

An International Journal of Analytical Chemistry

ΤΑΛΑΝΤΑ

talanta



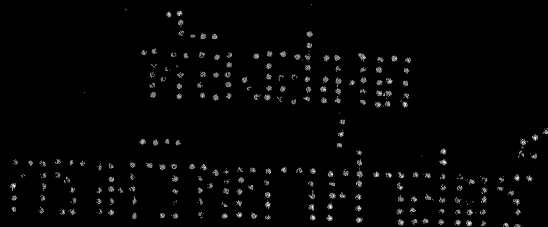
PERGAMON PRESS

LONDON NEW YORK PARIS LOS ANGELES

✓ 1963

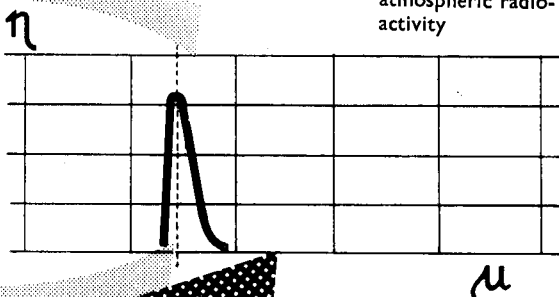
VOLUME 10

JANUARY



MEMBRANOUS ULTRAFILTERS

- V UFS (virology)
- H UFS (microbiology)
- A UFS (collection of aerosols and dust)
- R UFS (determination of atmospheric radioactivity)



solve a number of exacting tasks of microbiological and hygienico-epidemiological workplaces

Sole exporter

CHEMAPOL

Fine Chemicals and
Pharmaceuticals Division

**Panská 9, Prague I,
Czechoslovakia**

Telegrams:
Chemofarmacia Praha

Detailed prospectuses on request!

18 JAN 1963

2578

SUMMARIES FOR CARD INDEXES

Rapid analytical methods for the determination of metals and inorganic materials—XIII: Determination of tin in metallic antimony: Z. SULCEK, J. DOLEŽAL, J. MICHAL and V. SYCHRA, *Talanta*, 1963, 10, 3.

Summary—Tin^{IV} is held quantitatively on a silica gel column from a medium containing citric acid at pH 5.5. Antimony^{III} and antimony^V pass through the column. Interference from other metals can be masked with EDTA, and the tin, after elution, is determined polarographically. As little as $5 \times 10^{-4}\%$ of tin can be determined in antimony by this method.

New spectrophotometric methods for the determination of rhenium D. I. RYABCHIKOV and L. V. BORISOVA, *Talanta*, 1963, 10, 13.

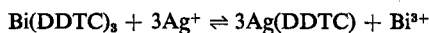
Summary—Recent spectrophotometric methods for the determination of rhenium are described and discussed.

Thermoanalytical investigations of high temperature fusion reactions L. ERDEY and S. GÁL, *Talanta*, 1963, 10, 23.

Summary—Derivatographic investigations are reported of acid-base reactions in solid and molten phases at high temperatures. It is established that the derivative thermogravimetric and differential thermal analysis peaks characterise the strengths of the bonds formed and broken during the reactions. The Lewis electron theory is extended to high temperature acid-base reactions. Fusion with soda and the Lawrence Smith fusion are investigated by derivatographic and other analytical methods.

Indirect polarographic determination of silver: M. KOPANICA and R. PŘIBL. *Talanta*, 1963, 10, 37.

Summary—Conditions for the indirect polarographic determination of silver, based on the substitution reaction of silver ions with bismuth diethyldithiocarbamate dissolved in carbon tetrachloride



are reported. Liberated bismuth^{III} ions can be determined polarographically in the supporting electrolyte containing EDTA. Using this principle a method has been developed for the determination of silver in galenite and in silver alloys.

A spectrophotometric study of *p*-nitrosodiphenylamine as a reagent for Rhodium: JAMES R. STOKELY and WILLIAM D. JACOBS, *Talanta*, 1963, 10, 43.

Summary—The red colour produced by heating excess *p*-nitrosodiphenylamine with rhodium has been studied to determine the optimum conditions for the analytical use of the reagent. The absorbance curve of the coloured complex shows an absorbance maximum at 520 m μ when measured against a reagent blank. The reaction is carried out in a buffered solution at pH 5.4 and is allowed to stand at room temperature for 1 hr for colour development. Beer's law is obeyed over the range investigated, 0.62 to 4.34 ppm, the optimum concentration range being 1.0 to 3.8 ppm. The sensitivity of the reaction is 0.0054 μ g per cm². Samples containing 3.12 ppm of rhodium gave absorbance readings showing average and maximum relative deviations of 0.69 and 1.22%, respectively. Interferences of other platinum metals have been investigated.

Differential coulometric analysis: A high-precision technique and its application to the determination of dichromate by constant-current generation of iron^{II} ion: R. G. MONK and G. C. GOODE, *Talanta*, 1963, 10, 51.

Summary—The application of the differential method of working to coulometric analysis is discussed. Experiments are described on the differential constant-current coulometric titration of potassium dichromate with iron^{II} ion to establish the validity and precision of the technique. Using "Primary Volumetric Standard" potassium dichromate as standard, "Analytical" and "Laboratory Reagent" grades of material were assayed and a relative standard deviation of 0.006% was obtained.

Analytical applications of the flame emission spectra of lead and titanium: C. L. CHAKRABARTI, R. J. MAGEE and C. L. WILSON. *Talanta*, 1963, 10, 57.

Summary—The flame emission spectra of lead and titanium, weak emitters in an oxy-hydrogen flame, have been studied with a view to their analytical applications. Interference effects, especially on the titanium emission band at 4518 m μ , and methods for eliminating or reducing them, have been investigated. Methods for determining lead and titanium in their respective alloys, by the use of a standard addition technique, have been developed. These methods have been tested on suitable alloys; the results have a reproducibility of $\pm 4-5\%$ (coefficient of variation). The advantages and the limitations observed in this study have a general bearing on the application of flame photometry to other elements.

L'oxalate de *p*-diméthylaminoaniline dans la colorimétrie des aldéhydes et des céto-stéroïdes: MAURICE PEREZ et JAROSLAV BARTOS, *Talanta*, 1963, 10, 69.

Summary—By reduction of *p*-nitrosodimethylaniline with alkali borohydride in the presence of copper, *p*-dimethylaminoaniline is formed, and can be isolated as the stable oxalate. In acetic acid medium, this reagent produces colours with aldehydes which permit them to be determined in amounts of the order of 10–30 μ g. In methanol, in the presence of perchloric acid, conjugated keto-steroids react in the same way as aldehydes, and can be determined in samples of less than 100 μ g.

Summaries for card indexes

Sodium peroxide as a flux in refractory and mineral analysis:
C. B. BELCHER, *Talanta*, 1963, **10**, 75.

Summary—The use of sodium peroxide as a flux in refractory and mineral analysis is reviewed. The rate of attack of sodium peroxide on various types of crucibles is compared and the influence of the impurities introduced into the assay by crucible attack and by sodium peroxide impurity is critically examined. The superior erosion resistance of zirconium crucibles at temperatures exceeding 550° is discussed. It is concluded that many fusion decompositions could be supplanted by sinter decomposition, thereby resulting in a significant reduction in blank levels. Some interferences caused by residual peroxide in extract solutions are also discussed.

Thermal neutron-activation analysis of titanium using 5.8-minute titanium-51 and rapid radiochemical separations; CHONG KUK KIM and W. WAYNE MEINKE, *Talanta*, 1963, **10**, 83.

Summary—A nuclear reactor has been used to determine trace amounts of titanium by neutron-activation analysis in a variety of samples. A 10-min radiochemical separation procedure coupled with gamma-ray spectrometry permitted measurement of 5.8-min titanium-51. With a neutron flux of about 10^{13} neutrons.cm⁻².sec⁻¹ the practical lower limit of detection was about 6×10^{-7} g of titanium.

Cation-exchange separation of bivalent metal ions from rare earths:
JAMES S. FRITZ and BARBARA B. GARRALDA, *Talanta*, 1963, **10**, 91.

Summary—The bivalent metal ions of calcium, magnesium, nickel and strontium are eluted from a cation-exchange column with 1.5M nitric acid and separated from trivalent rare earths, aluminium and yttrium. Prior sequential elution of other metal ions with hydrochloric acid in acetone-water or with dilute hydrofluoric acid does not interfere with the present separation method.

Photometric titration of alkyl aluminium compounds: COE W. WADELIN, *Talanta*, 1963, **10**, 97.

Summary—The end-point in the titration of alkyl aluminium compounds with isoquinoline can be detected photometrically. This enables their determination in the presence of oxygenated impurities with a standard deviation of 0.02 mmole per g. The method has been applied to trialkyl aluminium compounds and dialkyl aluminium hydrides in which the alkyl groups ranged from methyl to hexyl.

Summaries for card indexes

Determination of small amounts of calcium in the presence of large amounts of alkali metal salts by amperometric chelatometry: M. L. RICHARDSON, *Talanta*, 1963, 10, 103.

Summary—A rapid polarographic procedure for the determination of 0–50 ppm of calcium in alkali metal salts is described. It is selective and highly sensitive, with only strontium and barium causing interference to any marked degree. A cathode ray polarograph is used to measure the zinc peak current in a potassium chloride/hydroxide/zincate base electrolyte solution; a standard EDTA solution is added to the test solution; and the peak current of the zinc remains sensibly constant until all of the calcium has reacted, after which the peak current decreases as the zinc reacts with the EDTA. The end-point is found by extrapolation of the current-titration curves.

Precipitation of metal 8-hydroxyquinolates—VI: Zinc: J. PAUL JONES, ORVILLE E. HILEMAN, JR. and LOUIS GORDON, *Talanta*, 1963, 10, 111.

Summary—The precipitation of zinc 8-hydroxyquinolate from homogeneous solution with 8-acetoxyquinoline results in a precipitate with superior physical characteristics in comparison with that produced by the conventional method, and furnishes a much better separation of zinc from lead, calcium and magnesium.

Organic analysis—XXIX: A new spraying agent for reducing sugars on paper chromatograms: T. MOMOSE and M. NAKAMURA, *Talanta*, 1963, 10, 115.

Summary—An alkaline solution of 3,6-dinitrophthalic acid proves to be a very stable and sensitive spraying reagent for the detection of reducing sugars on paper chromatograms.

Use of compounds of the type $M^{II}TiO(C_2O_4)_2 \cdot xH_2O$ in analytical chemistry—I: The determination of potassium in barium titanate H. AREND and J. NOVÁK, *Talanta*, 1963, 10, 116.

