 1

Procedure

Digestion. Weigh 2–4 mg of the organic compound into a clean digestion tube.

For a series of determinations 8 tubes are used, 6 containing compounds for analysis and 2 for blank determinations (no organic compound present). Add 0·1 ml of concentrated sulphuric acid from a 1-ml graduated pipette, then seal the tube at a point 2·5–3 cm from the open end using an oxygen-gas flame. Place the sealed tube in a heating block at 420–430°. After 30 min remove the tube and allow it to cool in a metal block for a few min. Centrifuge for 5 min. Before opening, cool the tube in ice for 5 min then release the inside pressure, if any, by touching the glass just below the sealed end with a small oxygen-gas flame. Apply a molten soft-glass rod lightly to a moistened scratch made with a sharp glass knife about 2 cm below the point of sealing. Place the two parts of the opened tube in an oven at 90° for 5 min to remove any sulphur dioxide from the digest.

Column operation. Just before use, wash the ion-exchange column with 50 ml of water and determine the blank on 75 ml of water. If more than 0·2 ml of standard 0·05*N* sodium thiosulphate solution is required, further washing of the column is indicated. (Two ion-exchange columns should be prepared for a series of 8 determinations.)

Dilute the digest with 2 ml of water and transfer this solution to the ion-exchange column by means of a capillary teat pipette. Wash out the two parts of the opened digestion tube with four more 2-ml portions of water. Fit the water reservoir onto the column and use 75 ml of water to elute the column.

Titration. Treat the eluate from the ion-exchange column with 5 ml of bromine solution, allow to stand for about 1 min, then destroy the excess bromine by dropwise addition of formic acid until the colour of bromine disappears; add 2 drops of formic acid in excess. Stir magnetically for 5 min to remove bromine vapours from the titration flask. Add 2 ml of 10% potassium iodide solution and 2 ml of 4N sulphuric acid. Titrate the liberated iodine with standard 0·05N sodium thiosulphate solution using starch as indicator.

Deduct the titre of a blank determination and calculate the nitrogen content of the original organic compound:

$$1 \text{ ml of } 0{\cdot}05N\ Na_2S_2O_3 \equiv 0{\cdot}11673 \text{ mg of N.}$$

DISCUSSION

The proposed method combines the advantages of the sealed-tube digestion with the benefits from elimination of the distillation step in the normal Kjeldahl method. Four determinations can be easily made for one filling of an ion-exchange column. About 15 min are necessary for the 75 ml of water to elute the column.

The blank value from the concentrated sulphuric acid (0·1 ml) used for the digestion is rather high, *viz.* 0·48–0·50 ml of 0·05 N sodium thiosulphate solution (the slight variation in titre is caused by the change in quality of the distilled water from day to day). Attempts were made to reduce the blank by giving different treatments to the ion-exchange resin and also by improving the quality of the distilled water used for washing, but no significant change in the value could be effected.

Some results (± 0·3 absolute % of nitrogen) for various organic nitrogen-containing compounds are given in Table I. The method should be of value in the determination of small amounts of nitrogen.

TABLE I

Compound	Nitrogen content, %		
	Calculated	Found	Error
Ammonium sulphate	21·21	21·33	+0·12
Hippuric acid	7·82	7·95	+0·13
		7·72	−0·10
Phenyl thiourea	18·42	18·43	+0·01
		18·34	−0·08
α-Benzoin oxime	6·16	6·37	+0·21
		6·30	+0·14
DL-Lysine	15·38	15·30	−0·08
		15·15	−0·23
Phenacetin	7·84	7·55	−0·29
		7·54	−0·30
Diphenylamine	8·27	8·26	−0·01
		8·17	−0·10

Acknowledgement—The authors wish to record their grateful thanks to Dr. T. S. West for his helpful suggestions. They are also indebted to Mr. S. A. Jabbar for assistance in the work.

Zusammenfassung—Organischer Stickstoff wird bestimmt durch Aufschluß mit Schwefelsäure im Einschlußrohr und nachfolgenden Anionenaustausch an zwei übereinanderliegenden Säulen. Die obere Säule enthält das Harz in der OH-Form, die untere in der J-Form. Das so in NH_4J umgewandelte $(NH_4)_2SO_4$ aus dem Aufschluß wird nach der Methode von Leipert bestimmt.

Résumé—L'azote des composés organiques est dosé par décomposition de l'échantillon en tube scellé et passage sur deux colonnes contenant une résine échangeuse d'anions, placées l'une au-dessus de l'autre. La colonne supérieure contient la résine sous forme (OH) et la colonne inférieure sous forme d'iodure. Le sulfate d'ammonium par passage à travers ces deux colonnes est converti en NH_4I qui est dosé par la méthode d'amplification de Liepert.

REFERENCES

[1] L. M. White and M. C. Long, *Analyt. Chem.*, 1951, **23**, 363.
[2] B. W. Grunbaum, F. L. Schaffer and P. L. Kirk, *ibid.*, 1952, **24**, 1487.
[3] B. W. Grunbaum, P. L. Kirk, L. G. Green and C. W. Koch, *ibid.*, 1955, **27**, 384.
[4] P. R. W. Baker, *Analyst*, 1953, **78**, 500.
[5] R. Belcher, T. S. West and M. Williams, *J. Chem. Soc.*, 1957, 4323.
[6] R. Belcher, R. L. Bhasin and T. S. West, *ibid.*, 1959, 2585.

Talanta, 1963, Vol. 10, pp. 1087 to 1091. Pergamon Press Ltd. Printed in Northern Ireland

A SOLVATOCHROMIC CHELATING AGENT

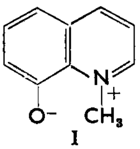
A. Mueller, J. Travis Leach and J. P. Phillips
Department of Chemistry, University of Louisville, Louisville 8, Kentucky
U.S.A.

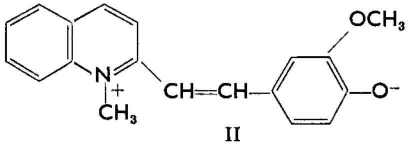
(*Received* 6 *May* 1963. *Accepted* 24 *May* 1963)

Summary—1-Methyl-2-[2-(8-hydroxy-5-quinolyl)vinyl]-8-hydroxyquinolinium chloride has been prepared as an example of a chelating agent for metals that changes colour with solvent polarity. As a chelating agent it has some selectivity, precipitating only the copper^{II} ion in an acidic solution and forming a distinctively coloured product with zinc in neutral solutions. In ammoniacal methanol it gives a red solution with magnesium and several other ions. A number of related solvatochromic compounds have also been prepared.

A SOLVATOCHROMIC compound undergoes a very large variation in colour as a function of the polarity of solvents. In positive solvatochromism the wavelength of maximum absorption increases with increasing dielectric constant (or other polarity measure) of the solvent, while a decrease is described as negative solvatochromism[1]; a mixed behaviour is not uncommon, the wavelength first increasing and then decreasing as the polarity rises, for example.[2]

Some efforts have been made to employ this phenomenon to analyse solvent mixtures[2,3] and in colour tests for type and degree of hydrogen bonding.[4,5] Among compounds explored for these applications have been the betaine of *N*-methyl-8-hydroxyquinolinium hydroxide (I)[3,4] and a variety of merocyanines such as II, the betaine of 2-(4-hydroxy-3-methoxy)styryl-*N*-methylquinolinium hydroxide:[5]


I


II

Both are negatively solvatochromic, I ranging from blue to yellow as the solvent dielectric constant rises from 2 to 80 and II from blue to red over the same range.

It is possible to prepare a single molecule containing both of the solvatochromic functions of I and II at once, *e.g.*, compound III and several related substances (VII-XV in Table I):

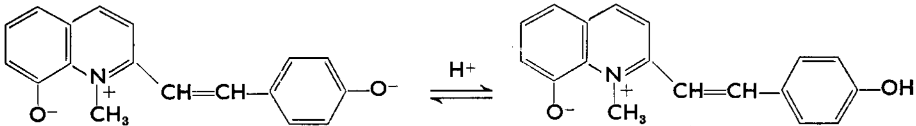
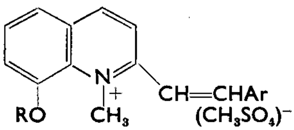

III IIIa

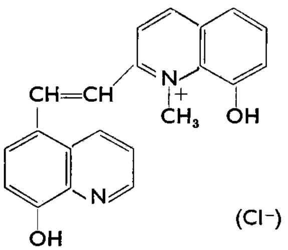
TABLE I—HYDROXY-*N*-METHYL-2-STYRYLQUINOLINIUM METHOSULPHATES



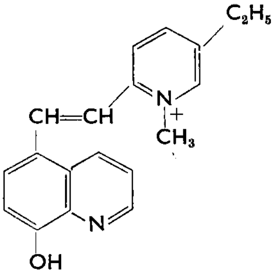
Compound	R	Ar	M.p., °*C*	Yield, %	N Calcd., %	N found, %
VII	H	4-HOC$_6$H$_4$	235–7	67	3·60	3·17
VIII	H	4-MeOC$_6$H$_4$	205–10	60	3·47	3·09
IX	Me	4-HOC$_6$H$_4$	196d.	89	3·47	3·39
X	H	C$_6$H$_5$	162–6[a]	90	3·75	3·71
XI	H	2-OH-1-naphthyl	155–6	88	3·19	2·89
XII	Me	2-OH-1-naphthyl	104–10	75	3·09	3·24
XIII	H	3-Me-4-OH-C$_6$H$_3$	170–3[b]	58	3·34	3·27
XIV	H	2-OH-5Cl-C$_6$H$_3$	229–31	65	3·31	3·39
XV	H	3-MeO-4-OH-5-Cl-C$_6$H$_2$	235d.[c]	60	3·09	3·42

[a] Betaine m. 82–3°.
[b] Betaine m. 98–100°.
[c] Betaine m. 168–9°.

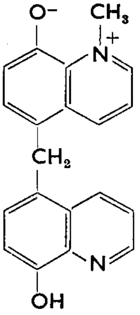
Attempts to prepare chelating agents related to the well-known 8-quinolinol but containing also the above solvatochromic functions led to compounds IV–VI:



IV



V



VI

As chelating agents these three compounds are distinct from each other. In an alkaline solution IV can form a diphenoxide anion which is similar to III in having two solvatochromic systems sharing a common quaternary nitrogen atom; however, chelation with a metal by the 8-quinolinol function eliminates the merocyanine function and the product can only be solvatochromic in the fashion of I. In V chelation again eliminates the potential merocyanine but the chelate cannot be solvatochromic; also, the chelates are cationic and should be soluble in polar solvents. In VI the solvatochromic function is simply added to an 8-quinolinol function and the two should be essentially independent. At the present time only IV has been investigated in much detail and the rest of this paper is therefore devoted to this compound and model compounds related to it.

The spectra of a number of model compounds like III were desired in order to gain an insight into the behaviour of IV. These substances were most conveniently isolated in the form of the yellow to red methosulphate salts (see Table I) from which the much more strongly coloured betaines (IIIa) could be generated in solution by the addition of an equimolar amount of base. Negative solvatochromism is characteristic of all of these betaines (Table II). All but VIII–X and XII can yield two

TABLE II.—CHARGE TRANSFER BANDS IN THE SPECTRA OF BETAINES OF COMPOUNDS VII–XV

Compound	Maximum, $m\mu$ (log ϵ)					
	Water	Methanol	Benzyl alcohol	Acetone	Chloroform	Benzene
VII		530 (1·77)	570 (2·43)	573 (2·26)	583 (2·48)	584 (1·08)
VIII	390s (3·77)	396s (3·79)	574 (3·66)	563 (3·26)	574 (3·20)	575 (2·99)
IX	484 (4·21)	543 (4·45)	574 (4·60)	576 (4·42)	586 (4·68)	587 (4·50)
X		513 (3·18)	545 (2·74)	610 (2·08)	615 (2·81)	
XI	525s (3·41)	566 (3·54)				
XII	550 (4·26)	587 (4·51)				
XIII	517s (2·89)	519s (2·96)				
XIV	520s (2·97)	530s (2·94)				
XV		560 (2·50)			600 (3·23)	

TABLE III.—SPECTRA OF THE HYDROXYSTYRYL-8-HYDROXYQUINOLINIUM BETAINE ANIONS

Compound	Maxima, $m\mu$ (log ϵ)	
	Aqueous 0·1N NaOH	Methanolic 0·1N NaOH
VII	347 (4·45), 382 (4·42), 500s (3·44)	353 (4·47), 393 (4·47), 550 (3·50)
XI	413 (4·18), 525s (3·41)	415 (4·21), 566 (3·54)
XIII	396 (4·27), 517s (2·89)	403 (4·32), 519s (2·95)
XIV	348 (4·44), 382 (4·43), 520s (2·97)	354 (4·49), 386 (4·48), 530s (2·94)
XV	347 (4·45), 382 (4·42), 500s (3·43)	353 (4·47), 393 (4·47), 550 (3·49)
IV	370 (3·97), 505 (4·43)	377 (4·06), 560 (4·57)

solvatochromic systems that share a common quaternary nitrogen atom in the presence of excess alkali, and the spectra of the resulting anions (III) were also obtained. The anion could not be extracted into non-polar solvents and these spectra were thus obtained in water and methanol solutions only. The expectation that the sharing of the solvatochromic systems would impair the intensity of each was fulfilled (Table III).

The number of metal ions that yield insoluble products with IV is certainly smaller than with 8-quinolinol. This may be partially accounted for by the very considerable differences in acid-base properties of the two reagents. The spectrophotometric method indicated three apparent pKa values for IV in the pH range 1–13, respectively 2·15, 5·35 and 8·5. The latter two are ionisations of the phenolic hydroxyls, with the 5·35 value assigned by analogy with the merocyanines of the preceding paragraph to the hydroxyl adjacent to the alkylated nitrogen atom.