Summary—The determination of potassium in barium titanate is the first example of the use of insoluble compounds of the type $M^{II}TiO(C_2O_4)_2 \cdot xH_2O$ in analytical chemistry. A simultaneous simple separation of barium and titanium is achieved, and no interference of oxalate ions in the determination of potassium by flame photometry is experienced.

Summaries for card indexes

Determination of boron in zirconium and Zircaloy: E. N. POLLOCK and L. P. ZOPATTI, *Talanta*, 1963, 10, 118.

Summary—The sample is dissolved in methanol and bromine. Boron is distilled out and collected in sodium hydroxide and methanol, then determined spectrophotometrically as the carminic acid complex.

Ion-exchange study of thiocyanatochloro complexes of rare earth elements: H. HAMAGUCHI, R. KURODA and N. ONUMA, *Talanta*, 1963, 10, 120.

Summary—The ion-exchange behaviour of several rare earths—La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er and Lu—on Diaion SK-1 cation-exchange resin with ammonium thiocyanate-hydrochloric acid solutions has been studied. The distribution coefficient (K_d) of the rare earth elements decreases with increasing atomic number. The differences in K_d value were found to permit separation of the lighter rare earths. The composition of the complex in the ammonium thiocyanate-hydrochloric acid medium is likely to be $M(\text{SCN})_2\text{Cl}$ or a similar compound, where M is the appropriate rare earth metal.

TALANTA

An International Journal of Analytical Chemistry



EDITOR-IN-CHIEF

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

ASSOCIATE EDITOR

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

REGIONAL EDITORS

Professor I. P. ALIMARIN, Vernadsky Institute of Geochemistry and
Analytical Chemistry, Academy of Sciences,
Vorobievskoe Shosse 47a, Moscow V-334, U.S.S.R.

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

Dr. R. PŘIBIL, Laboratory of Analytical Chemistry, Polarographic Institute, Czechoslovak Academy
of Sciences, Praha, 1, Jilská 16, Czechoslovakia.

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

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

EDITORIAL BOARD

Chairman: Mr. ROBERT MAXWELL, *Chairman and Managing Director, Pergamon Press Ltd.*

Professor C. L. WILSON, *Editor-in-Chief* Dr. M. WILLIAMS, *Associate Editor*

Professor L. GORDON, *representing Regional Editors*

Professor R. BELCHER, *representing Advisory Board*

Mr. G. F. RICHARDS, *Joint General Manager, Pergamon Press Ltd.*

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

Copyright © 1963

Pergamon Press Ltd.

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

ADVISORY BOARD

Chairman: Professor R. BELCHER University of Birmingham, England

Professor G. ACKERMANN	School of Mines, Freiberg, E. Germany
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. KORTÚM	University of Tübingen, W. Germany
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 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	University of Birmingham, 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

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 unbiased 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 fulfil 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 reproduced 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.

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.

TALANTA MEDAL

The Editorial Board of TALANTA has pleasure in announcing that, with the approval of the Advisory Board, the second award of the Talanta Medal has been made to

PROFESSOR GEROLD SCHWARZENBACH

of the Laboratorium für anorganische Chemie, Eidgenössische Technische Hochschule, Zürich, Switzerland.



In the opinion of the Editorial Board, Professor Schwarzenbach's studies have changed the face of titrimetric analysis. Determinations which were previously impossible can now be done simply, and determinations which were long and tedious have been made rapid. In addition, Professor Schwarzenbach's work has resulted in great strides being made in complex chemistry. His work has been followed up by so many other investigators that the number of papers of importance to analytical chemists must now run into thousands.

It is hoped that it will be possible to make a formal presentation of the Talanta Medal to Professor Schwarzenbach in Great Britain on some occasion during 1963.

RAPID ANALYTICAL METHODS FOR THE DETERMINATION OF METALS AND INORGANIC MATERIALS—XIII*

DETERMINATION OF TIN IN METALLIC ANTIMONY†

Z. ŠULCEK, J. DOLEŽAL, J. MICHAL and V. SYCHRA
Research Institute of Ores, Department of Analytical Chemistry, Charles University,
Central Geological Survey, Prague, Czechoslovakia

(Received 29 November 1961. Accepted 8 July 1962)

Summary—Tin^{IV} is held quantitatively on a silica gel column from a medium containing citric acid at pH 5.5. Antimony^{III} and antimony^V pass through the column. Interference from other metals can be masked with EDTA, and the tin, after elution, is determined polarographically. As little as $5 \times 10^{-4}\%$ of tin can be determined in antimony by this method.

In inorganic analysis silica gel has up to now been used only to a very slight extent. The present paper continues the systematic examination of the use of silica gel in this field, following on the work of Rezáč and Roubal¹ who describe the separation of small amounts of tin from tungsten utilising the adsorption of colloidal stannic hydroxide on a silica gel column.

In analytical methods for the determination of tin it is far more difficult to separate tin from accompanying elements, especially from the other elements of the second analytical group, than to perform the final determination. The isolation of tin is normally carried out by Scherrer's distillation method² or by precipitation according to Clark.³ These methods are very complicated, tedious, and not very exact. Because certain preliminary experiments showed that there was a possibility of the quantitative separation of tin from the other elements of the second analytical group (especially from antimony) on a silica gel column, this mode of separation was studied in the present work. As complex-forming agents, certain organic aliphatic oxyacids with more than one carboxyl group (tartaric, citric and oxalic acid), which form stable complexes with antimony and tin, even at high pH, were examined. Conditions were sought in which the sorption of tin on the silica gel column would be quantitative and all of the antimony would pass through the column.

EXPERIMENTAL AND RESULTS

Apparatus

The usual chromatographic columns were used, length 30 cm and cross-section area 1 cm².

* XXII: *Coll. Czech. Chem. Comm.*, 1961, **26**, 246.

† Dedicated to the 10th Anniversary of the Foundation of the Research Institute of Ores, Prague, Czechoslovakia.

Polarographic measurements were made with the Heyrovský V 310 polarograph with a 10-ml Novak cell. The sensitivity of the galvanometer was 6.2×10^{-9} A/mm/m. A dropping mercury electrode with a drop-rate of 2 sec at a reservoir-height of 80 cm was used.

pH measurements were made with a glass and a calomel electrode using a pH meter from the firm of Kovodružstvo. For calibration acetate and citrate buffers were used.

Reagents

Silica gel: The product of the firm Spolana of a grain-size of 0.06–0.18 mm (or 0.20–0.40 mm) was covered in a beaker with distilled water and left to stand for 12 hr (preferably overnight). The fine fraction was then washed out by decantation and the residue was repeatedly washed with dilute HCl (1 + 1) and distilled water until completely free from iron^{III} (almost no reaction with CNS⁻). The silica gel thus prepared was repeatedly decanted with distilled water and finally three times with 0.1M NH₄Cl, adjusted to the required pH by the addition of 0.1M HCl or dilute NH₄OH (1 + 5), and left in this solution for 2 hr. The pH value of the silica gel is then correct within ± 0.2 pH. The silica gel can also be prepared by shaking and decanting with 0.5 sodium citrate (adjusted to the required pH by the addition of citric acid or sodium hydroxide) until the solution over the solid phase reaches the same pH value as the used solution of citrate.

In preparing the gel it is necessary to stir it well with an overhead stirrer fitted with a glass-propeller. An electromagnetic stirrer is not suitable because the structure of silica gel is damaged and the stirrer crushes the grain to dust, which is washed out during decantation, so that severe losses occur. To obtain reproducible results it is necessary to work with a constant grain-size.

Standard solution of tin: This was prepared by dissolving exactly 10 g of the metal (p.a. Lachema) in 50 ml of conc. H₂SO₄ in a tall 100-ml beaker. The solution was evaporated to white fumes of sulphuric acid, the residue was dissolved in concentrated HCl, quantitatively transferred to a 1000-ml volumetric flask and made up to the mark in such a way that the final acidity of the solution was 4N in HCl. The factor of the solution was determined gravimetrically as SnO₂.

Solution of quinquevalent antimony: This was prepared by dissolving exactly 50 g of metallic antimony (p.a. Merck) in a mixture of 150 ml of conc. H₂SO₄ and 50 ml of conc. HNO₃ in a tall 500-ml beaker. After dissolution the solution was evaporated to fumes of sulphuric acid, the residue was carefully dissolved in conc. HCl, transferred quantitatively to a 1000-ml volumetric flask and made up with distilled water in such a manner to obtain a final acidity of the solution of 4N in HCl. The solution thus prepared is stable for a long time and does not hydrolyse.

Solution of trivalent antimony: This was prepared in the same manner but for dissolution only conc. H₂SO₄ was used.

Wash solution (0.5M sodium citrate): This was prepared by dissolving 242 g of the pure product (Lachema) and making up to 2 litres with distilled water.

For the preparation of all other solutions required, chemicals of the highest available purity were used.

Polarographic determination of tin

For the final determination of tin after its elution from the silica gel column the polarographic method was selected. Since the tin can be eluted with dilute hydrochloric acid (1 + 1) or dilute sulphuric acid (1 + 3), 1M hydrochloric acid + 3N ammonium chloride was used as supporting electrolyte. Tin gives in this medium a double step^{4,5} which corresponds to the reduction of $\text{Sn}^{\text{IV}} \rightarrow \text{Sn}^{\text{II}}$ and $\text{Sn}^{\text{II}} \rightarrow \text{Sn}^0$. The first step ($E_{\frac{1}{2}} = -0.25V$; SCE), is not well developed and is not suitable for evaluation. The height of the second step is measured ($E_{\frac{1}{2}} = -0.52V$; SCE). The same is true in a medium of 1M H_2SO_4 and 3N $(\text{NH}_4)_2\text{SO}_4$. It is difficult to dissolve 21 g of NH_4Cl —final concentration 4N—as proposed in the literature, in a 100-ml volumetric flask.

If the amount of tin adsorbed is less than 1 mg, it is necessary, after elution into a 100-ml volumetric flask, to record the polarogram at the highest sensitivity of the galvanometer, using compensation of the capacity current, which decreases the accuracy of the determination and makes it more difficult. If dilute sulphuric acid (1 + 3) is used for the elution, the volume of the eluate is the same (80 ml) and it can be evaporated in this case to a small volume, which cannot be done if dilute hydrochloric acid (1 + 1) is used for elution, because of the volatility of stannic chloride. The sensitivity of polarographic recording can thus be increased ten times.

Interference by possible traces of iron^{III} (from conc. hydrochloric acid or from silica gel) can easily be depressed with a small amount of ascorbic acid.

Sorption from Citric Acid

Results of preliminary experiments showed that it might be possible to separate even traces of tin from excessive amounts of antimony by the use of citric or tartaric acid as complexing agents. The sorption of tin and antimony on silica gel from a solution of citric acid was, therefore, studied thoroughly first.