In a series of tests with common metal ions at pH 2 only copper gave a precipitate, an intensely red compound that analysed for the expected 2:1 ratio of reagent to metal. At pH 4–6 a number of other bivalent and tervalent ions gave orange or red precipitates, but only zinc gave a violet-red product. This also analysed for the expected 2:1 mole ratio. In ammoniacal dioxan, pyridine or methanol, IV is green, but it yields orange, red, red or violet solutions with cobalt, copper, magnesium or zinc, respectively. An aqueous ammoniacal solution of IV is red, and there is thus no doubt that the reagent is solvatochromic; however, possible solvatochromism in the chelates was not striking, though the limited solubility of these substances in most solvents did not permit a thorough investigation.

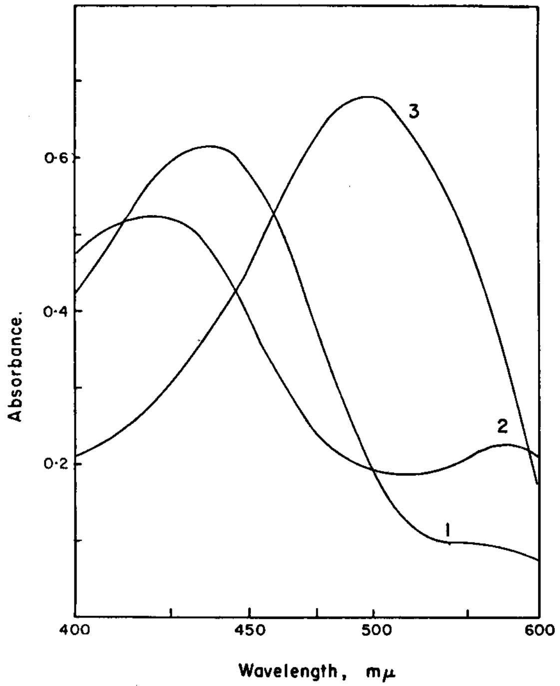


Fig. 1.—Spectra of IV in methanol (curve 1), in ammoniacal methanol of apparent pH 9 (curve 2) and in ammoniacal methanol 1×10^{-4} *M* in magnesium (curve 3), with a reagent concentration of *ca.* 2×10^{-4} *M*.

Spectra of IV in methanol, in ammoniacal methanol and after the addition of excess magnesium ion (Fig. 1) suggest a possible use of this reagent for the colorimetric determination of magnesium by measurements at two wavelengths.

EXPERIMENTAL

Preparation of compounds

Compounds VII–XV were obtained by quaternisation of the corresponding free bases[6] by the following general method: a mixture of 0·02 mole of the 2-styrylquinoline with an equimolar amount of dimethyl sulphate in about 10 ml of nitrobenzene was heated for 2 hr on a steam bath. After cooling the solution the methosulphate precipitated. It was filtered, washed well with ether and recrystallised from methanol or ethanol.

1-Methyl-2-[2-(8-hydroxy-5-quinolyl)vinyl]-8-hydroxyquinolinium chloride (IV) was prepared by condensing 5-formyl-8-quinolinol[7] with *N*-methyl-8-hydroxy-quinaldinium methosulphate in propanol solution with piperidine as catalyst. After refluxing 0·01 molar amounts of these reagents for 2 hr the precipitated product was filtered, dried, dissolved in methanol and recrystallised as the purple chloride by the addition of hydrochloric acid. A 60% yield of a product that, after several recrystallisations from methanol containing hydrochloric acid, melted with decomposition at 250–55° was obtained (calculated for N in $C_{21}H_{17}ClN_2O_2$: 7·68; N found by analysis: 7·87).

Spectra

The spectra in the visual region for each of the compounds in several solvents were recorded with a Beckman DK-2 Spectrophotometer. For compound IV spectra as a function of pH in aqueous solutions from pH 1 to 13 were recorded for over 20 different pH values and apparent ionisation constants calculated.[8] In acid solutions the principal absorption maximum was at 405, in neutral solutions at 425 and in base at 505 mμ.

Chelate formation

Spot tests with the bivalent ions of Cu, Ca, Mg, Fe, Co, Ni, Zn, Cd and Mn and the tervalent ions of Al, Cr and Fe with an aqueous solution of IV gave a precipitate at pH 2 only with copper. A sample of this chelate was prepared, dried and analysed for copper by ignition of weighed samples to the oxide [calculated for Cu in $Cu(C_{21}H_{16}N_2O_2)_2$: 8·9; Cu found by analysis (average of 3 trials): 9·0].

At pH 4 most of the bivalent ions gave orange or red precipitates except for the violet-red product with zinc. A dried sample of this compound was analysed for zinc by ignition to the oxide [calculated for Zn in $Zn(C_{21}H_{16}N_2O_2)_2$: 9·1; Zn found by analysis: 9·0].

Tests at pH 6 gave only minor changes from the results at pH 4. A number of the chelates were extracted into benzyl alcohol to test for solvatochromism but little effect on the colours could be detected.

In ammoniacal dioxan, pyridine or methanol, IV was green, but it gave red, orange or violet solutions with those bivalent ions that could be retained in solution at this basicity. Spectra of the reagent in methanol and in ammoniacal methanol and of the magnesium chelate in ammoniacal methanol were determined (see Fig. 1). A Beer's law test (after correction for reagent absorption) for several magnesium ion concentrations in the 10^{-6} to 10^{-5}-M region was successful.

Acknowledgment—This work was partly supported by the National Science Foundation (NSF–G 18559) and by the National Institutes of Health (CY-5607).

Zusammenfassung—1-Methyl-2-[2-(8-hydroxy-5-chinolyl)vinyl]-8-hydroxychinoliniumchlorid als Beispiel eines chelatbildenden Agens, das je nach Polarität des Lösungsmittels die Farbe ändert, wurde dargestellt. Es fällt in saurer Lösung nur Cu^{2+} und bildet mit Zn in neutraler Lösung ein deutlich gefärbtes Produkt. In ammoniakalischem Methanol gibt es mit Mg und einigen anderen Ionen eine rote Lösung.

Eine Anzahl verwandter solvatochromer Verbindungen wurde ebenfalls dargestellt.

Résumé—Le chlorure de méthyl-1-(hydroxy-8-quinolyl-5)2′-vinyl-2-hydroxy-8-quinoléine a été préparé comme exemple d'agent de chélation des métaux qui changent de couleur avec la polarité du solvant. Comme agent chélatant, il est assez sélectif, précipitant seulement l'ion cuivrique en solution acide et formant un produit coloré caractéristique avec le zinc en solution neutre. Dans le méthanol ammoniacal, il fournit une solution rouge avec le magnesium et de nombreux autres ions. Un certain nombre de composés apparentés ont pu également être préparés.

REFERENCES

[1] S. Hünig and O. Rosenthal, *Ann.*, 1955, **592,** 161.
[2] L. G. S. Brooker, G. H. Keyes and D. W. Heseltine, *J. Amer. Chem. Soc.*, 1951, **73,** 5350.
[3] J. P. Phillips and R. W. Keown, *ibid.*, 1951, **73,** 5483.
[4] J. P. Saxena, W. H. Stafford and W. L. Stafford, *J. Chem. Soc.*, 1959, 1579.
[5] J. T. Leach and J. P. Phillips, *J. Org. Chem.*, 1962, **27,** 3309.
[6] J. P. Phillips, R. Breese and E. M. Barrall, *ibid*, 1959, **24,** 1104.
[7] H. Zinner and H. Fiedler, *Arch. Pharm.*, 1958, **291/63,** 493.
[8] J. P. Phillips, J. F. Deye and J. T. Leach, *Analyt. Chim. Acta*, 1960, **23,** 131.

Talanta, 1963, Vol. 10, pp. 1093 to 1102. Pergamon Press Ltd. Printed in Northern Ireland

NON-DESTRUCTIVE ACTIVATION ANALYSIS OF ARSENIC AND ANTIMONY IN LEAD

F. ADAMS* and J. HOSTE
Institute for Analytical Chemistry, Ghent University, Belgium

(*Received* 13 *May* 1963. *Accepted* 31 *May* 1963)

Summary—A neutron-activation analysis has been devised for the non-destructive simultaneous determination of arsenic and antimony in lead. The ^{122}Sb and ^{76}As activities are computed by gamma counting at two discrete energies. The method has been tested with synthetic samples in the antimony and arsenic concentration range of 1 to 10^{-4}%. The reproducibility is generally better than 10%.

INTRODUCTION

NON-destructive gamma spectrometric analysis is rapidly growing in importance. In many cases the accuracy and precision are of the same order of magnitude as that obtainable with chemical separations.

In a previous paper[1] the determination of antimony in lead by radioactivation analysis was reported. The antimony content was computed from the height of the 0·566-MeV peak of ^{122}Sb, using the 0·411-MeV peak of ^{198}Au as an internal reference standard. The presence of arsenic, however, causes a serious interference because of the photopeak of ^{76}As at an energy of 0·55-MeV, which cannot be resolved from the 0·566-MeV peak of ^{122}Sb. Because arsenic is a common contaminant of lead, it appeared desirable to develop a gamma spectrometric activation analysis for the two elements without involving chemical separations.

The activation analysis of arsenic and antimony in various materials has been previously studied by numerous authors, but they all resorted to a chemical separation when arsenic and antimony were present simultaneously.

NUCLEAR DATA

Neutron irradiation of antimony and arsenic gives rise to a number of radioactive isotopes (see Table I). It appears that for relatively short irradiations the obtained activities will arise mainly from the ^{76}As and ^{122}Sb species. The activity from the matrix is negligible because the cross-sections of the lead isotopes are very small (^{208}Pb: 0·026 barn; ^{206}Pb: 0·0006 barn).

A number of other elements can, however, interfere with the antimony and arsenic determination. The nuclear properties of tin, copper, bismuth, iron, zinc and silver, which are all possible trace elements in lead are given in Table II. A number of isotopes formed from these elements have half-lives considerably smaller than ^{76}As and ^{122}Sb and their interference can be minimised by choosing an optimum cooling time. Moreover, if the irradiation time is short the activities from the longer lived species ^{65}Zn and ^{110m}Ag will also be negligible. The interference from ^{65}Zn, for example, is lower than 1% for a zinc:antimony ratio of 10:1.

---

* Research Fellow I.I.K.W.

TABLE I.—NUCLEAR PROPERTIES OF ANTIMONY AND ARSENIC ISOTOPES

Natural isotope	Occurrence, %	Activation cross-section, *barn*	Isotope formed	Half-life	Radiation and energy (*MeV*)
^{121}Sb	57·25	3·70	^{122}Sb	2·8 day	β^-: 0·740; 0·900; 1·40; 1·97 γ: 0·566; 0·686; 1·137; 1·256
		1·3	^{122m}Sb	3·5 min	I.T. e$^-$0·061; 0·075
^{123}Sb	42·75	1·1	^{124}Sb	61 day	β^-: 0·240; 0·610; 0·966; 1·60; 2·32 γ: 0·603; 0·641; 0·716; 1·68; 2·09
		0·013	$^{124m}{}_1$Sb	1·3 min	I.T. e$^-$(γ)0·012
		0·013	$^{124m}{}_2$Sb	21 min	I.T. e$^-$(γ)0·018
^{75}As	100	4·2	^{76}As	26·7 hr	β^-: 2·96; 2·41; 1·76; 0·880; 0·350 γ: 0·558; 0·660; 1·22; 1·76; 2·085

TABLE II.—INTERFERING ACTIVITIES

Natural isotope	Occurrence, %	Activation cross-section, *barn*	Isotope formed	Half-life	Gamma energy, *MeV*
^{63}Cu	69·1	3·0	^{64}Cu	12·8 hr	0·511; 1·34
^{65}Cu	30·9	0·65	^{66}Cu	5·1 min	0·83; 1·04
^{64}Zn	48·9	0·25	^{65}Zn	245 day	0·511; 1·11
^{68}Zn	18·6	0·02	^{69m}Zn	13·8 hr	0·438
^{70}Zn	0·62	0·048	^{71m}Zn	3 hr	0·38; 0·49; 0·61
^{107}Ag	51·53	23	^{108}Ag	2·3 min	0·430; 0·511; 0·600; 0·630
^{109}Ag	48·65	54	^{110}Ag	24·2 sec	0·660; 0·720 0·810; 0·880; 0·940
		1·4	^{110m}Ag	270 day	0·656; 0·681; 0·706; 0·764; 0·884; 0·940; 1·381; 1·481
^{112}Sn	0·95	0·013	^{113}Sn	112 day	0·260; 0·392
^{116}Sn	14·24	0·001	^{117m}Sn	14 day	0·161; 0·320
^{122}Sn	4·71	0·007	^{123}Sn	40 min	0·153
^{124}Sn	5·98	0·01	^{125m}Sn	9·5 min	0·326
^{23}Na	100	0·54	^{24}Na	14·8 hr	1·38; 2·76

NEUTRON SELF-SHIELDING EFFECTS

Although the cross-sections of the antimony isotopes are rather low, large self-shielding effects occur, caused by large resonance peaks at neutron energies in the epithermal region,[2] as shown by Plumb and Lewis[3] and Adams and Hoste.[1] The latter workers found that the antimony standards should be diluted with at least 50 parts of graphite or 100 parts of lead before a constant specific activity is reached.

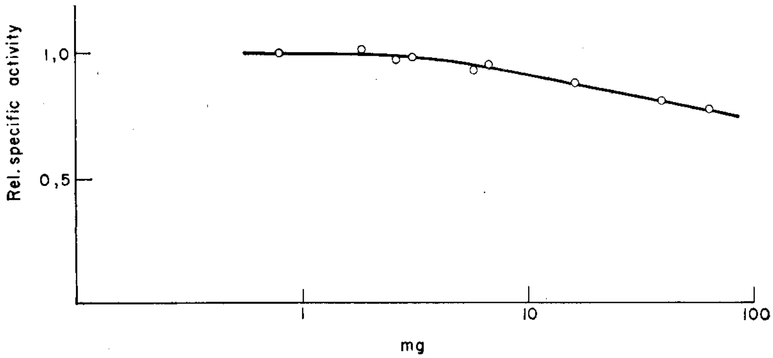


FIG. 1.—Neutron self-shielding in arsenic.

In arsenic, self-shielding is of minor importance. In Fig. 1 the specific activity of elementary arsenic is given as a function of sample size. It appears that for sample weights lower than 2 mg, self-shielding effects are negligible (particle size lower than 115 mesh).

Although an analysis of the composite decay curve of ^{76}As and ^{122}Sb can be analysed for the respective activities, a gamma spectrometric analysis was chosen because the half-life of ^{122}Sb is quite long and measurement during at least 14 days will be required.

From the decay schemes of ^{76}As and ^{122}Sb it appears that it will not be possible to resolve the predominant gammas at 0·55 and 0·56 MeV, respectively, as shown in

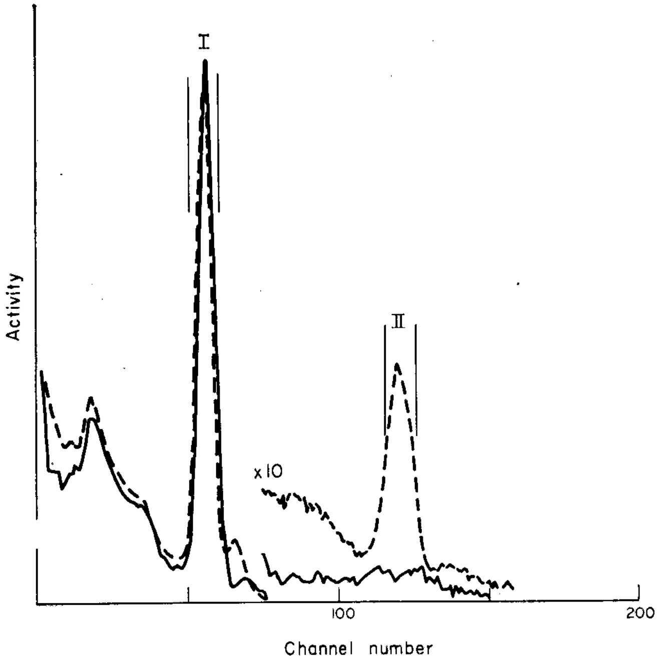


FIG. 2.—Gamma spectrum of ^{122}Sb and ^{76}As:
- - - - ^{76}As,
——— ^{122}Sb.

Fig. 2, giving the spectra after the irradiation of 1 μg of arsenic and 1·4 μg of antimony for 24 hr at 10^{12} neutrons. cm^{-2}. sec^{-1} and measurement after a decay of 12 hr. From Fig. 2 it is also apparent that the relative activities in the energy band of 0·51–0·61 MeV is 37 % for antimony and 30 % for arsenic. In the higher energy region the smaller 1·21-MeV peak of ^{76}As cannot be measured independently from ^{122}Sb because this isotope has gamma rays at 1·14 and 1·26 MeV, the relative activity in the energy band of 1·16–1·26 being 0·24 % for ^{122}Sb.

GAMMA SPECTROMETRIC ANALYSIS

The simultaneous determination of the two elements is thus possible by measurement in these two energy regions and solving the obtained equations as previously demonstrated by Adams *et al.*[4] for the simultaneous determination of ^{51}Cr and ^{131}I and by Öbrink and Ulfendahl[5] for mixtures of ^{24}Na and ^{42}K.

When the activity is measured at two different energy levels, I and II in Fig. 2, where both ^{122}Sb and ^{76}As contribute, the activities of the isotopes may be computed from equations (1) and (2):

$$(A_{Sb})_1 = \frac{(A_{Sb+As})_1\, K_{As} - (A_{Sb+})_{2As}}{K_{As} - K_{Sb}} \tag{1}$$

$$(A_{As})_1 = \frac{(A_{Sb+As})_2 - (A_{Sb+As})_1\, K_{Sb}}{K_{As} - K_{Sb}} \tag{2}$$

where

$$K_{Sb} = \frac{(A_{Sb})_2}{(A_{Sb})_1} \quad \text{and} \quad K_{As} = \frac{(A_{As})_2}{(A_{As})_1}$$

The constants K_{Sb} and K_{As} can easily be determined by irradiating suitable antimony and arsenic standards and counting under standard conditions. Both channels must be chosen so as to obtain absolute values of K_{Sb} and K_{As} as different as possible. It also advantageous to select rather wide channels giving high count rates and minimising minor errors from drift of the pulse height analyser. The band widths described above are perfectly suited for the purpose.

Remarks

1. Equations (1) and (2) must be corrected for the decay during the measurements of the second channel when a single channel analyser is used:

$$(A_{Sb})_1 = \frac{(A_{Sb+As})_1\, K_{As}\, e^{-\frac{0.693t}{T_{As}76}} - (A_{Sb+As})_2}{K_{As}\, e^{-\frac{0.693t}{T_{As}76}} - K_{Sb}\, e^{-\frac{0.693t}{T_{Sb}122}}} \tag{3}$$

$$(A_{As})_1 = \frac{(A_{Sb+As})_2 - (A_{As+Sb})_1\, K_{Sb}\, e^{-\frac{0.693t}{T_{Sb}122}}}{K_{As}\, e^{-\frac{0.693t}{T_{As}76}} - K_{Sb}\, e^{-\frac{0.693t}{T_{Sb}122}}} \tag{4}$$

2. In equations (1), (2), (3) and (4) the activity of the ^{124} Sb nuclide simultaneously produced with ^{122}Sb is neglected. For short irradiations the integral activity ratio of ^{122}Sb:^{124}Sb is 74, as can be computed from the nuclear data. Because the activity of ^{124}Sb is not the same at both energy levels, K_{Sb} will increase as a function of decay time whereas K_{As} remains constant. Experimental results are given in Fig. 3.

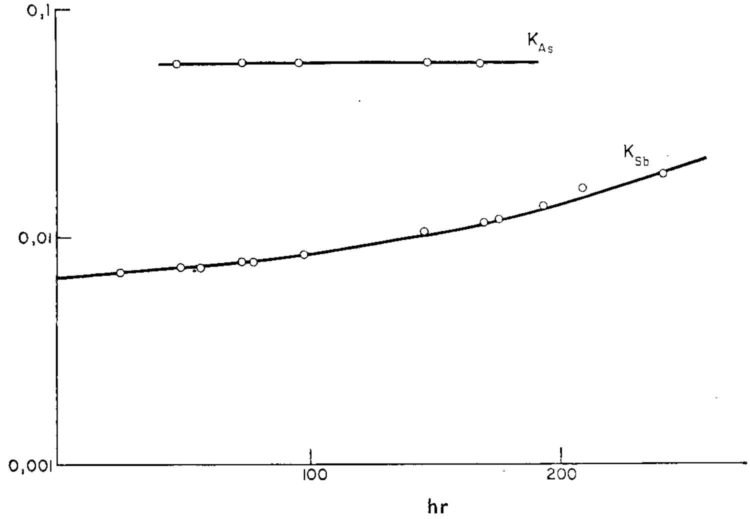


FIG. 3.—K_{As} and K_{Sb} as a function of decay time.

EXPERIMENTAL

Apparatus

Hilger and Watts crystal-photomultiplier Assembly P-1060*:* 3″ × 3″ *crystal and* EMI 9531A *photomultiplier.*

Nuclear Enterprises linear amplifier 5202 *and associated pulse-height analyser* 5102
Tracerlab precision high-voltage supply
Bell Telephone Mfg Cy Scaler Chronoscope NUK, 137 AI
Intertechnique 400 *channel analyser* SA-40

It is obvious that analyses using the proposed technique require a highly stable instrumentation. Using the above instruments in a temperature controlled room (±0·2°) the shift over a period of several weeks appeared to be $<1\%$. Shift as a function of count rate was not detected even for integral activities up to 5×10^5 cpm.

In subsequent analyses the 400-channel pulse-height analyser was used coupled to the same detector and high-voltage supply. The shift was within 1 channel over several weeks.

Determination of K_{Sb} *and* K_{As}

Although the efficiencies in channel II are rather low, namely 0·24 % of the integral activity for ^{122}Sb and 1·73 % for ^{76}As, the K_{As} and K_{Sb} values show a good reproducibility as seen from Table III, which gives the K-values obtained at an integral count rate of $1{\cdot}5 \times 10^5$ cpm, measured during 10 min in channel II, whereas 2 min in channel I proved to be adequate.

K_{As} and K_{Sb} are a function of the distance of the radioactive source to the detector. For source-detector distances larger than 3 cm, both ratios become constant.

Up to a total count rate of 2×10^5 cpm, K_{As} and K_{Sb} measured as a function of the total ^{122}Sb and ^{76}As activity remain constant. Above this activity level a systematic error occurs, caused by coincidence losses in the lower energy band when using the single channel analyser as can be seen from Fig. 4. With the SA-40 analyser equipped with a life timer, K_{Sb} and K_{As} remain constant up to a total count rate of 4×10^5 cpm.

Procedure

Synthetic samples were prepared by mixing antimony powder (200 mesh) and arsenic powder (100 mesh) with lead powder (below 100 mesh to dust) in a Spec-Mix, and pressing the mixture into pellets of 0·5″ diameter at a pressure of 1×10^5 lb. inch^2. Homogeneous mixtures with arsenic and antimony concentration below 0·01 % could not, however, be preparated. Concentrations between 0·01 and 0·0001 % were prepared by evaporation of a standardised solution of both elements in pure lead powder. Mixtures of Sb_2O_3 and As_2O_3 with graphite powder were used as standards. These were also used for the determination of K_{Sb} and K_{As}.

TABLE III. REPRODUCIBILITY OF K_{As} AND K_{Sb}

K_{As}	K_{Sb}
0·05700	0·006709
0·05779	0·006575
0·05787	0·006721
0·05760	0·006793
0·05788	0·006735
0·05803	0·006745
0·05751	0·006812
0·05767 ± 0·00035 s = 0·6 %	0·006727 ± 0·000075 s = 1 %

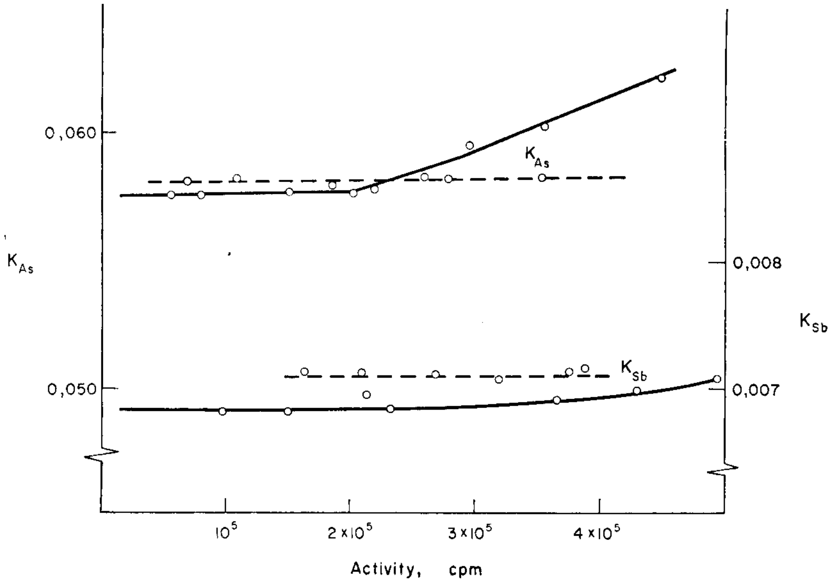


FIG. 4.—K_{As} and K_{Sb} as a function of activity:
- - - - Intertechnique SA-40,
——— Single Channel Analyser.

Samples and standards were wrapped in aluminium foil and irradiated in the core of BR-1 at a thermal neutron flux of 8 × 10^{11} neutrons. cm^{-2}. sec^{-1}. The irradiation time varied between 20 min and 24 hr according to the antimony and arsenic concentrations. Measurements were performed after the decay of ^{64}Cu, *i.e.*, 3 days after the end of the irradiation. In the absence of copper, measurements were begun after *ca.* 6 hr.

The method was tested on standard samples with a concentration ratio of antimony:arsenic of from 10:1 to 1:10.

RESULTS

The results of a number of analyses for concentrations of antimony and arsenic between 1 and 0·01 % are summarised in Table IV. The analyses in Table V were made with the SA-40 400-channel analyser and extend down to the ppm concentration range. As shown, the standard deviations are generally better than 10 %.