(a) Dependence of the sorption of tin and antimony-III and -V on pH

Experimental conditions: Length of the silica gel column 8 cm; volume 8 ml; grain-size 0.06–0.20 mm; the pH of the silica gel was adjusted as described.

Procedure: To 10 ml of the tin standard solution (1 ml contained 1 mg of Sn) were added 3 g of citric acid and 25 ml of 0.1M NH_4Cl ; the pH was adjusted within the range 3.0–10.0 with sodium hydroxide and the volume of the solution made up to 150 ml with distilled water. The solution was passed through the silica gel column at a flow-rate of 3 ml/min. After the solution had passed through, the column was washed with 100 ml of distilled water whose pH was adjusted to 5.5 with ammonium hydroxide. When the solution reached the top layer of silica gel, the adsorbed tin was eluted from the column with 10 ml of dilute HCl (1 + 1). The acid was left to react on the column for 3 min and then collected directly into a 100-ml volumetric flask containing 15 g of NH_4Cl . The column was washed thoroughly with 70 ml of distilled water and after the dissolution of the NH_4Cl , was treated with 1 ml of 0.25% gelatine, and the contents of the volumetric flask were made up to the mark with distilled water. Tin was determined by a polarographic method.¹

The sorption of antimony-III and -V from hydrochloric acid medium was followed polarographically. From Fig. 1 it is seen that quadrivalent tin can be quantitatively

separated from ter- and quinquevalent antimony. This was confirmed by the investigation of the completeness of the sorption of tin in the presence of varying concentrations of ter- and quinquevalent antimony.

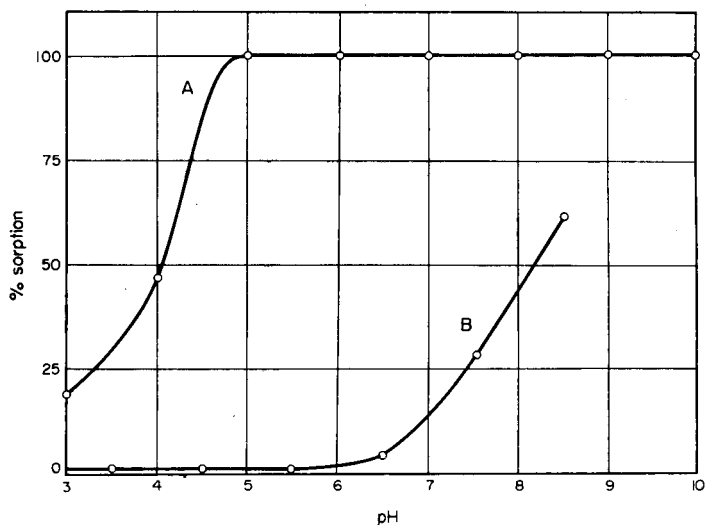


FIG. 1.—Dependence of the sorption of tin (A) and antimony (B) on pH in the presence of citric acid as complex-forming electrolyte.

(b) *Dependence of the sorption of tin on the concentration of citric acid*

The experimental conditions were the same as above. The concentration of citric acid was measured from 0.1M to 0.5M. The pH of the solutions was adjusted, in all cases, to 5.5 with sodium hydroxide. From the experiments, whose results are listed in Table I, it is seen that even a high concentration of citric acid in the solution does not affect the quantitative sorption.

TABLE I.—DEPENDENCE OF THE SORPTION OF TIN ON THE CONCENTRATION OF CITRIC ACID

Conc. of citric acid M	Sn taken, mg	Sn found, mg	Error %
0.1	1.00	0.98	-2.0
0.2	1.00	0.98	-2.0
0.3	1.00	0.98	-2.0
0.4	1.00	0.98	-2.0
0.5	1.00	0.98	-2.0

(c) *Influence of the concentration of the electrolyte on the sorption*

Řezáč and Roubal¹ observed in their work a marked influence of the concentration of neutral salts on the completeness of the sorption of tin. From our experiments it appeared that under the given conditions the sorption of tin does not depend at all on the concentration of the electrolyte, and that even a high concentration of salts in the solution does not affect the sorption. To 150 ml of a solution, containing 4 mg of tin,

were added 3 g of citric acid and varying amounts of ammonium sulphate the pH of which was adjusted to 5.5. The other conditions were the same as in (a).

(d) *Separation of tin from antimony*

A sample solution containing known amounts of tin and antimony was treated with an excess of citric acid (at least a five-fold excess over that of antimony) and diluted to a definite volume. The pH of solution was adjusted with sodium hydroxide to 5.5. The solution was passed through the column at a rate of 3 ml/min. Then the column was washed with 150 ml of the wash solution and 150 ml of distilled water. All other experimental conditions were the same as above.

As can be seen from Table II, it was possible to determine 0.1 mg of tin in the presence of 20 g of antimony, which corresponds to 0.0005% of tin in antimony, with a mean error of 3–5%.

TABLE II.—DETERMINATION OF TIN IN THE PRESENCE OF A LARGE EXCESS OF ANTIMONY

Sb taken, mg	Sn taken, mg	Sn found, mg	Error %
1 Sb ^v	1.00	0.97	−3.0
10	1.00	0.97	−3.0
100	1.00	0.97	−3.0
1000	1.00	0.985	−1.5
10000	1.00	0.97	−3.0
1	0.20	0.195	−3.0
10	0.20	0.195	−3.0
100	0.20	0.19	−4.5
1000	0.20	0.19	−4.5
10000	0.20	0.195	−3.0
20000	0.20	0.19	−4.5
20000	0.10	0.095	−5.0
1 Sb ^{III}	1.00	0.97	−3.0
10	1.00	0.955	−4.5
100	1.00	0.97	−3.0
1000	1.00	0.97	−3.0
10000	1.00	0.97	−3.0
1	0.20	0.195	−3.0
10	0.20	0.195	−3.0
100	0.20	0.19	−4.5
1000	0.20	0.19	−4.5
10000	0.20	0.19	−4.5

(e) *Influence of the grain-size of silica gel, flow rate and volume of the sorbed solution*

Silica gel prepared from water glass, which is very fine, cannot be used in practice. Its fine structure prevents good decantation and an 8-cm column of silica gel will clog. The solution flows only at low flow-rates. Silica gel of grain-size 0.06–0.20 mm, manufactured by the firm Lachema proved to be the best.

The narrowest adsorption zone is created at low flow-rates (1 ml/min) and small grain-size (a larger surface of silica gel). Since it is often necessary to sorb from larger volumes (500–1000 ml), the flow-rates used were, for practical reasons, 3–5 ml/min. The sorption itself was not affected at all.

The completeness of the sorption is not affected by either a large volume of the

analysed solution or of the wash solution. It was found that the results obtained by the use of a volume of the analysed solution of 1000 ml, which contained 5 mg of tin, are completely quantitative after washing with 400 ml of wash solution at a flow-rate of 3 ml/min. This means that no apparent shifting of the adsorption zone of tin takes place.

Generally it can be said that the adsorption zone of tin on silica gel is prolonged with an increasing grain-size and an increasing flow-rate. The extreme conditions which must be maintained to render the sorption of tin quantitative are, for a silica gel column 8 cm long, a volume of 8 ml and a grain-size of 0.06–0.20 mm, the following: volume of solution 1200 ml, flow-rate 5 ml/min, volume of wash solution 500 ml; the maximum amount of tin which can safely be quantitatively retained under these conditions is 10 mg.

(f) Determination of tin in the presence of antimony and in the presence of certain other elements

Accompanying elements normally encountered do not interfere in citric acid solution if sufficient EDTA is added (5 g in a final solution volume of 250–400 ml.)

Alkali metals do not in the slightest interfere with the determination of tin even when present in a thousand-fold excess. Complex ions of the alkaline earths also pass the silica gel column. Tin can easily be determined even in the presence of a large excess of metals of the first and second sub-groups of the Periodic System (Cu^{2+} , Ag^+ , Cd^{2+} , Zn^{2+} , Hg^{2+}). In the presence of silver ions and chloride ions the solution becomes turbid from AgCl , which settles on the bottom of the beaker. Adsorption of tin on the precipitated AgCl was not observed. Iron^{III}, chromium^{III}, manganese^{II}, nickel^{II}, cobalt^{II} and aluminium ions form the corresponding complexes, iron and nickel giving particularly stable citrates⁶ which pass the silica gel column and do not interfere. Large amounts of vanadium, arsenic, molybdenum, tungsten and lead can also be tolerated.

The determination of tin in the presence of beryllium, titanium, thorium, zirconium and uranium is more difficult, because these metals sorb completely or partially on silica gel from EDTA solution even in the presence of a complexing agent.^{6,7} In the presence of citric acid the corresponding citrate complexes are formed and these are only partially adsorbed on silica gel at pH 5.5. Thus it was possible to determine tin quantitatively even in a hundred-fold excess of these metals with a maximum error of –3%. Since these metals are present only in traces in most materials containing antimony as the main constituent, they do not affect the determination of tin.

Even larger amounts of the commoner anions do not interfere with the determination.

Sorption from Tartaric Acid

In a study of the sorption of tin and antimony on silica gel from a solution of tartaric acid, which also forms soluble complex ions with antimony, it was found that the sorption of tin is quantitative in the pH range 7.0–10.0, and decreases with an increasing acidity of the solution to less than 7% at pH 3. The quantitative sorption of tin at pH 7.5 is not influenced even by an extremely high concentration of tartaric acid and ammonium chloride or ammonium sulphate in the solution.

The assumption that the tartrate complex of ter- and quinquevalent antimony will not be adsorbed on silica gel proved to be erroneous. Experimentally it was proved

that partial sorption of antimony takes place, even if the complexing agent—tartrate—is present in large excess, and increases with an increasing pH of the solution.

Practical Application

Determination of small amounts of tin as impurities in metallic antimony

(a) *Weight of the sample:* The sample weight is chosen according to the expected tin content, determined for instance spectrographically or from the height (or capacity) of the used silica gel column (Table III). In the final polarographic determination of

TABLE III.—CHOICE OF THE WEIGHT SAMPLE
ACCORDING TO THE EXPECTED TIN CONTENT

Expected tin content, %	Weight of sample, g
1.0–5.0	0.1–0.5
0.1–1.0	0.5–5.0
0.01–0.1	5.0–20.0
<0.01	20.0

tin the amount of tin adsorbed on the silica gel column from one sample should preferably be not smaller than 1 mg and not larger than 10–20 mg (sensitivity of the galvanometer 1/5 and 1/70, respectively). Smaller amounts of tin require a further increase in the sensitivity of the galvanometer and the use of compensation of the capacity current, decreasing the accuracy of the determination. Amounts larger than 20 mg from one sample are too great because of the capacity of the silica gel column.