TABLE IV.—ACTIVATION ANALYSIS OF LEAD ALLOYS (SINGLE CHANNEL ANALYSER)

Sb and As taken, %	Sample weight, *g*	Sb found, %	As found, %	Sb and As taken, %	Sample weight, *g*	Sb found, %	As found, %
1·083 As	0·56728	0·958	1·084	0·0730 As	0·40404	0·773	0·0752
0·956 Sb	0·56306	0·932	1·100	0·769 Sb	0·45357	0·756	0·0734
	0·58476	0·927	1·047		0·50342	0·800	0·0693
		0·939	1·077			0·777	0·0726
		s = 1·8 %	s = 2·5 %			s = 3 %	s = 10 %
0·6065 As	0·73323	0·569	0·616				
0·595 Sb	0·68851	0·566	0·624	0·566 As	0·32773	0·0381	0·533
	0·75398	0·564	0·613	0·0324 Sb	0·34537	0·0335	0·537
	0·70538	0·581	0·601		0·34832	0·0245	0·639
		0·570	0·613			0·0320	0·570
		s = 1·3 %	s = 1·5 %			s = 5 %	s = 10 %
0·617 As	0·34742	0·313	0·642	0·309 As	0·34794	0·0445	0·314
0·313 Sb	0·30700	0·321	0·636	0·0334 Sb	0·39784	0·0450	0·311
	0·38778	0·304	0·561		0·30497	0·0424	0·295
		0·313	0·613			0·0440	0·307
		s = 2·7 %	s = 7 %			s = 5 %	s = 3 %
0·134 As	0·40621	0·101	0·132	0·172 Sb	0·31116	0·184	0·275
0·1006 Sb	0·42475	0·104	0·126	0·293 As	0·33745	0·182	0·293
	0·39255	0·096	0·132	0·193 Cu	0·29452	0·188	0·273
		0·100	0·130			0·185	0·280
		s = 4 %	s = 3·5 %			s = 1·7 %	s = 4 %
0·1020 As	0·45509	0·533	0·0915	0·594 Sb	0·31077	0·559	0·491
0·520 Sb	0·45806	0·460	0·109	0·473 As	0·37119	0·564	0·502
	0·46917	0·530	0·100	0·450 Cu	0·30090	0·579	0·517
		0·508	0·100			0·567	0·503
		s = 8 %	s = 8·7 %			s = 2 %	s = 2·3 %

Using this technique a complete analysis of arsenic and antimony can be performed in 0·5 hr, excluding irradiation time.

A series of 4 commercial lead alloys was analysed using the method described. Only one of the lead samples could be analysed without chemical separation of copper. In the other samples the copper content was 10–50 times the antimony concentration, and a separation of copper prior to the antimony and arsenic measurements was therefore necessary. For this purpose a liquid-liquid extraction procedure with 2,2′-biquinolyl in isoamyl alcohol was used.[6] Two successive extractions gave a decontamination of 99·8 % in the presence of g-amounts of lead, whereas no losses of antimony and arsenic could be observed.

TABLE V.—ACTIVATION ANALYSIS OF LEAD ALLOYS (400 CHANNEL ANALYSER)

Sb and As taken, %	Sb found, %	As found, %
3·35 × 10^{-3} Sb	3·20 × 10^{-3}	3·54 × 10^{-3}
3·15 × 10^{-3} As	3·44 × 10^{-3}	3·96 × 10^{-3}
	3·54 × 10^{-3}	2·84 × 10^{-3}
	3·46 × 10^{-3}	4·02 × 10^{-3}
	3·54 × 10^{-3}	4·30 × 10^{-3}
	3·48 × 10^{-3}	3·73 × 10^{-3}
	s = 4 %	s = 7·7 %
9·24 × 10^{-4} Sb	9·2 × 10^{-4}	8·6 × 10^{-4}
8·4 × 10^{-4} As	9·4 × 10^{-4}	8·4 × 10^{-4}
	9·0 × 10^{-4}	9·4 × 10^{-4}
	9·6 × 10^{-4}	7·8 × 10^{-4}
	11·8 × 10^{-4}	7·6 × 10^{-4}
	9·6 × 10^{-4}	8·4 × 10^{-4}
	s = 11 %	s = 8·5 %
2·99 × 10^{-3} Sb	2·70 × 10^{-3}	6·2 × 10^{-4}
4·86 × 10^{-4} As	3·06 × 10^{-3}	4·2 × 10^{-4}
2 × 10^{-3} Ag	2·92 × 10^{-3}	5·8 × 10^{-4}
	3·06 × 10^{-3}	4·6 × 10^{-4}
	3·10 × 10^{-3}	4·0 × 10^{-4}
	2·74 × 10^{-3}	5·4 × 10^{-4}
	2·94 × 10^{-3}	5·0 × 10^{-4}
	s = 6 %	s = 17 %
6·64 × 10^{-3} Sb	6·32 × 10^{-3}	3·40 × 10^{-3}
3·14 × 10^{-3} As	6·92 × 10^{-3}	3·28 × 10^{-3}
2 × 10^{-3} Ag	6·86 × 10^{-3}	3·32 × 10^{-3}
	6·72 × 10^{-3}	3·30 × 10^{-3}
	6·68 × 10^{-3}	3·46 × 10^{-3}
	6·70 × 10^{-3}	3·36 × 10^{-3}
	s = 4 %	s = 2 %
3·68 × 10^{-4} Sb	3·8 × 10^{-4}	1·76 × 10^{-3}
1·65 × 10^{-3} As	4·2 × 10^{-4}	1·72 × 10^{-3}
2 × 10^{-3} Ag	4·0 × 10^{-4}	1·62 × 10^{-3}
	4·6 × 10^{-4}	1·64 × 10^{-3}
	4·2 × 10^{-4}	1·68 × 10^{-3}
	s = 7 %	s = 4 %

Procedure

The irradiated lead samples (*ca.* 1 g) were dissolved in 40 ml of 1*M* nitric acid and 20 μg of copper-carrier added. The solution was neutralised with 30% sodium hydroxide to pH 4·5, then 200–300 mg of hydroxylamine hydrochloride added to reduce the copper to the univalent state. Copper was extracted twice with 10 ml of a 0·02% solution of 2,2′-biquinolyl in isoamyl alcohol. The arsenic and antimony activities were measured with a SA-40 multichannel analyser. Because the concentrations of the two elements were rather low (0·05 ppm of antimony in two of the samples) measurements of 1–2 hr were used. Two of the samples showed a negligible arsenic concentration.

The gamma spectrum showed a considerable activity from ^{203}Pb. This isotope is formed by a (n, 2n) reaction of ^{204}Pb. Because of the low energy of the gamma radiation (max. 420 KeV) ^{203}Pb does not interfere with the antimony and arsenic determination.

TABLE VI.—DETERMINATION OF ANTIMONY AND ARSENIC IN COMMERCIAL LEAD SAMPLES

Commercial lead sample	Weight of sample, *g*	As found, *ppm*	Sb found, *ppm*	Sb by sum-coincidence method, *ppm*
1	0·8265	0·0033	0·063	0·074 ± 0·013
	1·2381	0·0054	0·053	
	1·2262	0·0009	0·060	
	1·1202	0·0030	0·058	
	1·0496	0·0036	0·061	
	1·0844	0·0009	0·073	
	1·0952	0·0010	0·054	
	1·0451	0·0007	0·063	
	0·9431	0·0018	0·052	
	1·0920	0·0024	0·0049	
		Av. 0·0023 ± 0·0016	0·056 ± 0·009	
2	0·7123	0·180	1·30	1·34 ± 0·1
	1·2109	0·070	1·13	
	1·1441	0·140	1·08	
	0·8054	0·090	1·32	
	0·6162	0·290	1·38	
	0·5588	0·250	1·33	
	0·4352	0·170	1·45	
	0·6747	0·240	1·34	
		Av. 0·180 ± 0·08	1·29 ± 0·11	
3	0·9562	< 0·002	0·0143	0·015 ± 0·005
	0·8602		0·0185	
	0·7540		0·0123	
	0·8923		0·0113	
	0·9200		0·0133	
			Av. 0·014 ± 0·03	
4	1·203	< 0·001	0·016	0·014 ± 0·003
	1·227		0·011	
	0·947		0·014	
	1·117		0·020	
			Av. 0·015 ± 0·004	

Table VI gives the results of a number of analyses of arsenic and antimony in commercial lead samples. The antimony analyses were controlled with an independent gamma spectrometric technique, namely by sum-coincidence measurement of ^{124}Sb.[7] This method will be described separately in due course.

Acknowledgments—This investigation was carried out as part of the research programme sponsored by "Het Interuniversitair Instituut voor Kernwetenschappen". Thanks are due to Miss R. Aerts for technical assistance and to Mr. Steylemans and the "Studiecentrum voor Kernenergie" for performing the irradiations.

Zusammenfassung—Eine Neutronenaktivierungsanalyse für die gleichzeitige zerstörungsfreie Bestimmung von As und Sb in Pb wurde entwickelt. Die ^{122}Sb- und ^{76}As-Aktivitäten wurden aus Gamma-Zählungen bei zwei Energien berechnet. Die Methode wurde an künstlichen Proben mit Sb- und As-Konzentrationen zwischen 1 und 10^{-4}% getestet. Die Reproduzierbarkeit war im allgemeinen besser als 10%.

Résumé—Une analyse par activation de neutrons a été imaginée pour le dosage simultané et récupératif de l'arsenic et de l'antimoine dans des échantillons de plomb. Les activités de Sb^{122} et As^{76} sont calculées par comptage gamma à deux énergies séparées. La méthode a été testée au moyen d'échantillons synthétiques contenant de l'antimoine et de l'arsenic de concentration de l'ordre de 1 à 10^{-4}%. La reproductibilité est généralement supérieure à 10%.

REFERENCES

[1] F. Adams and J. Hoste, *Talanta*, 1962, **9**, 827.
[2] D. J. Hughes and J. A. Harvey, *Neutron Cross-sections*. McGraw-Hill, 1955.
[3] R. C. Plumb and J. E. Lewis, *Nucleonics*, 1955, **13**, 45.
[4] R. Adams, J. D. Woodward, M. G. Crane and J. E. Holloway, *J. Appl. Rad. Isotopes*, 1958, **3**, 156.
[5] K. J. Öbrink and M. R. Ulfendahl, *ibid.*, 1959, **5**, 99.
[6] J. Hoste, *Analyt. Chim. Acta*, 1950, **4**, 23.
[7] A. M. Hoogenboom, *Nuclear Instruments*, 1958, **3**, 57.

Talanta, 1963, Vol. 10, pp. 1103 to 1105. Pergamon Press Ltd. Printed in Northern Ireland

PRELIMINARY COMMUNICATION

Systematic titration errors in titrimetric analysis

(*Received* 20 *May* 1963. *Accepted* 22 *May* 1963)

In titrimetric analysis a certain amount of titrant (x mequiv) is added to a solution containing an amount of material to be determined (a mequiv); a is therefore a constant and x is variable. The *equivalence point* of the titration is reached when the amount of titrant added is exactly equivalent to the amount of material to be determined, *i.e.*, when $x = a$. In general, the indicator-system used will give a signal to indicate that the titration is finished when $x \neq a$. This point is called the *end-point* of the titration.

By the term *systematic titration error*, also called titration error[1] or chemical error,[2] is meant the error caused by the fact that the equivalence point and end-point do not coincide because of errors inherent in the titration system. Therefore, when a titration is finished ($x \neq a$), a systematic titration error is introduced

$$\Delta = (x - a) \text{ mequiv} \tag{1}$$

giving the number of mequiv that has been added in excess. The purpose of the present study is to express Δ as a function of the characteristics of the titration system and to calculate its value for different values of these characteristics.

In this preliminary note a short survey is given of the equations derived for Δ for precipitation, complex formation and redox titrations with visual end-point detection and an indication of the way in which further evaluation may be carried out. Neutralisation titrations have not been considered because some information about them has already appeared in the literature; a complete treatment of these titrations will be given in the subsequent detailed publication.

Precipitation titrations

Consider the precipitation titration

$$\alpha A^{p+} + \beta B^{q-} \rightleftharpoons A_\alpha B_\beta \tag{2}$$

for which the solubility product is

$$L_{A_\alpha B_\beta} = [A^{p+}]^\alpha \cdot [B^{q-}]^\beta \tag{3}$$

When a choice can be made between an indicator I^+ reacting with B^{q-} according to

$$I^+ + B^{q-} \rightleftharpoons IB^{(q-1)-} \tag{4}$$

and an indicator J^- reacting with A^{p+} according to

$$J^- + A^{p+} \rightleftharpoons JA^{(p-1)+} \tag{5}$$

it is possible to derive a generally and exactly valid equation for the systematic titration error, *viz.*,

$$\Delta = \pm v\{q(B + IB) - p(A + JA)\} \tag{6}$$

where v is the volume (ml) at the end-point of the titration. The plus sign in equation (6) is valid for a titration of A with B and the minus sign for the opposite case. It is self-evident that in all calculations, whether theoretical or practical, either IB or JA cancels.

In equation (6) A, B, IB and JA are expressed in moles/l.; if the indicator-compound IB or JA is insoluble, the term in question gives the detection limit in moles/l. The same notation has been used for the equations derived below; square brackets, denouncing concentrations, have been omitted when no mistake is possible.

Elaboration of equation (6) is carried out by substituting equation (3) and the data known about the indicator reaction. It can be shown that in many cases the terms IB or JA are more significant than A and/or B, which means that the treatment normally given is wholly unsatisfactory.

Complex formation titrations

Consider the complex formation titration

$$\alpha A^{p+} + \beta B \rightleftharpoons A_\alpha B_\beta \tag{7}$$

for which the dissociation constant of the complex formed is

$$K = \frac{[A^{p+}]^\alpha \cdot [B]^\beta}{[A_\alpha B_\beta]} \tag{8}$$

When the complex compounds directly preceding and following $A_\alpha B_\beta$ are given by $A_\alpha B_{\beta-1}$ and $A_\alpha B_{\beta+1}$, respectively, an approximately valid, but very reliable equation for the systematic titration error is given by

$$\Delta = \pm v \frac{p}{\beta} (\alpha B - \beta A + \alpha A_\alpha B_{\beta+1} - \alpha A_\alpha B_{\beta-1}) \tag{9}$$

the plus sign being used for a titration of A with B and the minus sign for the opposite case.

The right-hand side of equation (9) is multiplied by p/β because with complex formation titrations the equivalent weight is defined as the weight of the substance which contains or reacts with $1/p$ g ion of a p-valent cation A^{p+}. The Δ-formula is elaborated with the help of the complex formation constants and the data concerning the indicator reaction of either A or B. When a compound like IB or JA is formed in the indicator reaction [see equations (4) and (5)], this can be worked into equation (9) by introducing a term $p/\beta.(\alpha.IB)$ or $-p/\beta\ .\ (\beta.JA)$, respectively.

Redox titrations

Let the two half-reactions involved in a redox titration be

$$\alpha ox_1 + p\,.\,e \rightleftharpoons \beta red_1 \tag{10a}$$

$$\gamma red_2 \rightleftharpoons p\,.\,e + \delta ox_2 \tag{10b}$$

$$\alpha ox_1 + \gamma red_2 \rightleftharpoons \beta red_1 + \delta ox_2 \tag{10}$$

As an exactly valid equation for the systematic titration error one finds

$$\Delta = \pm v\,.\,p(\frac{1}{\alpha} ox_1 - \frac{1}{\gamma} red_2) \tag{11}$$

where the plus sign must be used for a titration of red_2 with ox_1 and the minus sign for the reverse titration.

In this case the Δ-equation can be elaborated using the Nernst equation for both half-reactions (10a) and (10b); apart from Δ, other criteria, *e.g.*, the potential at the equivalence point and the quantitativeness of the reaction, that can be readily calculated are used for the determination of systematic errors.[3]

Chemical Laboratory, Free University
Amsterdam, The Netherlands

U. A. TH. BRINKMAN

Summary—A brief summary is given of the formulae that can be derived for the systematic titration error for different types of titration using visual end-point detection. The methods by which these formulae can be elaborated to make them suitable for calculations are indicated. Mention is made of the introduction of the indicator-compound into the formula used for precipitation titrations.

Zusammenfassung—Es wird ein überblick gegeben über die Formeln für die systematischen Titrationsfehler für verschiedenen Typen von Titrationen mit visueller Endpunktsbestimmung. Die Methoden, die benutzt werden für weitere Entwicklung dieser Formeln, werden angegeben. Speziell genannt wird das in Betracht ziehen der Indikatorverbindung in Fällungstitrationen.

Résumé—On étude les formules pouvant être dérivées des erreurs systématiques de dosage apparaissant dans divers types de dosages utilisant une détermination visuelle du point équivalent. Les méthodes pour lesquelles ces formules ont pu être élaborées et rendues applicables au calcul sont indiquées. L'introduction d'un composé indicateur dans la formule utilisée pour les dosages par précipitation sont examinés.

REFERENCES

[1] I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis.* Interscience, New York, 2nd Ed., 1942 Vol. 1, p. 143.
[2] E. Bishop, *Analyt. Chim. Acta,* 1960, **22,** 205.
[3] U. A. Th. Brinkman, *Chem. Weekblad,* 1963, **59,** 9.

Talanta, 1963, Vol. 10, pp. 1107 to 1114. Pergamon Press Ltd. Printed in Northern Ireland

SHORT COMMUNICATIONS

The dissolution of alunite employing hot concentrated perchloric acid: Determination of silica and aluminium

(*Received* 4 *May* 1963. *Accepted* 20 *May* 1963)

INTRODUCTION

ALUNITE (hydrated potassium aluminium sulphate, $K_2Al_6(OH)_{12}(SO_4)_4$) is an important naturally occurring source of aluminium with potash salts as valuable associated ingredients. Large deposits of this mineral are found in Nevada. Production of aluminium using alunite as a substitute for bauxite has been proposed. Potash salts would thus be a natural by-product.

As alunite is ordinarily encountered, the potassium may be replaced in part by sodium, aluminium by iron, and 3–5% of silica may be present. The alumina content approximates to 35%, potassium oxide to 10–11%, and sulphuric acid anhydride to 35%, together with 12·5% of water.

Because of the high aluminium content, alunite is not soluble in mineral acids, such as hydrochloric acid, and dissolution would ordinarily follow a sodium carbonate fusion. The determination of potassium would ordinarily follow the J. Lawrence Smith procedure.

Finely ground alunite is soluble, however, in hot 72·5% perchloric acid. The determination of silica and the R_2O_3 metals present can thus be carried out without recourse to a sodium carbonate fusion.

ANALYSIS OF ALUNITE

The composition of a representative sample of alunite is given in Table I.

Examination of the results in Table I shows that there is good agreement between the macro and micro techniques. The sample may thus be used as a standard for reference in characterising effective dissolution using hot 72·5% perchloric acid.

DEMONSTRATION OF COMPLETE DISSOLUTION OF ALUNITE

Grind the sample for analysis in a mechanically driven agate mortar until it passes completely through a 200-mesh sieve. A large sample need not be prepared if the preliminary grinding has provided a large sample of sufficient fineness (80–100-mesh) to ensure uniformity.

Treat a 0·5-g sample of the 200-mesh material with 10 ml of 70–72% C.P. perchloric acid in a 100-ml beaker covered closely with a clock glass. Heat the contents of the beaker just to boiling, and maintain at the boiling point for 1 hr. The perchloric acid fumes in the beaker should reflux down the beaker walls from a point not less than 1 inch from the top of the beaker. Little acid is thus lost by volatilisation. A small stirring rod is kept in the beaker so that an occasional drop of cold, dilute acid dropping from the cover glass returns to the beaker down the stirring rod. Under these conditions the sample does not "bump" or spatter, but simmers gently to effect complete solution of everything but dehydrated silica, giving an acid concentration of 72·5%. The stated amount of perchloric acid is required to keep the aluminium salts in solution. If the solution tends to froth and throw out insoluble aluminium salts, too much perchloric acid has been volatilised, and a little more is added, or complete solution will not result. Under proper conditions additional acid will not be required. The aluminium sulphate is not dehydrated to the insoluble form by this process, and the progress of the dissolution of the sample is readily followed. For low silica contents (less than 5%) the solution at the end of 1 hr is practically clear and is slightly yellow in colour.

Cool the hot solution of the sample somewhat, and treat it at once with 50 ml of water, washing down the cover glass and the beaker walls. Heat the diluted solution just to boiling, and filter at once through a 5·5-cm C.S. and S. blue ribbon filter in a small funnel, receiving the filtrate in a 400-ml beaker. Wash the insoluble matter into the filter, and wash further 10–12 times with hot 1% hydrochloric acid solution. Complete the washing of the precipitated silica by a final wash with

TABLE I.—THE ANALYSIS OF ALUNITE EMPLOYING STANDARD METHODS OF PROCEDURE

	Sodium Carbonate Fusion							J. Lawrence Smith Method		
Percent	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	H_2O	Na_2O	K_2O	Total
	3·70	35·01	1.10	Absent	Absent	36·48	12·42	0·41	10·56	
	3·65	35·05	1·21	Absent	Absent	36·59	12·54	0·47	10·71	
	—	—	—			—	—	0·39	10·67	
	3·66	35·03	1·16	Absent	Absent	36·54	12·48	0·42	10·65	99·94
Average theory	None	36·92	None	None	None	38·66	13·05	None	11·37	100·00
Microtechnique*	3·65	35·21	1·16	Absent	Absent	36·17	12·63	0·36	10·51	99·69

* Sample weights for Na_2O and K_2O, 7·625 mg; Al_2O_3, Fe_2O_3 and SiO_2, 9·143 mg; SO_3, 4·011 mg; and H_2O, 5·206 mg.

1% ammonia solution. Dry and ignite the filter and precipitate in a weighed platinum crucible, heating in an electric muffle furnace for 30 min at 1000–1100°. Cool, and weigh for the determination of impure silica. If the true silica content is known, the impure silica should not weigh more than 2–3% in excess of the value for pure silica if dissolution of the sample has been complete. If the silica content is not known, treat the platinum crucible and ignited precipitate with 5 ml of water, 2 drops of 1:1 sulphuric acid and 5 ml of 40% C.P. hydrofluoric acid. Evaporate the solution thus obtained to dryness, fuming off the sulphuric acid, and heat the residue to 1000°. Weigh the impurities in the silica to obtain the corrected silica content.

Carry out the R_2O_3 determination, employing the filtrate from the silica determination, by the conventional method, details of which need not be given.

Results obtained in the determination of silica and R_2O_3 employing the reference sample of Table I were found to be: silica = 3·72%; R_2O_3 = 36·09%. These values are in close agreement with those found following the conventional sodium carbonate dissolution procedure. Perchloric acid dissolution is thus shown to be complete.

A study is proposed of the use of perchloric acid in sealed tubes in contact with insoluble products such as bauxite and other refractory materials, at temperatures in the 300–350° range.

Summary—Finely ground alunite (hydrated potassium aluminium sulphate) can be dissolved in hot 72·5% perchloric acid. Determinations of silica and R_2O_3 in samples of alunite so dissolved agree closely with similar determinations following a sodium carbonate fusion procedure.

Zusammenfassung—Fein gemahlener Alunit (hydratisiertes Kaliumaluminiumsulfat) läßt sich in heißer 72,5%iger Überchlorsäure lösen. Bestimmungen von Kieselsäure und R_2O_3 in so gelösten Alunitproben stimmen gut mit ähnlichen Bestimmungen nach Sodaschmelze überein.

Résumé—En poudre fine, l'alunite (sulfate d'aluminium et de potassium hydraté) se dissout à chaud dans l'acide perchlorique à 72,5%. Les dosages de silice et R_2O_3 dans les échantillons d'alunite ainsi dissous sont en bon accord avec les résultats obtenus par le procédé de fusion au carbonate de sodium.

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

G. Frederick Smith
W. H. Taylor

The determination of thiomalic acid

(*Received* 15 *May* 1963. *Accepted* 18 *June* 1963)

The iodometric method proposed by Busev and Chzhan Fan'[1] for the determination of thiomalic acid has been found unsatisfactory by the critical re-examination of Aravamudan and Rama Rao.[2] In connection with the latter study, a number of other oxidants (potassium iodate, potassium bromate, potassium periodate and chloramine-T) were examined for their potential applicability in determining thiomalic acid; none of these titrants, however, permitted the development of a reliable analytical method. Failure of these attempts has prompted us to publish a simple and rapid titrimetric method, used for the determination of thiomalic acid in our laboratories for some time.

This method is based on the titration of the —SH group of thiomalic acid with a solution of sodium *o*-hydroxymercuribenzoate in the presence of thiofluorescein as indicator. The principle of this method had been worked out earlier by Wroński[3] and applied to the determination of some aliphatic thiol-compounds, such as cysteine, thioglycolic acid, alkylmercaptanes, *etc.* When applied to the determination of thiomalic acid, this method gives reproducible results and with regard to simplicity and accuracy it compares favourably with the acrylonitrile procedure.[4]

EXPERIMENTAL

Reagents

Pure thiomalic acid (*Fluka*): Recrystallised twice from water (m.p. 153–154°).[5]

0·05*M solution of sodium o-hydroxymercuribenzoate* (*HMB*): Prepared from the corresponding anhydride (POCH Gliwice, Poland) and standardised by the method previously described.[3]

Thiofluorescein (Lachema, Brno, Czechoslovakia): Used in the form of a 0·02% solution in 0·1*M* aqueous ammonia and stabilised by the addition of 0·2% of disodium ethylenediaminetetra-acetate. The solution is stable for several days.

Procedure

In the preliminary experiments the standard thiomalic acid solution was used as described previously.[1,2] The results obtained, however, differed considerably even when this solution was stored in a well-stoppered flask. The recovery of thiomalic acid decreased to 99·1% and 96·8% after storage for 6 hr at 20° and 30°, respectively. Because of this, only solid samples were used in the later experiments.

The sample (100–200 mg) of thiomalic acid was dissolved in 100 ml of water, which was about 0·2% in sodium sulphite to minimise oxidation effects. On adding 10 ml of 1*M* aqueous ammonia and a few drops of indicator solution the thiomalic acid was titrated with 0·05*M* HMB solution. The end-point colour change from sky-blue to colourless was sharp.

RESULTS

Results of the individual determinations in comparison with the acrylonitrile method are listed in Table I. The tabulated values (columns 1, 2 and 4) are averages of six determinations. The scatter of results of individual titrations is represented by the limits of the confidence interval (w.t_w, columns 3 and 5), in which the "true" central value could be expected with a 95% probability.[6]

TABLE I

TMA[a] taken, *mg*	Acrylonitrile method		HMB method	
	TMA found, *mg*	Confidence interval, *mg*	TMA found, *mg*	Confidence interval, *mg*
100·00	99·92	±0·44	99·95	±0·07
200·00	199·78	±0·48	200·05	±0·16

[a] TMA = thiomalic acid

DISCUSSION

The determination of thiomalic acid has received considerable attention in view of its increasing biochemical importance. To-date, however, only the acrylonitrile method[4] has been of practical value for this purpose. The method described in the present paper is an improvement on the acrylonitrile procedure, both as regards accuracy and simplicity (the method involves the application of a precisely standardised titrant, so that blank determinations are unnecessary). Furthermore, non-volatile and less toxic reagents are employed. The method is applicable to both solid samples of thiomalic acid and its aqueous solutions.