(b) *Decomposition of the sample with conc. hydrochloric acid and bromine:* Transfer a weighed sample to a 250-ml beaker, add conc. HCl, and cover with a watch glass. Add bromine carefully and with constant swirling. For 100 ml of conc. HCl add 10 ml of bromine. A vigorous reaction takes place; the reaction mixture becomes very hot and often spatters on the lid. A sample weight of 10 g dissolves completely in 10–15 min. The solution is always orange-yellow from dissolved bromine. Excess of acid and of bromine should be avoided, since it is necessary to neutralise the acid without too great an increase in volume and in the concentration of salts. When decomposition is complete, the excess of bromine must be removed by warming or simmering (2–3 min) and the addition of ascorbic acid (the solution is decolorised). Small amounts of precipitated silicic acid need not be removed because of the small silica content of metallic antimony.

At first sight this mode of decomposition seems very complicated and unsuitable for the given material. If, however, the conditions of the decomposition are strictly maintained it is possible to decompose the sample quickly and no loss of tin need be feared. The warming must, however, last only for a few min and be used only to remove the excess of bromine but not to accelerate or complete the decomposition, which should take place by itself in the cold.

The advantage of the decomposition with bromine-hydrochloric acid lies in the fact that it is very rapid and that readily water soluble salts are formed. It requires, however, greater manual skill.

(c) *Decomposition with conc. sulphuric acid and conc. nitric acid*

Transfer a weighed sample to a 250-ml beaker, add 3 parts of conc. H_2SO_4 and 1 part of conc. nitric acid, cover with a watch glass and warm on a hot plate until no black particles can be seen in the reaction mixture. The concentration of sulphuric acid is diminished by partial evaporation of the solution. To the remaining solution add conc. HCl carefully, while swirling, and dilute with water. This mode of decomposition is very simple but rather tedious. The complete decomposition of a 10-g sample takes at least 2 hr.

The further procedure is the same whatever the method of dissolution. To the acid sample solution add the required amount of citric acid (at least a five-fold excess over the antimony present) and 25–50 ml of 0.1M NH_4Cl , dilute with distilled water and

TABLE IV.—RESULTS OF ANALYSES OF METALLIC ANTIMONY

No	Sn content, %	No	Sn content, %
1.	0.103	5.	0.098
	0.103		0.094*
2.	0.100	6.	0.098
	0.100		0.096
3.	0.098	7.	0.094
	0.098		0.092
4.	0.098	8.	0.094
	0.092*		0.095

* Checked by standard addition after decomposition.

adjust the pH to 5.5 with sodium hydroxide. Pass the solution thus prepared through a silica gel column of 8 cm length, 8 ml volume and with a grain size of 0.06–0.29 mm at the flow rate of 3 ml/min. When the solution has passed through, wash the column with 200 ml of the wash solution (0.5M sodium citrate; pH = 5.5) and then with 100 ml of water, the pH of which has been adjusted to 5.5 with a few drops of very dilute HCl . In the presence of large amounts of impurities in antimony, sufficient excess of EDTA should be added. When the solution reaches the top layer of the silica gel, elute the tin from the column with 10 ml of dilute HCl (1 + 1) directly into a 100-ml calibrated flask containing 15 g of NH_4Cl . Wash the column well with 70 ml of distilled water, add gelatine as before, make up to the mark and determine the tin.

The rapid adjustment of the pH to the required value can easily be made visually, using methyl red as indicator. The neutralisation with hydroxide is stopped at the first colour change of the indicator. At this point the pH, measured potentiometrically, is found to be 5.6–5.8. The dye is partially sorbed on the column in the acid form, colouring the column red.

The results are evaluated from a calibration curve and may be checked by standard addition. Table IV shows the analyses of eight samples from one specimen.

DISCUSSION

For the determination of trace amounts of tin in metallic antimony up to now normally the spectrographic method has been used. This does not guarantee accurate results even if perfect instruments are used. All other methods cited in the literature are very tedious.

The newly proposed method fulfils all requirements for the determination of trace elements. It is very selective and sensitive; it is possible to determine as little as $5 \times 10^{-4}\%$ of tin in antimony. The interference of other components in the analysed material is eliminated by adding EDTA.

Since the final determination is made polarographically the method is suitable even for routine laboratories. The interfering antimony can be completely removed by washing the column with 0.5M sodium citrate of pH 5.5.

Tartaric acid was not suitable as a complex forming electrolyte. Even if an optimal pH value is maintained and if the washing is thorough, a considerable amount of antimony remains adsorbed on the silica gel column together with tin and interferes with the polarographic determination of tin. This concentration could, of course, be decreased by repeated sorption, but the time necessary for analysis would then be much increased.

The study of other aliphatic acids (oxalic, maleic) as complex forming electrolytes showed no substantial improvement over citric acid for the separation. Both acids are even less suitable than tartaric acid. From a medium of oxalic acid the sorption of tin is quantitative at pH 5.5; at this pH, however, the sorption of antimony is 40%, and at pH 7.5 65%. From a medium of maleic acid the sorption of tin was not quantitative and the results were not reproducible.

It should be possible to use the method for the determination of tin in various alloys and metals, and this, and the sorption of other ions from EDTA citrate medium, will be the subject of further study.

Zusammenfassung—Zinn(IV) wird aus einem Zitronensäuremedium von pH 5.5 an einer Silicagelsäule quantitativ festgehalten. Sb(III) und Sb(V) laufen durch die Säule. Störungen durch andere Metall können mittels ÄDTE ausgeschaltet werden. Das Zinn wird nach Elution polarographisch bestimmt. Noch $5 \times 10^{-4}\%$ Sn können so in Antimon bestimmt werden.

Résumé—L'étain^{IV} est retenu quantitativement sur une colonne de gel de silice en présence d'acide citrique à pH 5,5. L'Antimoine III et l'Antimoine IV ne sont pas fixés. En présence d'E.D.T.A les autres métaux ne gênent pas et l'étain, après élution, est dosé par polarographie. Il est possible par cette méthode, de doser $5 \cdot 10^{-4}\%$ d'étain dans l'antimoine.

REFERENCES

- ¹ Z. Rezáč and M. Roubal, *Chem. Listy*, 1957, **51**, 884.
- ² J. A. Scherrer, *J. Res. Nat. Bur. Stand.*, 1936, **16**, 253; 1938, **21**, 95.
- ³ S. W. Clark, *Chem. News*, 1870, **21**, 124.
- ⁴ A. Vlček, *Chem. Listy*, 1956, **50**, 400.
- ⁵ J. J. Lingane, *J. Amer. Chem. Soc.*, 1945, **67**, 919.
- ⁶ J. Bjerrum, G. Schwarzenbach and L. Sillén, *Stability Constants*, Part I. The Chemical Society, London, 1958.
- ⁷ Z. Šulček, J. Michal and J. Doležal, *Coll. Czech. Chem. Comm.*, 1959, **24**, 1815.
- ⁸ *Idem, ibid.*, 1961, **26**, 246.

NEW SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF RHENIUM

D. I. RYABCHIKOV and L. V. BORISOVA

V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry
Academy of Sciences, Moscow, U.S.S.R.

(Received 28 May 1962. Accepted 18 June 1962)

Summary—Recent spectrophotometric methods for the determination of rhenium are described and discussed.

IN connection with the use of rhenium in new fields of engineering and in the production of refractory alloys, studies on the analytical chemistry of this element have been recently developed on a large scale.¹⁻⁹

The practical trend of these analytical studies is determined by the fact that natural materials contain very small amounts of rhenium. On the other hand, both in natural and in industrial materials rhenium is in a complex mixture with other metals: with Mo and W which have many common chemical properties with rhenium, as well as with Ni, Co, Cu, Cr, Ti, Zn, Ag, Pb and other elements.

From an analytical point of view rhenium is a very interesting element, as it may exist in seven valency states. But bearing in mind that most of the analytical determinations of rhenium are carried out in aqueous solutions, it is expedient to use the more stable valency states, Re^{VII} , Re^{V} and Re^{IV} . The conversion of rhenium into Re^{V} and Re^{IV} states is achieved by reduction of Re^{VII} with various chemical reagents.

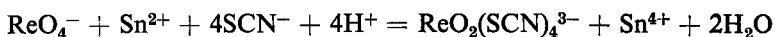
It is particularly important that rhenium of lower valencies readily interacts with many inorganic and organic reagents forming coloured complex compounds. Almost all the reagents (dioximes, thiocyanate, sulphite, thiourea, diethyldithiocarbamate, diethyldithiophosphoric acid, *etc.*) contain nitrogen, sulphur, oxygen and phosphorus atoms in one or another combination; and, apparently bonding through them is characteristic for rhenium.

A detailed review of analytical methods for rhenium determination was given by the authors¹⁰ in 1961.

Our studies on rhenium complexing are directed to the solution of analytical problems.

Recently¹¹ work has been carried out to elucidate the composition of a coloured rhenium-thiocyanate complex compound: one of the most widely used methods for the determination of rhenium is based on spectrophotometric measurement of this compound. Various authors have suggested various compositions for the compound: Druce¹²— $\text{ReO}(\text{SCN})_4$, Bibikova¹³— $\text{Re}(\text{SCN})_3$, Tarayan and co-workers¹⁴— $\text{Re}(\text{SCN})_4$.

Our investigation shows that the coloured compound exists in solution as a complex anion $\text{ReO}_2(\text{SCN})_4^{3-}$, and rhenium in this anion is in the quinquivalent state. Taking this into account, the reaction producing it can be represented by the following equation:



Our recent investigations also provided an opportunity to discover a number of new colour reactions of rhenium which may successfully be used for the photometric determination of this element. The majority of the reagents used were sulphur-containing compounds.

The rhenium-sulphite reaction was described¹⁵ in 1959. By a more thorough study of rhenium interaction with sulphites and thiosulphates, it has been found that rhenium forms three complex compounds in a hydrochloric acid medium in the presence of SnCl_2 . The maximum absorbance of the first compound is located at $460 \text{ m}\mu$, of the second at $420 \text{ m}\mu$, and of the third at $520 \text{ m}\mu$. The optimum conditions for formation of these compounds are as follows: the HCl concentration should be $1\text{--}2N$ for the first, $5N$ for the second, and $9N$ for the third; the concentration of reactants 1.4×10^{-3} mole/litre for the first, and 7×10^{-3} mole/litre for the second and third compounds, in the presence of excess of SnCl_2 .