Spolana N.C.
Research Centre of the Lachema Plant
Brno, Czechoslovakia

V. CHROMÝ
V. SVOBODA

Summary—A titrimetric method for the determination of thiomalic acid is described. It is based on the titration of the —SH group of thiomalic acid with a solution of sodium *o*-hydroxymercuribenzoate in the presence of thiofluorescein as indicator. The method is simple and rapid, and it allows the determination of thiomalic acid with an accuracy of ±0·1%.

Zusammenfassung—Es wurde eine Methode für die Bestimmung der Thioäpfelsäure beschrieben. Die Methode beruht auf der Titration der —SH Gruppe der Thioäpfelsäure mittels einer Lösung des Natrium o-Oxymerkuribenzoats in Anwesenheit des Thiofluoresceins als Indikator. Die Methode ist sehr einfach und schnell, und ermöglicht die Thioäpfelsäure-Bestimmung mit der Genauigkeit ±0·1%.

Résumé—Les auteurs présentent une méthode de dosage de l'acide thiomalique. La méthode consiste en titration du —SH groupe de cet acide avec la solution du sel sodique de l'acide o-hydroxymercuribenzoique en présence de thiofluoresceine comme indicateur. Cette méthode est simple et rapide et permet la détermination avec une précision de ±0·1%.

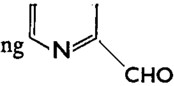
REFERENCES

[1] A. I. Busev and Chzhan Fan', *Talanta*, 1961, **8**, 470.
[2] G. Aravamudan and C. Rama Rao, *ibid*, 1963, **10**, 231.
[3] M. Wroński, *Chem. Analit.*, 1961, **6**, 859.
[4] S. I. Obtemperanskaja, A. P. Terentjev and M. M. Buzlanova, *Vestnik Moskov. Univ., Ser. mat., mech., astronom., fiz., chim.* 1957, No. 3, 145.
[5] A. Emr and F. Roubínek, *Chem. Listy*, 1956, **50**, 664.
[6] R. B. Dean and W. J. Dixon, *Analyt. Chem.*, 1951, **23**, 636.

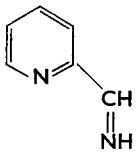
Spot tests for pyridine aldehydes, pyridine-2-aldehyde, phenylhydrazine, phenylhydrazones and osazones

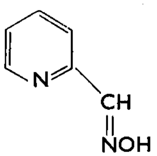
(*Received* 11 *June* 1963. *Accepted* 25 *July* 1963)

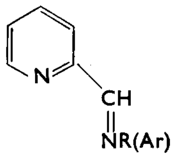
Summary—Spot tests for the detection of the three isomeric pyridine aldehydes and for pyridine-2-aldehyde are described. The tests are based on colour reactions with phenylhydrazine and with iron-, sulphate and hydroxylamine respectively. The chemical basis of te-colour reactions is discussed and the pertinent procedures are outlined. The colour reaction between pyridine-2-aldehyde and phenylhydrazine makes possible the detection of the latter as well as of phenylhydrazones and osazones after their acidic hydrolytic cleavage.

A DEEP red colour was observed to appear upon the addition of a solution of an iron^{II} salt to an aqueous solution of pyridine-2-aldehyde. Solutions of the isomeric 3- or 4-pyridine-aldehydes remain unaltered. This difference in behaviour indicates the participation in the colour reaction of the atomic grouping  , which exists only in pyridine-2-aldehyde. We assume that the N- and O-atoms in this group chelate with iron^{II} to form a red complex cation, $[Fe(Pyr.\ ald)_x]^{2+}$, where the value of x is either 2 or 3.

In accordance with this assumption it was observed that crystalline violet salts precipitated on the addition of a solution containing voluminous complex anions, such as $[CdI_4]^{2-}$, $[Hg(CNS)_4]^{2-}$, $[TlBr_4]^1$ and $[Co(NO_2)_6]^{3-}$, to the coloured solution. Because the colour reaction between pyridine-2-aldehyde and iron^{II} salts occurs only in relatively concentrated solutions, small amounts of the aldehyde cannot be detected. It is therefore possible to prepare a stable colourless solution containing both the aldehyde and iron^{II} sulphate. Such a solution shows remarkable behaviour towards ammonium salts, salts of hydroxylamine, salts of primary aliphatic and aromatic amines (and also their respective free bases), and amino acids. When a small amount of any of these undissolved compounds is placed on a spot plate or in a micro test tube and a drop of the aldehyde-iron^{II} solution is added a red, violet or blue colour appears immediately.* A plausible explanation for these colour reactions is that the basic pyridine aldehyde liberates ammonia, hydroxylamine or amines which in turn condense with the aldehyde, thereby forming the imide (I), aldoxime (II), or Schiff bases (III) of pyridine-2-aldehyde:

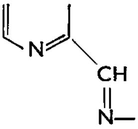

I


II

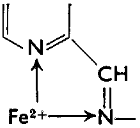

III

*According to observations made by S. Yariv (Jerusalem), it seems that a preliminary test for organic derivatives of ammonia can be based on this effect.

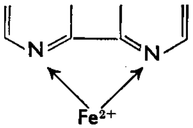
As the constitution of I–III shows, these compounds contain the atomic group IV which may chelate iron^{II} ions to complex cations with the schematic structure V. Similar chelate cations with bipyridyl and its derivatives (VI) are red in colour; their formation is the basis for well-known colour tests for iron^{II} ions:[1]



IV



V



VI

It is evident that if the condensations which lead to I–III are carried out in the presence of iron^{II} ions, then the coloured complex iron cations are formed directly from the components. It is possible that the presence of iron^{II} ion may facilitate the condensation through the formation of the complex salts*.

We have tried to develop a test for the detection of pyridine-2-aldehyde and its differentiation from its isomers, based on the formation of coloured complex iron^{II} cations of type V. It was found that the best conditions are obtained when a mixture of the aldehyde, iron^{II} salts and hydroxylamine chloride is made alkaline with pyridine. In this way the red product is formed almost immediately, even with micro quantities of the aldehyde.

When the behaviour of the pyridine-2-aldehyde-iron^{II} sulphate towards compounds containing —NH_2 groups was examined, it was found that salts of phenylhydrazine (as well as the base) produce an intense yellow colour. This is not caused by the formation of a complex iron^{II} cation, because the same colour appears in the absence of iron^{II} salts. Furthermore, all three isomeric pyridine aldehydes show the same behaviour. The colour reactions are therefore based on the formation of the phenylhydrazones of pyridine aldehydes:

$$C_6H_5NCHO + NH_2NHC_6H_5 \rightarrow C_6H_5NCH{=}N{-}NHC_6H_5 + H_2O.$$

This condensation takes place rapidly in aqueous solution and makes possible the spot test detection of pyridine aldehydes as well as of phenylhydrazine and its salts.

EXPERIMENTAL

Detection of pyridine aldehydes

Procedure: Mix 1 drop of the aqueous test solution and 1 drop of 0·1% solution of phenylhydrazine hydrochloride on a spot plate or in a micro test tube. A positive response is indicated by the appearance of a yellow colour, the intensity depending on the quantity of the aldehyde.

Limit of identification: 0·5 μg of 2-, 3-, or 4-pyridine-aldehyde.

This colour reaction does not occur in the case of aliphatic and aromatic aldehydes, except for furfural, which, in quantities above 200 μg, gives a faintly pinkish colour within about 15 min.

Detection of pyridine-2-aldehyde

Procedure: Mix 1 drop of the aqueous test solution with a few mg of hydroxylamine hydrochloride and 1 drop of a 5% solution of ammonium iron^{II} sulphate on a spot plate. When the mixture is made alkaline with 1 drop of pyridine, a red or pink colour is formed almost instantaneously.

Limit of identification: 5 μg of pyridine-2-aldehyde.

Detection of phenylhydrazine

Procedure: Add to 1 drop of the aqueous test solution, containing a salt of phenylhydrazine or the solution of the base in excess acetic acid. on a spot plate, 1 drop of a 1% solution of pyridine-2-aldehyde. The presence of phenylhydrazine is indicated by the almost immediate appearance of a yellow colour, the intensity depending on quantity.

Limit of identification: 0·5 μg of phenylhydrazine.

It is highly probable that the above colour reaction may appear in the case of colourless alkyl and aryl hydrazines containing a free -NH_2 group. If so, a general test for these compounds may be

*The colour reaction of pyridine-2-aldoxime with iron^{II} ions was first observed by Hartkamp[2] and recommended for the colorimetric determination of iron.

obtained. Because of lack of test material, we have so far been able to examine only the behaviour of *p*-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine. Because these compounds and their salts are orange-coloured, it was not possible to observe a colour change.

Detection of phenylhydrazones and osazones

The test described above for phenylhydrazine makes possible the detection of phenylhydrazones of aldehydes and ketones and of osazones of sugars. These compounds are easily hydrolysed by the action of dilute acid to give an acid solution of phenylhydrazine salts. In these solutions the yellow pyridine-2-phenylhydrazone is formed on addition of pyridine-2-aldehyde and making alkaline with pyridine.

Procedure: Place 1 drop of the aqueous or alcoholic test solution in a micro test tube together with 1 drop of $2M$ hydrochloric acid and heat for a few min in a water bath. Add 1 drop of 1% aqueous pyridine-2-aldehyde solution followed by 1 drop of pyridine. A positive response is indicated by the appearance of a yellow colour.

The following were detected:

2 μg of phenylhydrazone of benzophenone,
1 μg of osazone of arabinose.

Acknowledgment—We thank Professor B. Kirson (Jerusalem) for his private communication, informing us that mixtures of diluted aqueous solution of pyridine-2-aldehyde and ammonium iron^{II} sulphate become red when made alkaline. The aim of the present investigation was the clarification of this effect and its possible analytical application. We are also grateful to the Conseillo National de Perquisas (Rio de Janeiro) and the Department of Inorganic and Analytical Chemistry of the Hebrew University (Jerusalem) for financial support.

Department of Inorganic
and Analytical Chemistry
Hebrew University
Jerusalem, Israel

F. FEIGL*
L. BEN-DOR

Summary—Spot tests for the detection of the three isomeric pyridine aldehydes and for pyridine-2-aldehyde are described. The tests are based on colour reactions with phenylhydrazine and with iron^{III} sulphate solution and hydroxylamine, respectively. The chemical basis of the colour reactions is discussed and the pertinent procedures are outlined. The colour reaction between pyridine-2-aldehyde and phenylhydrazine makes possible the detection of the latter as well as of phenylhydrazones and osazones after their acidic hydrolytic cleavage.

Zusammenfassung—Es werden Tüpfelnachweise für die drei isomeren Pyridinaldehyde und für Pyridin (2) aldehyd beschrieben. Die Nachweise beruhen auf Farbreaktionen mit Phenylhydrazin bzw. mit Ferrosulfat und Hydroxylamin. Der Chemismus der Farbreaktionen und deren Ausführung wird angegeben. Die Umsetzung zwischen Pyridin(2) aldehyd und Phenylhydrazin ermöglicht den Nachweis von Phenylhydrazin, sowie von Phenylhydrazonen und Osazonen nach deren hydrolytischen Spaltung durch Säuren.

Résumé—Des réactions à gouttes pour la détection des trois isomères de la pyridine-aldéhyde et pour la pyridine-2-aldéhyde ont été décrites. La détection est basée sur la réaction de couleur avec la phénylhydrazine et avec une solution de sulphate ferreux et l'hydroxylamine respectivement. La base chimique des réactions de couleur est discutée, et la méthode de travail est donnée. La réaction de couleur entre la pyridine-2-aldéhyde et la phénylhydrazine rend possible la détection de la dernière, ainsi que celles des hydrazones et osazones après leur hydrolyse acidique.

*Permanent address: Laboratorio da Produçaõ Mineral, Ministerio das Minas e Energia, Rio de Janeiro, Brazil.

REFERENCES

[1] F. Feigl, *Chemistry of Specific, Selective and Sensitive Reactions.* Academic Press, 1949, p. 375.
[2] H. Hartkamp, *Z. analyt. Chem.*, 1959, **170,** 399.
[3] A. Kaufmann and L. G. Vallette, *Ber.*, 1913, **46,** 49; G. Lénàrt, *Ber.*, 1914, **47,** 808; *Ann.*, 1915, **410,** 115; J. P. Wibant *et al.*, *Rec. trav. chim.*, 1945, **64,** 30.

Talanta, 1963, Vol. 10, pp. 1115 to 1117. Pergamon Press Ltd. Printed in Northern Ireland

LETTERS TO THE EDITOR

Murexide as an indicator in thorium-EDTA titration

SIR:

Beck[1] has noted the reaction between Murexide (ammonium purpurate) and scandium, rare earths, zirconium and thorium, and has described a titrimetric method for scandium. Murexide has now been found to function as an indicator for the complexometric determination of thorium.

Ammonium purpurate forms a yellow complex with thorium which turns pink when an excess drop of EDTA is added to it. To obtain very sharp end-points 0·1 ml of Murexide (0·04%) is recommended for each titration. It is possible to titrate down to a dilution of 0·005*M* of thorium at any temperature between 0° and 100°, at pH 2·5.

There is no interference in this titration from Li, Na, K, Ag, Ca, Sr, Ba, Mg, Hg^{II}, Al, As^{III} or Mn^{II}; the following ions interfere: Cu^{II}, Au^{III}, Be, Zn, Cd, Ti^{IV}, Zr^{IV}, Sn^{IV}, Sn^{II}, Pb, V^{V},Sb ^{III}, Bi^{III} Cr^{VI}, Mo^{VI}, W^{VI}, Fe^{III}, Co^{II}, Ni, Ce^{IV}, UO$_2$^{II}, tartrate, citrate, borate, phosphate, and fluoride. It is possible to perform titrations in the presence of Fe^{III}, which can be masked by ascorbic acid.