A molar ratio of Re to sulphite and thiosulphate of $1:4$ for the two rhenium concentrations of 6.6×10^{-5} and 3.3×10^{-5} mole/litre in a $1.6N$ HCl medium has been found for the first complex compound by the method of varying the concentration of one of the reagents. The anionic nature of the coloured components of all the compounds has been established by means of ion-exchange resins. The solutions follow Beer's law (Fig. 1); the molar extinction coefficients are found to be 1×10^4 for the

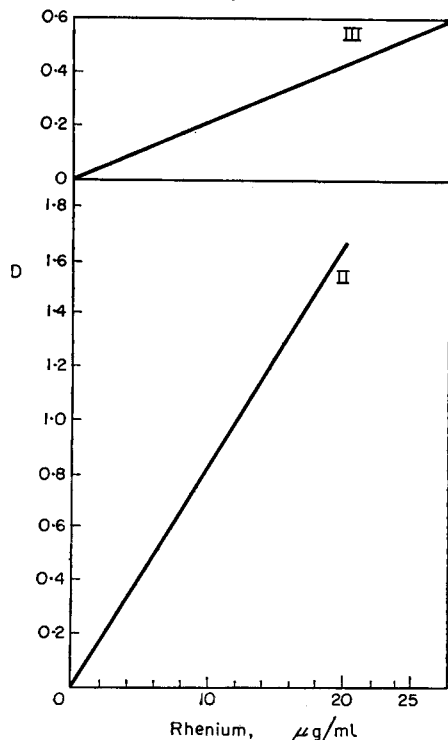


FIG. 1.—Relationship of optical density and rhenium concentration for the second and third complex sulphites

first, 1.5×10^4 for the second, and 4×10^3 for the third compound, and this therefore permits determination down to 1 mg of Re in 25 ml with an accuracy of $\pm 0.5\%$ (by

the third complex compound). The preliminary separation of Re from Mo and W is necessary when rhenium is determined by the sulphite method; separation is carried out chromatographically.¹⁶ We have determined rhenium by this method in a number of alloys.

Some interesting results have been obtained in the study of the interaction of rhenium with thiourea. This reaction was suggested¹⁷ in 1955 for the photometric determination of rhenium. The sensitivity of the thiourea method is $0.2 \mu\text{g/ml}$. The solutions obey Beer's law over a wide range of rhenium concentrations, the optical density being measured with a violet filter (at $413 \text{ m}\mu$). This method may be used for the determination of larger quantities of rhenium than is possible by the thiocyanate method. A spectrophotometric modification of the thiourea method for the analysis of alloys and perrhenates has been described.¹⁹ The optical density has been measured at $390 \text{ m}\mu$. The cationic nature of the compound has been unequivocally proved by testing the coloured compound with ion-exchange materials when the complex composition has been studied.^{17,18}

We have recently found that rhenium forms five complex compounds with thiourea, and solutions of these have different absorption spectra (Fig. 2). The absorbance maxima in the visible range of the spectrum are at $390, 420, 520, 570$ and $700 \text{ m}\mu$. The solutions of the complexes are yellow, orange, pink, blue and green in colour. The first two compounds are formed on adding three or more equivalents of SnCl_2 as reducing agent in the presence of excess of thiourea, and contain rhenium^{IV}; that one with the maximum absorbance at $390 \text{ m}\mu$ is formed in $4\text{--}6N$ HCl, the second one ($\lambda_{\text{max}} = 420 \text{ m}\mu$) in $8N$ HCl.

The other three compounds are formed on adding two or less equivalents of SnCl_2 in the presence of excess of thiourea and contain rhenium^V. The first of these ($\lambda_{\text{max}} = 520 \text{ m}\mu$) is obtained in $4\text{--}6N$ HCl, the second ($\lambda_{\text{max}} = 570 \text{ m}\mu$) in $8N$ HCl, and the third ($\lambda_{\text{max}} = 700 \text{ m}\mu$) in $10\text{--}11N$ HCl. It has been found that thiourea may reduce rhenium to rhenium^V, forming complex compounds with absorbance maxima at $520, 570$ and $700 \text{ m}\mu$, depending on the acidity of the medium.

The formation of these compounds takes place in the absence of SnCl_2 when HReO_4 and thiourea solutions are mixed together, thiourea in this case serving both as a reducing and a complexing agent.

We have succeeded in isolating all these complex compounds in a solid state. When a HReO_4 solution and an excess of thiourea are mixed in $8N$ HCl, yellow-greenish brilliant crystals with a tabular form are deposited. Their chemical composition corresponds to the formula $[\text{Re}(\text{OH})_2(\text{Thio})_4]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$. The compound is almost immediately hydrolysed in water, so we have not succeeded in obtaining any data on either its molecular conductivity or its cryoscopic molecular weight. The magnetic susceptibility is $\chi \approx 0.21 \times 10^{-6}$, which shows that this compound is diamagnetic, and it is additional proof that rhenium is in a quinquevalent state. When these crystals are dissolved in $2\text{--}4N$ HCl, the solution has a bright pink colour, the maximum absorbance being at $520 \text{ m}\mu$. When the acidity is increased to $8N$ HCl, the colour changes from pink to blue. Pale blue crystals separated from this solution ($\lambda_{\text{max}} = 570 \text{ m}\mu$) and the composition of these is being studied.

When the pale blue crystals are dissolved in water the colour of the solution rapidly changes through pink to brown, suggesting that the compound is hydrolysed in water.

แผนกห้องสมุด กรมวิทยาศาสตร์
กระทรวงอุตสาหกรรม

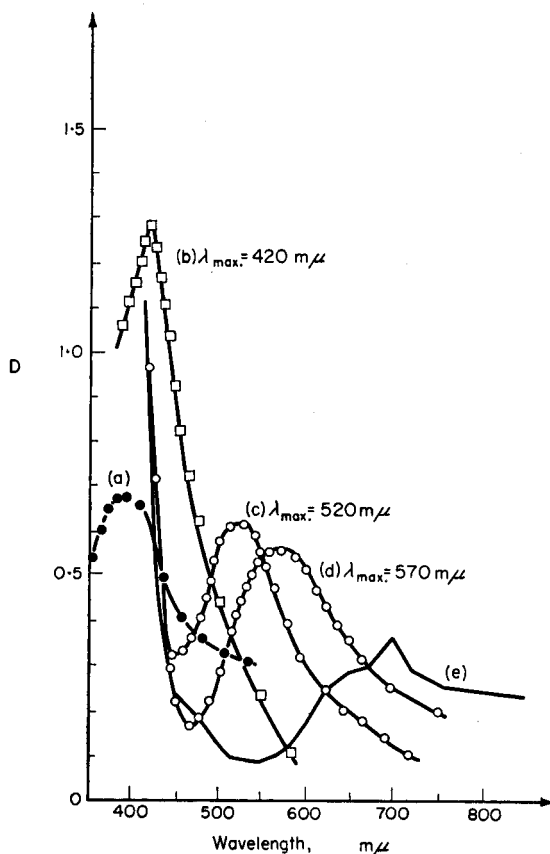


Fig. 2.—Absorption spectra of rhenium-thiourea complexes:

- (a) 1.5–6*N* HCl, large excess of SnCl₂: $\lambda_{\max} = 390 \text{ m}\mu$
- (b) 7–8*N* HCl, Re:Sn = 1:1.5 (moles)
- (c) 1.5–6*N* HCl, Re:Sn = 1:1 (moles)
- (d) 7–8*N* HCl, Re:Sn = 1:1 (moles)
- (e) 11*N* HCl, Re:Sn = 1:1 (moles)

When the pale blue crystals are dissolved in concentrated HCl, green solutions are formed, of which the maximum absorbance is at 700 $\text{m}\mu$. Red crystals crystallise from such solutions and the composition of these is being studied by us at present.

Compounds of rhenium^{IV} have also been separated by us. They are obtained by mixing together HReO₄, thiourea and an excess of SnCl₂. When the brown crystals which are obtained are dissolved in water, the solution develops a yellow-green colour. The absorption spectrum of this solution is given in Fig. 3. The composition and characteristics of this compound are being studied.

All the compounds described have different molar extinction coefficients, and may be used for the colorimetric determination of rhenium. The "blue" solution has been found to follow Beer's law (Fig. 4). The molar extinction coefficient is $\epsilon = 1 \times 10^2$, so that the method may be recommended for the determination of microgram quantities of rhenium (1–7 μg in a sample). In the analytical determination of rhenium the addition of SnCl₂ is recommended to speed the reaction, as is the case in Os and Ru determinations.²⁰

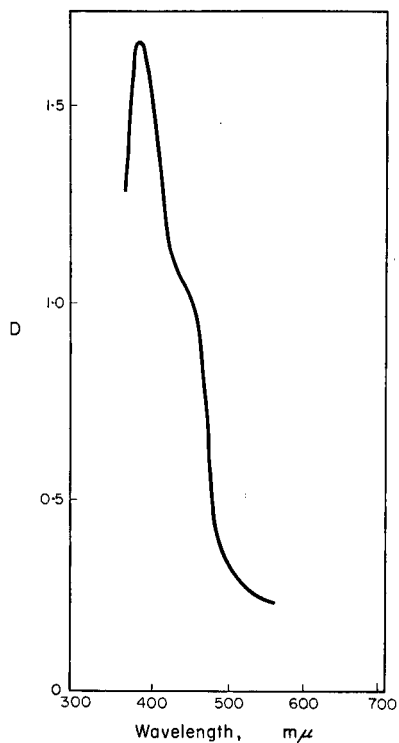


FIG. 3.—Absorption spectrum of aqueous solution of Re^{IV} -thiourea compound ($\lambda_{\text{max}} = 390 \text{ m}\mu$)

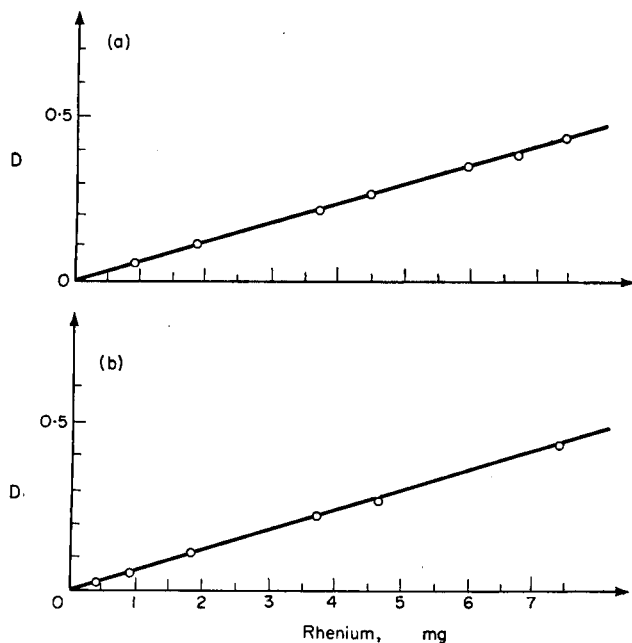


FIG. 4.—Relationship of optical density of "blue" complex solutions and rhenium concentration:

(a) $\text{Re} : \text{Sn} = 1 : 1$ (moles)

(b) In the absence of SnCl_2 .

Now we shall deal briefly with the reaction with *o*-mercaptocresol²¹ which, in certain conditions, is a selective reagent for rhenium and may be used for its determination in the presence of large quantities of Mo and W, as we have recently proved. Extraction of a violet compound with chloroform is carried out from 10*N* HCl. The chloroform extract is measured photometrically.

We have also established that rhenium forms a coloured compound with dithizone. The compound is extracted with chloroform from a solution which is 9*N* in respect to HCl. The maximum absorbance is at 530 *mμ*.

Besides the above reagents containing sulphur, we have studied the reactions of rhenium with phosphorus- and nitrogen-containing compounds.

A pyrophosphate complex compound is formed on heating HReO₄, H₃PO₄ and NH₄OH until a dark cherry-coloured melt is formed.²² The maximum absorbance of the aqueous solution is at 490 *mμ*. The maximum colour intensity develops when the ratio of the components of the initial mixture is H₃PO₄:HReO₄ ≈ 100, and in excess of ammonia.

A similar compound, judging from the absorption spectrum, is obtained in pyrophosphate acid medium when HReO₄ is treated with FeSO₄ as reducing agent. A barium salt of this compound has been separated from aqueous solutions of the melt, which proves that the rhenium is in a complex anion. In addition, the anionic nature of the coloured part has been confirmed by means of ion-exchange resins. The determination of the rhenium valency state has been carried out by the Noddack method,²³ and it has been found to be 5. Chemical analysis of the barium salt has shown a mole ratio of Ba:Re:P = 1:1:2, which corresponds to a possible formula, Ba[ReO(OH)P₂O₇]. Besides the barium salt, two more salts with NH₄⁺ and [Pt(NH₃)₄]⁺⁺ cations have been isolated. According to results of analysis their formulae may be (NH₄)₂[ReO(OH)P₂O₇] and [Pt(NH₃)₄][ReO(OH)P₂O₇]. The ratio of the molecular weights of the postulated salts is:

$$\frac{\text{Ba}[\text{ReO}(\text{OH})\text{P}_2\text{O}_7]}{[\text{Pt}(\text{NH}_3)_4][\text{ReO}(\text{OH})\text{P}_2\text{O}_7]} = 0.876$$

The weight ratio obtained in practice for the precipitates of these salts corresponding to a single rhenium value is 0.882. These close values suggest that the hypothetical formulae may be correct. The cherry-violet colour of the melt is very stable and, apparently, in certain cases it may be used for photometric determination of rhenium.

Finally, we refer to the reaction of rhenium with diphenylcarbazide;²⁴ on the basis of this reaction we have developed a very selective method for rhenium determination. It has been established that Re^{VII} does not react with diphenylcarbazone (DN) (m.p. 127°), but reacts with diphenylcarbazide (DD) (m.p. 173°) forming a violet compound with maxima of absorbance at 420 and 540 *mμ*. The optimum conditions for the reaction are: 8*N* HCl, a 100- to 150-fold excess of DD and 40% (by vol.) of acetone. For analytical purposes it is better to use the chloroform extract of the compound. In this case the molar extinction coefficient ϵ is 1.78×10^5 , the working acidity range is from 7.6*N* to 8.3*N* in respect of HCl. The composition of the compound has been determined by the isomolar series method, and a ratio of Re:DD = 1:1 has been found when the total concentration of Re^{VII} and DD is equal to 2.5×10^{-3} mole/litre (Fig. 5). The formation of only one complex, with the composition Re:DD = 1:1 has been proved by the identity of the absorption spectra

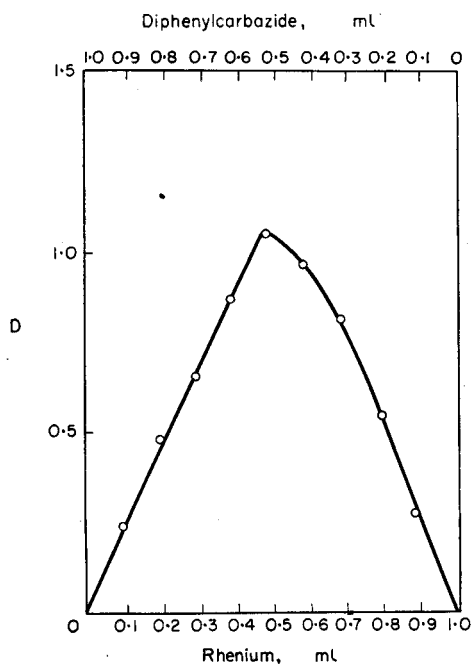


FIG. 5. Isomolar series of Re^{VII} -diphenylcarbazide at the total concentration of 2.5×10^{-3} mole/litre.

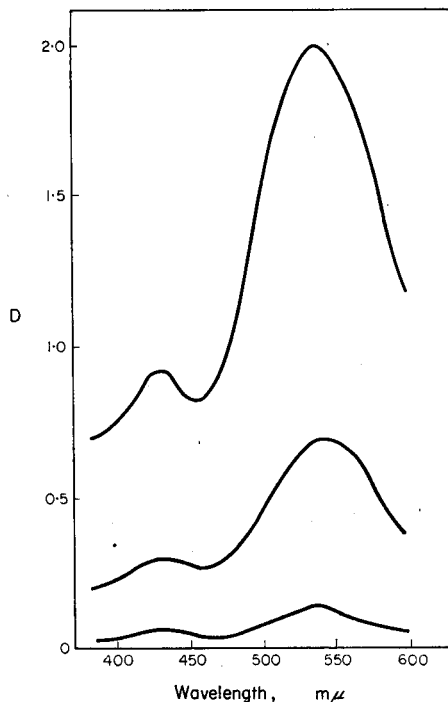


FIG. 6. Absorption spectra at molar ratios of Re^{VII} : DD = 1:1, 1:10 and 1:100.

of the solutions in which the ratios Re^{VII} :DD are 1:1, 1:10 and 1:100, other conditions being equal (Fig. 6). In addition, the isomolar series results agree with the suggested reaction mechanism; this is that in the interaction of Re^{VII} with DD rhenium is reduced to Re^{V} , and DD is oxidised to DN; in this way the transfer of two electrons takes place, corresponding to participation of Re^{VII} and DD in the ratio of 1:1. The products of the reaction between Re^{V} and DN react with each other forming a coloured compound.

The quinquevalent state of rhenium in the compound has been confirmed by studying the interaction of Re^{V} with DD and DN. Re^{V} did not react with DD and the solution remained colourless for some time; in the reaction of Re^{V} with DN a violet colour developed immediately, and the absorption spectrum of the compound is identical with that of the compound obtained by the reaction of Re^{VII} with DD. The results on the diamagnetism of the compound obtained by mixing together Re^{VII} and DD confirm the quinquevalent state of rhenium in the complex.²⁴

To determine whether rhenium is a component of the coloured compound, the distribution of rhenium between the aqueous and chloroform phases during extraction has been studied. It has been found that rhenium passes completely into the chloroform phase in a 100- to 150-fold excess of DD. Thus the coloured compound is a complex rhenium compound.

The extraction of this compound from 8N HCl with chloroform proved to be very selective; this allowed the development of a sensitive extraction-photometric method for the determination of rhenium. The sensitivity of the method is $3 \mu\text{g}$ in 25 ml;

the colour intensity of the solution is stable for 24 hr (in the chloroform extract). The solutions obey Beer's law (Fig. 7). The main advantage of this method is the possibility of determining rhenium in the presence of any amount of tungsten. This method has

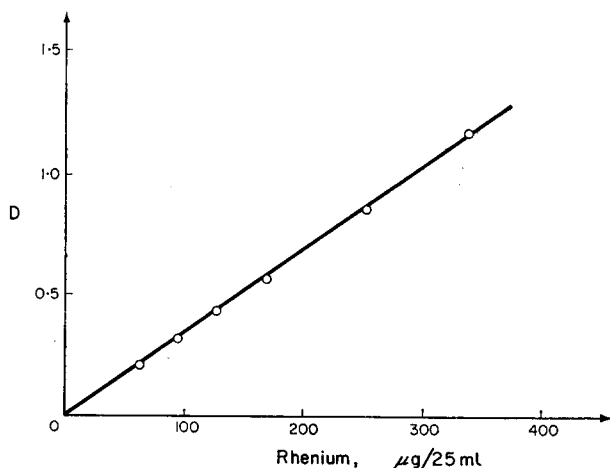


FIG. 7.—Relationship of optical density of rhenium-diphenylcarbazide complex solutions and rhenium concentration.

been developed for the analysis of rhenium-tungsten alloys. But the method proved to be valid for rhenium determination in a number of other alloys²⁵ since Co, Ni, Zn, Bi, Pb, Cr^{III}, Fe, Al, Ag, Ti, Cd and a 5-fold excess of Mo do not interfere in the reaction. Cu, V and Cr^{II} interfere.

In conclusion, it should be noted that rhenium has a great ability for complexing and all the possibilities, presented by the numerous complex rhenium compounds of lower valent states, with very varied properties, are far from being exhausted. When they have been fully studied, some of them will undoubtedly be used for the development of new methods for the determination of rhenium.

Zusammenfassung—Neuere spektrophotometrische Methoden zur Bestimmung von Rhenium werden beschrieben und diskutiert.

Résumé—Les méthodes spectrophotométriques récentes de dosage du rhénium sont décrites et discutées.

REFERENCES

- ¹ A. G. Philipenko and V. A. Obolonchik, *Ukrain. khim. Zhur.*, 1958, **24**, 506; 1959, **25**, 359.
- ² A. I. Lazarev and V. V. Rodzaevsky, *Zhur. analit. Khim.*, 1961, **16**,
- ³ W. Geilman and R. Neeb, *Z. analyt. Chem.*, 1956, **151**, 401.
- ⁴ V. A. Zarinsky and V. A. Frolkina, *Zhur. analyt. Khim.*, 1962, **17**, 75.
- ⁵ D. I. Ryabchikov, V. A. Zarinsky and I. I. Nazarenko, *ibid.*, 1960, **15**, 752.
- ⁶ D. I. Ryabchikov and L. V. Borisova, *ibid.*, 1958, **13**, 155, 492.
- ⁷ Y. A. Banovsky, A. F. Ievinsk and E. A. Luksha, *ibid.*, 1959, **14**, 714.
- ⁸ I. P. Kharlamov and P. Y. Yakovlev, *Zavodskaya Lab.*, 1961, **27**, 141.
- ⁹ T. I. Beckmann and M. Lederer, *J. Chromatog.*, 1961, **5**, 341.
- ¹⁰ D. I. Ryabchikov and Y. B. Gerlit, *Sb. Metody Opredeleniya Redkikh Elementov*. M. Izd. AN U.S.S.R., 1961, p. 528.
- ¹¹ D. I. Ryabchikov, V. A. Zarinsky and I. I. Nazarenko, *Zhur. neorg. Khim.*, 1961, **3**, 641.
- ¹² F. Druce, *Rec. Trav. chim.*, 1935, **54**, 334.