The authors are thankful to the Council of Scientific and Industrial Research for an award of a fellowship to one of them (S. P. S.)

SATENDRA P. SANGAL
ARUN K. DEY

Department of Chemistry
University of Allahabad
Allahabad, India
25 *June* 1963

REFERENCE

[1] G. Beck, *Analyt. Chim. Acta*, 1947, **1**, 69.

The stability constant of the complex of Zr^{IV} with EDTA

SIR:

Zr^{IV} is known to form with EDTA a stable complex with the mole ratio 1:1; and several modifications[1,2] of the complexometric titration of Zr^{IV} with EDTA solutions have been proposed. For the stability constant K$_{ZrY}$ two values are found in the literature: log K$_{ZrY}$ = 19·4[3] and log K$_{ZrY}$ = 21·9.[4] These seem to agree reasonably with each other. It is rather surprising, however, that the complex ZrY should be less strong than, for instance, ThY, because in other cases the stabilities[5] of Th^{IV}, U^{IV} and Pu^{IV} complexes with EDTA (1:1) regularly rise with decreasing ionic radii. Furthermore, if we note that log K$_{ThY}$ = 23·2 and accept that log K$_{ZrY}$ lies between 19 and 22, it is strange that Th (10 mg) does not[1,2] interfere in the titrimetric determination of Zr (2–20 mg) with EDTA solutions.

In a study of Zr^{IV} sorption on silica gel in 1*N*–5*N* HNO$_3$ medium, in the presence of EDTA, we have found that all necessary conditions are fulfilled which would allow calculation of the value of K$_{ZrY}$ from the dependence of partition coefficient on EDTA concentration.

From our results the following formation constants have been determined (20°): log K_{ZrY} = 28·5 ± 0·3 (1*N* HNO$_3$); 30·6 ± 0·2 (5*N* HNO$_3$). 29·5 ± 0·5 (μ = 0·1). These results are in very good agreement with solvent extraction[6] and spectrophotometric[7] data.

According to our findings, the stability constants (K$_{MeY}$) and ionic radii (r, Å) of the four quadrivalents ions can be correlated by the following semiempirical equation:

$$\log K_{Me^{IV}Y} = -16{\cdot}9 + 38\frac{1}{r}, \quad (\mu = 0{\cdot}1;\ \mathrm{Me} = \mathrm{Th, U, Pu, Zr})$$

the value for K$_{ZrY}$ being the highest of the four constants. Our value for the ZrY stability constant seems to eliminate the contradictions mentioned above. It is believed that the low values of K reported for K$_{ZrY}$ have been produced by neglecting Zr^{IV} hydrolysis.

The use of silica gel for the study of stability constants of complexes does not appear to have been mentioned in the literature.

A detailed report of this work will be published later.

REFERENCES

[1] J. Körbl, R. Přibil and A. Emir, *Chem. Listy*, 1956, **50**, 1440; *Coll. Czech. Chem. Comm.*, 1957, **22**, 961.

[2] A. E. Klygin and N. S. Kolyada, *Zavodskaya Lab.*, 1961, **27**, 23.

[3] L. O. Morgan and N. L. Justus, *J. Amer. Chem. Soc.*, 1956, **78**, 38.

[4] A. Iwase, *Nippon Kagaku Zasshi*, 1959, **80**, 1142: *Chem. Abs.*, 1961, **55**, 4250.

[5] N. N. Krot, N. P. Ermolagev and A. D. Gelman, *Zhur. neorg. Chim.*, 1962, **7**, 2054.

[6] M. Kyrš and R. Caletka, *Coll. Czech. Chem. Comm.*, in press.

[7] A. K. Babko and M. I. Shtokalo, *Ukrain. khim. Zhur.*, 1961, **27**, 566.

Institute of Nuclear Research
Řež by Prague
Czechoslovakia
16 *June* 1963

M. Kyrš
R. Caletka

A source of error in the use of a cathode-ray polarograph

Sir:

It is well known that when a mercury-pool anode is used to determine half-wave potentials the anode potential must be measured against a standard reference electrode, if reproducible results are to be obtained. The inconvenience of using a reference electrode has led to the practice of using the mercury-pool anode in a synthetic sample solution as the reference for analytical purposes.

Recent work in this Laboratory has shown that this practice can lead to appreciable errors in determining concentrations when a cathode-ray polarograph is used for the measurement of wave heights. These errors arise from a change in the position of the polarographic wave on the cathode-ray screen. This effect was observed with a K 1000 cathode-ray polarograph; it was even more marked with a Davis differential cathode-ray polarograph (DDCRP) used "single ended", *i.e.*, with only a single dropping-mercury electrode.

The position of the polarographic wave on the screen is governed not only by the half-wave potential of the ion concerned, but also by the sweep-start potential and the potential of the mercury-pool anode. Hence small variations in the latter potential from one solution to the next give rise to changes in the growth time of the drop to the point at which the polarographic wave occurs.

Furthermore, the wave height depends upon the surface area of the drop, which is related to growth time. A convenient way of illustrating this dependence of wave height on the distance of the wave across the screen, and hence on drop-growth time, is to measure wave heights for a given solution at a number of sweep-start potentials. Some results obtained in this way with cadmium and thallium solutions and with the two cathode-ray polarographs are given in Table I.

Table I

	Wave height, *scale units*		
Start potential, *volts*	K 1000 Cd^{2+}	DDCRP Tl^{+}	DDCRP Cd^{2+}
0·05		6·8	
0·10		6·6	
0·15		6·4	
0·20		6·15	7·6
0·25		6·0	7·35
0·30	8·9	5·85	7·1
0·35	8·7	5·65	6·9
0·40	8·5		6·7
0·45	8·35		6·5
0·50	8·2		6·35
0·55	8·0		6·1
0·60	7·8		5·9

It can be seen that a movement of the polarographic wave on the screen equivalent to 0·1 volt produces a change of the order of 5% in the measured wave height.

For maximum accuracy in the determination of ion concentration it is necessary to measure the height of the wave at a standard drop-growth time. This can be achieved either by using a standard reference electrode in the cell, combined with a fixed setting of the sweep-start potential, or by adjusting the sweep-start potential for each sample solution to bring the wave to the same position on the cathode-ray screen.

J. M. Bakes
G. R. E. C. Gregory
P. G. Jeffery

Warren Spring Laboratory, D.S.I.R.
Stevenage, Herts., England
17 *July* 1963

Talanta, 1963, Vol. 10, pp. i to iii. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(*Material for this section should be sent directly to the Associate Editor*)

DEUTSCHE DEMOKRATISCHE REPUBLIK

24. und 25. Oktober 1963: Merseburger Hochschultagung über **Moderne Methoden der analytischen Chemie** in der Technischen Hochschule für Chemie Leuna-Merseburg.

Vortragsfolge

	Donnerstag, 24. *Oktober*	Hörsaal 1
9.00 Uhr	R. Geyer	*Die analytische Chemie, ein selbständiges Teilgebiet Chemie?*
10.00 Uhr	L. Erdey und F. Paulik	Thermoanalytische Untersuchungen mit Hilfe des Derivatographen.
11.00 Uhr	R. Kalvoda	*Oszillographische Polarographie.*

Parallelveranstaltungen

	Vortragsreihe A	Hörsaal 1
14.00 Uhr (A)	A. Bardocz	*Spektrenanregung und ihre zeitlich aufgelöste Wahrnehmung.*
15.00 Uhr (A)	F. Günther	*Die Bedeutung der Röntgenspektroskopie für die analytische Chemie.*
16.00 Uhr (A)	V. M. Potapow	*Spektralpolarimetrische Analyse.*
16.30 Uhr (A)	G. Klose	*Die Anwendung der hochauflösenden paramagnetischen Kernresonanz zur chemischen Analyse.*

	Vortragsreihe B	Hörsaal 5
14.00 Uhr (B)	J. Bognar	*Auf katalytischer Wirkung begründete Analysenverfahren.*
15.00 Uhr (B)	N. P. Rudenko	*Anwendung radioaktiver Isotope und radioaktiver Strahlung in der analytischen Chemie.*
16.00 Uhr (B)	S. Spauszus	*Ergebnisse bei der Analyse metallurgischer Produkte nach der Rückstreumethode.*
16.30 Uhr (B)	F. Paulik und L. Erdey	*Einiges über die Auswahl der Versuchsbedingungen in der Thermoanalyse.*
17.00 Uhr (B)	E. Rexer und G. Ehrlich	*Probleme bei der Analyse von Reinststoffen.*

	Freitag, 25. *Oktober*	Hörsaal 1
9.00 Uhr	K. Schwabe	*Uber amperometrische Analysenverfahren zur Betriebskontrolle.*
10.00 Uhr	A. I. Busev	(Thema steht noch aus)
11.00 Uhr	M. Juřecek	*Methoden der organischen Analyse in der Praxis und im Unterricht*

Parallelveranstaltungen

	Vortragsreihe V	Hörsaal
14.00 Uhr (A)	H. Schlegel	*Edelmetalle als Werkstoffe in der modernen chemischen Technik.*
15.00 Uhr (A)	A. P. Kreschkow	*Titration in wasserfreien Medien.*
16.00 Uhr (A)	B. Philipp	*Zur Analytik faserbildender Hochpolymerer.*
17.00 Uhr (A)	Z. G. Szabo und L. G. Bartha	*Titrimetrische, auf Reduktion durch Eisen (II)-hydroxid beruhende Verfahren zur Bestimmung des Nitrations.*
18.00 Uhr (A)	P. I. Woskressenski	*Analytische Reaktionen zwischen festen Stoffen.*

	Vortragsreihe B	Hörsaal 5
14.00 Uhr (B)	H. Eckstein	*Bedeutung der analytischen Chemie im Mansfeld-Kombinat.*
15.00 Uhr (B)	S. Rennhak	*Die "technische" Gasanalyse.*
16.00 Uhr (B)	H. Hennicke	*Automatisierung von Analysenverfahren.*
17.00 Uhr (B)	P. Szolczanyi	*Chemische Betriebsanalyse als Grundlage der Regelung von Reaktionsapparaten.*

HUNGARY

Wednesday–Wednesday 15–22 *April* 1964: **Third Festival of Technical-Scientific Films:** Budapest, The festival will include, on the basis of reports by experts from the universities of various countries, a discussion on *The Technical and Natural Scientific Film in the University and Higher Education*, and, with the participation of foreign firms, a show on *Means of Technical-Scientific Cinematography and Photography*.

Only films produced after 1 January, 1962, can be entered, even if they have been shown at other festivals. Participation must be announced not later than 31 December, 1963, to Filmklub—Fesztivál Iroda, Budapest V, Szabadság-tér 17, Hungary. Films should be sent not later than 31 January, 1964.

UNITED KINGDOM

Wednesday 9 *October* 1963: *Thin Layer Chromatography: Society for Analytical Chemistry:* Imperial College of Science and Technology, London S.W.7: 6.30 p.m.

The following papers will be presented and discussed:

General Aspects.	L. J. Morris
Specific Separations on Impregnated Thin Layers.	L. J. Morris
Application of Thin Layer Chromatography to Inorganic Systems.	K. Burton, D. Lyons, G. Nickless and F. H. Pollard
Effects of Alkyl and Alkenyl Substitution on the Chromatography of Quinols and Related Compounds.	D. McHale
Steroids.	P. Oxley
Thin Layer Chromatography of Lipids.	B. W. Nichols

Wednesday 16 *October* 1963: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemistry Group: The Feathers*, Tudor Street, London E.C.4: 6.30 p.m.

Tuesday 22 *October* 1963: **Use of Plasma Jets,** I. L. Jones; **Fast-Neutron Activation Methods of Determining Oxygen in Steel,** A. L. Gray; *Society for Analytical Chemistry, Physical Methods Group* and *North of England Section*, and *Sheffield Metallurgical Association, Modern Methods of Analysis Group:* B.I.S.R.A. Laboratories, Hoyle Street, Sheffield: 7.00 p.m.

Wednesday 23 *October* 1963: Meeting on **Assay of Virus Vaccines,** F. Perkins and A. J. Beale: *Society for Analytical Chemistry, Biological Methods Group:* Burlington House, London W.1: 7.00 p.m.

Friday 25 *October* 1963: **The Atom and the Analyst—Some Confessions of an Unqualified Chemist,** J. M. A. Lenihan: *Society for Analytical Chemistry, Scottish Section:* Royal Society of Edinburgh, Edinburgh: 7.15 p.m.

Thursday 7 *November* 1963: Meeting on **Gas Analysis:** *Society for Analytical Chemistry:* Wellcome Building, Euston Road, London N.W.1: 3.00 p.m.

Thursday 14 *November* 1963: **Some Observations on the Use of Ion Exchange in Analytical Chemistry,** J. E. Salmon: *Society for Analytical Chemistry, Midlands Section:* Lanchester College of Technology, Coventry: 7.00 p.m.

Friday 22 *November* 1963: **The Presentation of Scientific Papers,** J. D. Nisbet: **Editing a Scientific Journal,** J. B. Attrill: *Society for Analytical Chemistry, Scottish Section:* Royal College of Science and Technology, Glasgow: 6.00 p.m.

Tuesday 26 *November* 1963: **Annual General Meeting** followed by **Address of Retiring Chairman,** W. Cule Davies: *Society for Analytical Chemistry, Physical Methods Group:* Burlington House, London W.1: 6.30 p.m.