- ¹³ V. I. Bibikova, *Redkie Metally*, 1935, **6**, 24.
- ¹⁴ V. M. Tarayan, E. N. Ovsepyan and M. G. Ekimyan, *Doklady Akad. Nauk. Armyansk. S.S.R.*, 1957, **25**, 7; 1958, **27**, 33.
- ¹⁵ A. I. Lazarev, *Zhur. analit. Khim.*, 1959, **14**, 362.
- ¹⁶ D. I. Ryabchikov, L. V. Borisova and Y. B. Gerlit, *ibid.*, in the press.
- ¹⁷ D. I. Ryabchikov and A. I. Lazarev, *ibid.*, 1955, **10**, 228.
- ¹⁸ D. I. Ryabchikov and L. V. Borisova, *Doklady Akad. Nauk. S.S.R.*, 1962, **145**, 355.
- ¹⁹ T. M. Malutina, B. M. Dobkina and Y. A. Chernichov, *ibid.*, 1960, **26**, 259.
- ²⁰ E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 2nd Edition. Interscience, New York, 1950.
- ²¹ V. M. Dzionko, *Tezisy Dokladov na Soveshchaniy po Extraktzii v Analit. Khim.*, 1961.
- ²² D. I. Ryabchikov and L. V. Borisova, *Sb. Renii. M. Izd. AN U.S.S.R.*, 1961, p. 227.
- ²³ I. Noddack and W. Noddack, *Z. anorg. Chem.*, 1933, **215**, 129.
- ²⁴ R. D. Daftary and B. C. Haldar, *J. Indian Chem. Soc.*, 1960, **12**, 803.
- ²⁵ D. I. Ryabchikov and L. V. Borisova, *Zavodskaya Lab.*, in the press.

THERMOANALYTICAL INVESTIGATIONS OF HIGH TEMPERATURE FUSION REACTIONS

L. ERDEY and S. GÁL

Institute for General Chemistry, Technical University, Budapest XI
Gellért tér 4, Hungary

(Received 18 June 1962. Accepted 16 July 1962)

Summary—Derivatographic investigations are reported of acid-base reactions in solid and molten phases at high temperatures. It is established that the derivative thermogravimetric and differential thermal analysis peaks characterise the strengths of the bonds formed and broken during the reactions. The Lewis electron theory is extended to high temperature acid-base reactions. Fusion with soda and the Lawrence Smith fusion are investigated by derivatographic and other analytical methods.

FOR some time we have been carrying out a systematic investigation of the basic methods of gravimetric analysis to obtain statistically evaluable data on their accuracy. A number of precipitates as well as reaction mixtures have been examined for this purpose at high temperatures to determine the optimal conditions of heat treatment.^{1,2,3} For these experiments a universal thermobalance, the derivatograph, was developed with which thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermoanalytical (DTA) examinations could be carried out simultaneously on the same sample.^{4,5} The results reported in this paper were obtained with this thermobalance.*

HIGH TEMPERATURE REACTIONS

The derivatograph has been found suitable for the investigation of analytical reactions taking place at high temperatures. These reactions can be divided into:

1. acid-base reactions,
2. redox reactions.

High temperature acid-base reactions occur without any changes in oxidation numbers, and only the co-ordination relations of the atoms or ions are changed during the process. The interpretation of these reactions can be made either by the introduction of ionisation potentials, electron affinities and ionic potentials, by the concept of electronegativity, by the polarity of chemical bonds, with deformability and polarisation, or by complex chemical treatments. However, the solution of the chemical problems is tedious using any of the mentioned theories. The temperature intervals of energy and weight changes occurring in high temperature reactions are relatively easily measurable by the different methods of thermal analysis and, in our experience, the maxima of differential thermal analysis as well as derivative thermogravimetric curves characterise well the strengths of the bonds which are formed and broken

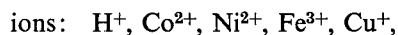
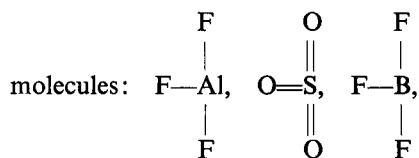
* The industrially produced derivatograph (system: Paulik-Paulik-Erdey, Type Orion-Gyem 676) was employed.

during the reactions. It became apparent to us to use the maxima of thermoanalytical curves for characterising the reaction ability of the components taking part in high temperature reactions.

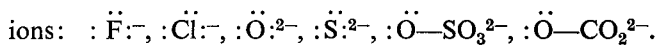
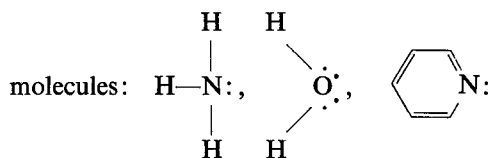
This idea can be supported theoretically by the fact that according to the principle of equipartition, apart from the degrees of freedom of transition and rotation there is also energy corresponding to the degree of freedom of oscillation, which is mostly important from the view of chemical bonds. This is proportional to the temperature. That temperature, therefore, at which a chemical bond disappears and a new one is formed is proportional to the strength of the chemical bond, or at least there exists some dependence between these two data.

All analytical acid-base reactions are connected with changes in the co-ordination relations, both if volatilisation, precipitation or dissolution as well as proton exchange, complex formation or complex decomposition takes place. The most general interpretation of these reactions, valid also for high temperature systems, can be made, in our opinion, in terms of the Lewis acid-base or electron theory. It is interesting, that while this theory made clear a number of organic reactions, for inorganic and all high temperature reactions it was hardly used. This is because for reactions taking place in solutions the Brönsted, Lowry, Franklin and Uszanovits theories give fairly descriptive pictures, and because of the nivellating and differentiating effect of the solvents the phenomena can be treated relatively simply. In high temperature reactions, however, the protolytic and solvolytic effect of the solvent fails in most cases, and so it is very difficult to find an adequate measure for the relative strengths of acids and bases.

According to the Lewis electron theory, bases are those atoms, ions or molecules, which have donatable electron pairs, while acids are those entities which are able to accept these electron pairs. According to this theory, some examples of acids are as follows:



and of bases:

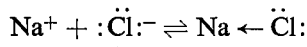


THEORY OF ACID-BASE REACTIONS

The essence of acid-base reactions is, therefore, the formation of a co-ordinative covalent (dative) bond. The result of the reaction is in most cases a complex, which may have further acid-base characteristics; thus, the reaction is not finished by the formation of a so-called neutral, salt-like product. According to the Lewis theory, cations are

generally acids. These are able to form strong co-ordinative covalent bonds, and the stronger their polarising effects are, the stronger the acids. A cation, therefore, can be regarded as a stronger acid the smaller is its diameter and the higher is its charge. Thus the proton is one of the strongest acids. Regarding the long periodic system, the acid strengths of cations in their most positive valencies increases from left to right. For this reason, for example, the cations S^{6+} , P^{5+} and N^{5+} are not stable, and always occur as neutralised forms containing oxygen ions, like SO_4^{2-} , PO_4^{3-} and NO_3^- ions. Sidgwick recognised that the ions of transitional metals are able to accept donatable electron pairs when co-ordinative covalent bonds are formed, and at the same time their incomplete electron shells are stabilised. The transitional metal ions, therefore, are strong acids.

Because the co-ordinative covalent bond is the stronger, the stronger a base (the ligand) can be polarised, therefore the strength of acids depends also on the strength of the bases bound to them. Among the elementary anions the halide ions and the amphoteric elements are the strongest bases and of these the fluoride and oxygen ions are the strongest. The base strength of strongly polarisable ions, having a great diameter, increases more strongly with increase of temperature, in our experience than that of less deformable ones. In the heating of cation acids, electrons in the outer shell become excited, they jump into the outermost orbit and so it becomes possible for the electron shell to accept an electron pair. This means that the acid strength of cations having a stable s^2p^6 -electron shell also increases at higher temperatures, and so the ion should be able to form a co-ordinative covalent bond under these circumstances. The volatilisation of ionic-type salts can be explained by the same principles. Thus, for example, in the volatilisation of sodium chloride the following reaction takes place



and so the process can be regarded as a chemical process, as a neutralisation. This explanation is supported by the fact that the distance of the nuclei in sodium chloride vapour is 2.5 Å while that in the sodium chloride crystal is 2.8 Å, which corresponds to fairly overlapped electron orbits, *i.e.* formation of a strongly covalent-type bond in the vapour.

From the view of fusion reactions it is essential that the covalent character of the acid-base bond increases with increase of temperature; the greater the increase, the more covalent is the character of the bond at low temperatures, the extent depending on the covalent character. At a sufficiently high temperature the orbit of that electron pair, which produces the bond, becomes deformed to such an extent that it will go round both nuclei. At this critical temperature the substance volatilises. The boiling point of substances, therefore, is reversely proportional to the strength of the acid-base bond between the ions. These phenomena can be well illustrated for the halides of the rubidium and thallium^I ions. Although the radii of the ions are almost the same, the boiling points of the thallium halides are much lower (see Table I). This means that in these compounds thallium^I is a stronger acidic cation than rubidium. Indeed, in spite of the equal ionic potentials (e/r) the thallium^I ion is more able to accept electron pairs than the rubidium ion, which has a closed electron octet, because the outer electron shell of thallium^I is incomplete. The fact that in the vapour phase the distances of nuclei are much smaller than in the crystal phase, which has the more close structure supports this theory. The order of base strengths of halides is the