British Standards Institution has announced the following *New British Standard:*

B.S. 3631*:* 1963*: Method for the determination of the ash content of paper.* This describes the apparatus and procedure as well as the method of reporting the results. Appendices give notes on the determination of ash in "ashless papers" and on the qualitative analysis of ash from loaded and coated papers. (*Price* 4s.)

The following *Amendment Slips* have also been announced: *B.S.* 1016*: Methods for the analysis and testing of coal and coke: Part* 8*:* 1959*: Chlorine in coal and coke. Amendment No.* 2*: PD* 4949. *B.S.* 3156*:* 1959*: Methods for the sampling and analysis of fuel gases. Amendment No.* 2*: PD* 4946.

UNITED STATES OF AMERICA

Wednesday–Friday 6–8 *November* 1963: **Pittsburgh Diffraction Conference:** Mellon Institute, Pittsburgh, Pa.

Wednesday–Friday 13–15 *November* 1963: **1963 Eastern Analytical Symposium:** *American Chemical Society, Analytical Chemistry Groups of N.Y. and N.J. Sections, Society for Applied Spectroscopy* and *American Microchemical Society:* Statler Hilton Hotel, New York City.

Monday–Wednesday 18–20 *November* 1963: *The Robert A. Welch Foundation Conferences on Chemical Research:* **VII. Modern Developments in Analytical Chemistry:** Rice Hotel, Houston, Texas.

The programme is as follows:

Monday, 18 *November*

10.00 a.m. *Isotopes in Analysis.* H. Eyring
Discussion Leaders: I. M. Kolthoff and A. D. Suttle, Jr.
2.00 p.m. *Polarography.* P. Delahay
Discussion Leaders: D. J. Fisher and D. N. Hume

Tuesday, 19 *November*

10.00 a.m. *Activation Analysis.* W. W. Meinke
Discussion Leaders: G. E. Boyd and V. P. Guinn
2.00 p.m. *Microanalysis.* O. Lowry
Discussion Leaders: D. Glick and C. L. Wilson

Wednesday, 20 *November*

10.00 a.m. *Nuclear Magnetic and Paramagnetic Resonance,* H. S. Gutowsky
Discussion Leaders: F. Bloch and J. N. Shoolery
2.00 p.m. *Mass Spectrographic Analysis.* K. Biemann
Discussion Leaders: J. L. Franklin and D. P. Stevenson

Thursday–Friday 7–8 May 1964: **Fourth Informal Conference on Vacuum Microbalance Techniques:** Mellon Institute Auditorium, 4400 Fifth Avenue, Pittsburg, Pa.

Papers are invited on the following topics: Theory, New Types of Balance, Difficulties, Associated Equipment, Other Microweighing Methods, Applications. The title and abstract must be submitted by 26 March, 1964, to Mr. F. A. Brassart, Westinghouse Research and Development Centre, Beulah Road, Churchill Borough, Pittsburgh 35, Pa., U.S.A. The written papers will be required at the meeting for inclusion in the *Fourth Volume on Vacuum Microbalance Techniques.*

22–27 *August* 1965: **1965 International Symposium on Microchemical Techniques:** *American Microchemical Society* (formerly *Metropolitan Microchemical Society*): Pennsylvania State University. University Park, Pennsylvania.

The symposium will be similar to that in 1961. Details will be available in due course from C. W. Pifer, Hoffmann–La Roche Inc., Nutlet 10, New Jersey, U.S.A..

The **American Society for Testing and Materials** has announced that the following publication is now available:

Manual on Hydrocarbon Analysis, STP 332. The first part of the manual covers considerations in choosing methods of analysis and in interpreting results obtained by them. Analysis of three basic types of hydrocarbon is covered: Chapter I—Gas Analysis: Analysis of C_5 and Lighter Hydrocarbons; Chapter II—Analysis of Gasoline and Other Distillate Fuels; Chapter III—Analysis of Viscous Oils. (*Prices if prepaid:* $14.00; $9.80 *to ASTM members.*)

ERRATUM

Volume 10, *page* 711: the second author of the letter should read *V. Marková.*
Volume 10, *page* 1039: the footnote to Table V should read
Sample No. 1: *total* 66 *ppm, Ca* 55 *ppm.*
Sample No. 2: *total* 379 *ppm, Ca* 205 *ppm.*

Talanta, 1963, Vol. 10, p. iv. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Reaction of iron^{III} with hydroxyaminoacids: *N*, *N*-Dihydroxyethylglycine-iron^{III}: E. R. NIGHTINGALE, JR. and R. F. BENCK. (22 *July* 1963)

The determination of chlorosuccinic acid in aqueous solutions: R. ANNINO and T. J. BERAS. (27 *July* 1963).

Phase titrations—IV: New applications and the phase titration of binary solutions of chemically similar components: D. W. ROGERS, A. OZSOGOMONYAN and A. SUMER. (29 *July* 1963).

Photochemical studies of organic compounds with vanadium^{V}—I: Oxidation of some carbonyl compounds: K. S. PANWAR and J. N. GAUR. (29 *July* 1963).

Some sulphur-containing organic compounds as reagents for the photometric determination of selenium: A. I. BUSEV. (29 *July* 1963).

Effects of adsorbed films of camphor and thymol on kinetics of the titanium^{IV}-titanium^{III} electrode reaction: H. A. LAITINEN, K. EDA and M. NAKANISHI. (5 *August* 1963).

The chemical compounds formed during the precipitation of cations with sulphides: N. A. RUDNEEV and G. I. MALOFEEVA. (8 *August* 1963).

Aluminium oxinate: A thermogravimetric study: C. J. KEATTCH. (8 *August* 1963).

The purification of Calcein: C. J. KEATTCH. (8 *August* 1963)

Chronopotentiometric study of thallium^{I} ion in glacial acetic acid: S. BRUCKENSTEIN, T. O. ROUSE and STEPHEN PRAGER. (12 *August* 1963).

Theoretical considerations in the indirect determination of anions: The determination of sulphate with barium chloranilate: J. AGTERDENBOS and N. MARTINIUS. (15 *August* 1963).

Separation of the oligophosphates: HERBERT L. ROTHBART, HENRY W. WEYMOUTH and WM. RIEMAN III. (15 *August* 1963).

The determination of trimetaphosphate ion in the presence of linear phosphates: HERBERT L. ROTHBART, and WM. RIEMAN III. (15 *August* 1963).

The determination of thiourea using chloramine-T: G. ARAVAMUDAN and V. R. SATYANARAYANA RAO. (18 *August* 1963).

Potentiometric study of the complexes of mercury^{I} with pyrophosphate, triphosphate and tetraphosphate: JAMES I. WATTERS and RICHARD A. SIMONAITIS. (19 *August* 1963).

Talanta, 1963, Vol. 10, pp. v to vi. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Standard Methods of Chemical Analysis: Sixth Edition. D. Van Nostrand Company, Inc., Princeton, Toronto, London, New York. **Vol. I—The Elements.** Edited by N. HOWELL FURMAN. 1962. Pp. xix + 1401. $25.00. **Vols. IIA and IIB. Industrial and Natural Products and Non-Instrumental Methods.** Edited by FRANK J. WELCHER. 1963. Pp xiv + 1282. £9-9s.

Contents: Volume I: The Alkali Metals: Aluminum: Antimony: Arsenic: Barium: Beryllium: Bismuth: Boron: Bromine: Cadmium: Calcium: Carbon: Cerium and the Rare Earth Metals: Chlorine: Chromium: Cobalt: Copper: Fluorine: Gallium: Germanium: Gold: Hydrogen: Indium: Iodine: Iron: Lead: Magnesium: Manganese: Mercury: Molybdenum: Nickel: Niobium and Tantalum: Nitrogen: Oxygen: Phosphorus: The Platinum Metals: Radium: Rhenium and Technetium: Scandium: Selenium and Tellurium: Silicon: Silver: Strontium: Sulfur: Thallium: Thorium: Tin: Titanium: Tungsten: Uranium: Vanadium: Zinc: Zirconium and Hafnium: Appendix (Qualitative Tests of Substances: Tables of Reactions: Tables and Useful Data: Reagents, Standard Solutions, and Indicator Solutions: Standard Laboratory Constants: Standardization of Weights: Common Logarithms of Numbers: Index.)

Volume IIA: Part I: Apparatus, General Operations and Reagents: Standard Laboratory Apparatus: Sampling: Detection of the Cations and Anions: Mechanical Separation: Separation by Precipitation: Separation by Electrolysis: Solvent Extraction: Separations by Distillation and Evaporation: Chromatography: Ion Exchange Methods in Analysis: Final Gravimetric Treatment: Titration Methods: Acid-Base Titrations in Nonaqueous Solvents: Determination of pH by the Colorimetric Method: Electrometric Hydrogen Ion Measurements: Statistical Interpretations: The Analytical Use of the Microscope: Quantitative Organic Analysis: Solubility Measurements: Determination of Water.

Part II: Special Techniques for Industrial Products and Other Special Substances: Commercial Acids and Bases: Air Pollutants: Alloys (Iron and Steel): Alloys (Ferro-Alloys): Alloys (Non-ferrous): Amino Acid Analysis of Protein Hydrolyzates: Bituminous Substances, including Asphalts, Tars, and Pitches: Portland Cement: Chemical Analysis in Clinical Medicine: Coal and Coke.

Volume IIB: Explosives and Propellants: Natural Fats: Fertilizers: Fuel Gases and Related Products: Gas Analysis—Vacuum Techniques: Paint, Varnish and Lacquer: Paper, Wood, and Pulp: Pesticides: Petroleum and Petroleum Products: Plastics: Poisons: Rubber and Rubber Products: Silicates (Glasses, Rocks, and Ferrous Slags): Soap and Detergents: Soils: Vitamins: Water Analysis: Water (Bacteriological Examination): Water (Biological Examination): Index.

Russian-English Chemical Reader: A. KRAMER. D. Van Nostrand Company Inc., Princeton, Toronto, London, New York, 1963. Pp vii + 311, 58s. 6d.

Left-hand pages: Chemical topics in Russian. **Right-hand pages:** Word for word English translations in parallel paragraphs.

Contents: Atomic-Molecular Theory and Basic Laws of Chemistry: Inorganic Chemistry: Organic Chemistry: Nuclear Reactions: Short Russian-English Chemical Dictionary.

Particle Size: Measurement, Interpretation and Application: RIYAD R. IRANI and CLAYTON F. CALLIS: John Wiley and Sons, London and New York, 1963. Pp. viii + 165. 60s.

Contents: Applications of Particle Size Distribution Measurements: Definitions: Methods of Data Presentation: Distribution Functions Applicable to Particle Size Distributions: Sedimentation Techniques: Microscopy: Sieving: Miscellaneous Techniques: Comparison of Particle Size Distribution Data from Various Methods: Procedure for Choosing the Appropriate Method of Particle Size Measurement: Index:

Steroid Reactions: An Outline for Organic Chemists: Edited by CARL DJERASSI: Holden-Day. Inc., San Francisco, 1963. Pp vi + 657. $9.75.

Contents: Editor's Introduction: Glossary of Abbreviations: The Protection of Carbonyl and Hydroxyl Groups: Selective Oxidations of Polyhydroxy Steroids and Non-catalytic Selective Reduction of Polycarbonyl Steroids: Introduction of Fluorine into the Steroid System: Preparation and Dehydrohalogenation of α-Bromo, α-Chloro and α-Iodo Ketosteroids: The Introduction of Double Bonds: The Birch Reduction and Partial Synthesis of 19-Nor-Steroids: Metal Ammonia Reductions of Steroidal Enones, Saturated Ketones and Ketols: Recent Applications of Photolytic and Related Preparative Methods in the Steroid Field: Selective Aromatizations of Steroids: Conversion of 20-Ketosteroids to 17-Ketosteroids: Ring Contraction of Steroids: Insertion of Hetero Atoms into the Steroid Nucleus: Preparation of Steroidal α-Hydroxy and α-Acetoxy Ketones: Formation and Reactions of Epoxides and Episulfides.

An International Quarterly Journal

DISARMAMENT AND ARMS CONTROL

Editorial Board: Dr. Donald Brennan, President, The Hudson Institute, New York; The Hon. Alastair Buchan, Director, The Institute of Strategic Studies, London; Professor Bernard T. Feld, Massachusetts Institute of Technology; Professor Henry Kissinger, Center for International Affairs, Harvard University; Professor Sir Nevill Mott, The Cavendish Laboratory, Cambridge University; Wayland Young (Executive Editor).

DISARMAMENT AND ARMS CONTROL has been launched to provide an international forum for the discussion of disarmament, arms control and related topics as a means of reducing the manifest dangers in which mankind now stands. Such work has, in the past, been largely undertaken and published within the haven of the research worker's own country, and makes its greatest impact there. It is hoped that this new medium will encourage the exchange of ideas, insights and experience between workers in different countries. It seeks to establish the understandings through which voluntary limitation and elimination of armaments may be reached.

Contents of the first issue

First Step—Sealed Records Caches?, *John C. Polanyi*; The Role of the Neutrals in the Geneva Negotiations, *M. Samir Ahmed*; Violations of Disarmament Agreements, *Richard J. Barnet*; The International Control of Fissile Material Production, United Kingdom Atomic Energy Authority; A Proposal for an African and Near-Eastern Zone Free from Certain Weapons, *David H. Frisch*; Obituary: A. V. Topchiev, *C. F. Powell*; Note: Perjury before International Tribunals; Book Reviews; Current Literature and Research.

Write for a free inspection copy and full details of the subscription rates, mentioning this journal

PERGAMON PRESS

Headington Hill Hall, Oxford
122 East 55th Street, New York 22, N.Y.

VOLUME 10, NO. 10 OCTOBER 1963

CONTENTS