TABLE I

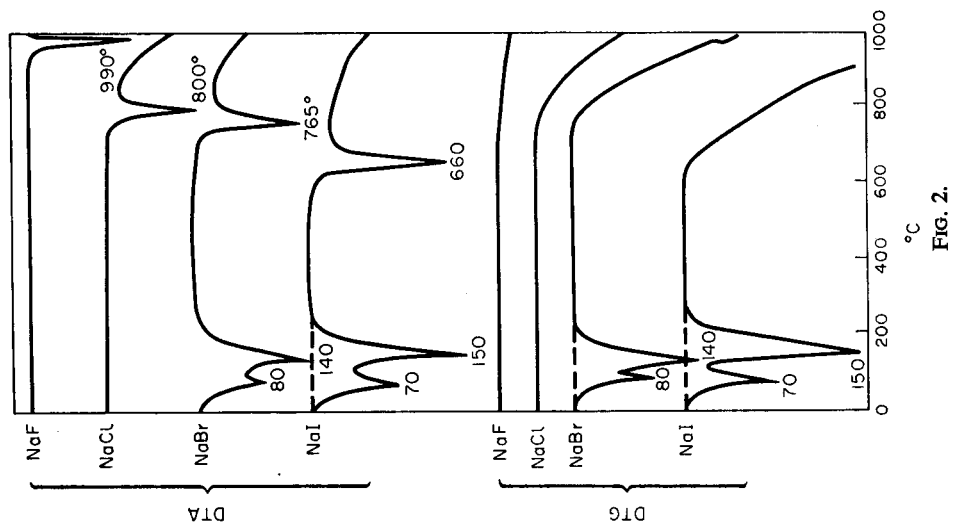
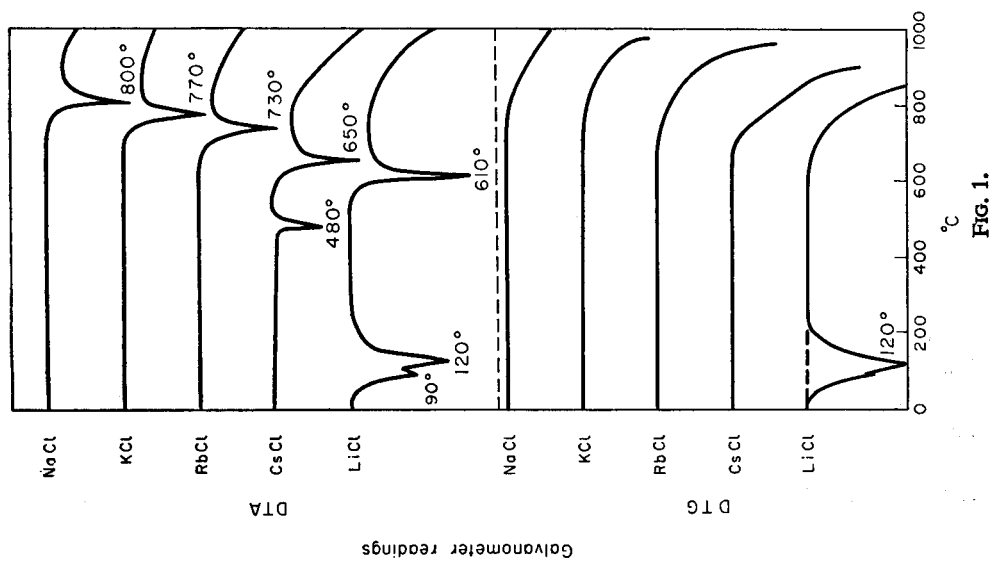
	Ionic radius, \AA	Boiling point, $^{\circ}\text{C}$		
		Cl^-	Br^-	I^-
Rb^+	1.49	1383	1350	1305
Ti^+	1.51	806	815	824

same as the order of ionic diameters, *i.e.* deformability; chloride is the weakest and iodide is the strongest base. The boiling points of the rubidium halides also decrease in the same order. With the thallium^I halides the order is reversed, because the thallium ion deforms more the chloride, having a smaller diameter, than the iodide with a greater diameter. Therefore, the thallium^I ion is a stronger acid in thallium^I chloride than in thallium^I iodide.

From the thermoanalytical curves in Fig. 1 the order of acid strength of the alkali metal ions can be read. The DTA and DTG maxima of lithium chloride at 90° indicate the departure of mechanically bound water, while those at 120° show the removal of crystalline water. The DTA maximum of caesium chloride at 480° indicates a modification-change. DTA maxima in the range $610\text{--}800^{\circ}$ correspond to the melting of the salts. The strongest cation acid is the sodium ion, while the weakest is the lithium ion. The DTG curves of the halides of the same alkali ion (see Fig. 2) show the order of base strengths of the halide ions. The strongest anion base among them is the fluoride ion, while weakest is the iodide ion. The DTA and DTG maxima at $70\text{--}80^{\circ}$ correspond to the departure of mechanically bound water, while those at $140\text{--}150^{\circ}$ show the departure of crystalline water. The DTA maxima at $660\text{--}990^{\circ}$ are from the melting of the salts.

The order of cation strength of the same cation in compounds with various anion bases may be different, which indicates that the temperatures corresponding to the maxima of thermal decomposition curves are a measure of the strength of the acid-base bond, but not the strengths of the individual cation acids and anion bases. A similar phenomena to this is that the order of acid strengths of proton acids can be changed by change of the solvent.

Among the proton-containing high temperature systems the ammonium phosphates of zinc, magnesium, cadmium and manganese are most important. In Fig. 3 DTG curves of these precipitates are to be seen. The precipitates were dried previously at low temperatures. From the decomposition curves it can be seen that the precipitates first loose their crystal water, and ammonia is removed only at higher temperatures. In every case the hydrogen phosphate ion is formed, and this ion loses its structural water only at still higher temperatures with formation of the corresponding pyrophosphate. The maximum corresponding to the departure of ammonia is correlated with the strength of the corresponding cation acid from which the following order was obtained: zinc > magnesium > cadmium > manganese. It is interesting that in this case the acid strength of magnesium is much greater than would be expected from its place in the Periodic System. The effect of cation acids appears in this case also in that they decrease the base strength (proton affinity) of phosphate ion, and so they increase the temperature of departure of ammonia. The dimerisation of phosphate takes place at lower temperatures in the case of transition metal ions than in that of magnesium ions. In these reactions, therefore, magnesium behaves like a weak acid.



Water is a typical amphoteric molecule, even according to the electron theory, because it is able to both accept electron pairs with formation of hydrogen bridge bonds, and donate the free electron pair on the oxygen. In crystal-water-containing substances water behaves in many cases both as an acid and as a base. Potassium is a

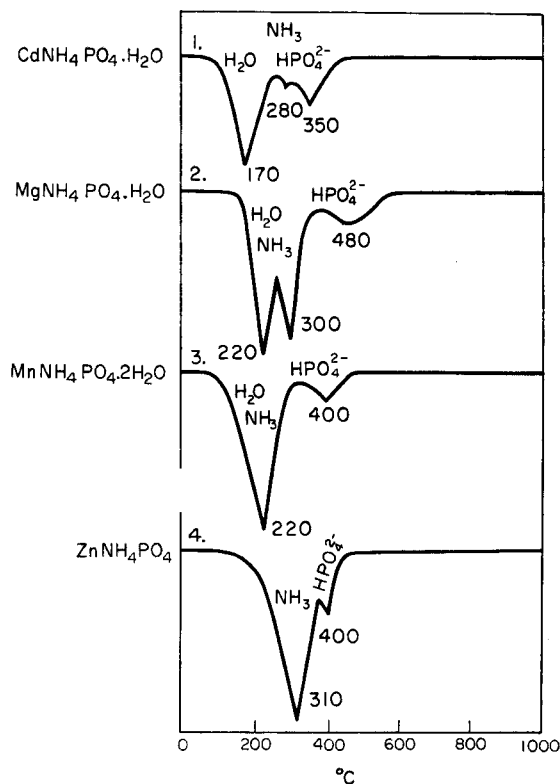


FIG. 3.

very interesting example of this behaviour (see Fig. 4). The potassium ion is fairly weak as a cation acid and therefore it lets free the four water molecules bound to it as bases. Aluminium, as a stronger acid cation, loses its six water molecules at much higher temperatures. Water, bound by hydrogen bridge bonds to the sulphate anion base, departs at an even higher temperature; this acid-base bond is therefore even stronger than the former ones. The strength of the aluminium cation acid is indicated also by the fact that at 760° (see the maximum at this temperature) aluminium takes up an oxygen ion from the sulphate ion and sulphur trioxide is partly removed, while for the potassium, being a weaker cation acid, the same reaction is not possible even at 1000°; therefore at this temperature the residue is a mixture of aluminium oxide and potassium sulphate.

Ammonium alum is analogous to potassium alum with the exception that in this case ammonium sulphate decomposes at first and aluminium sulphate only later, for the same reason as described before.

Systems containing no protons can also be treated in terms of the same theory. From the view of acidic and basic fusions the most important are those fusion agents

which are able to accept and donate oxygen ions. Among the alkaline fusion agents, alkali metal hydroxides and carbonates are the most important. In the melt of these, alkali metal cations and oxygen-containing anions are to be found.⁶ The acid strengths of alkali metal ions are the least among all other metal ions; in their presence therefore, all other metal ions are stronger acids. Alkaline fusion, according to the acid strengths of the Lewis acids present in the sample to be fused, may take place in three ways:

(a) In samples containing strongly acidic cations the cation tries to take up oxygen ions corresponding to its maximal co-ordination number, and so an exocomplex is

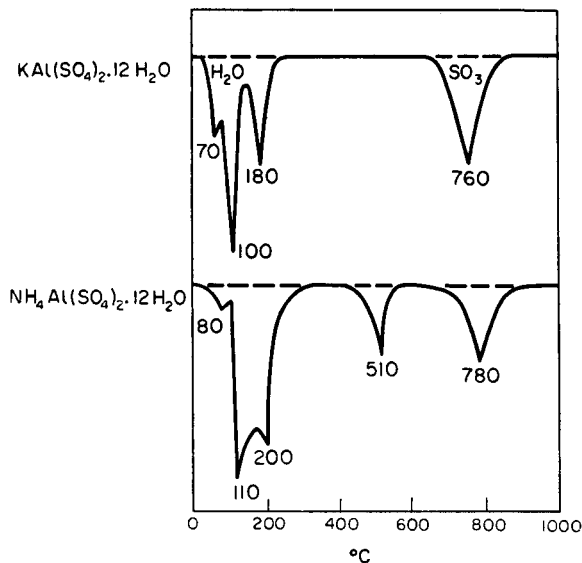
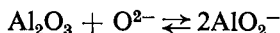
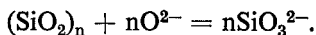


FIG. 4.

formed, which dissolves well in the melt and in water. Such a process takes place, for example, in the fusion of aluminium oxide with sodium carbonate, when a water-soluble sodium aluminate is formed (Fig. 6):



(b) Acids of medium strength try to form even by themselves a structure corresponding to the maximal co-ordination number:



(c) In the alkali fusion of samples containing weak acid cations an oxide or carbonate phase is formed, which does not dissolve either in the ionic-type melt or in water.

INVESTIGATION OF FUSION REACTIONS

Among the high temperature acid-base systems we investigated fusion with sodium carbonate more thoroughly. In the melt of sodium carbonate the oxygen ion activity is especially high, and therefore it is a very good alkaline fusion agent. In Fig. 5 TG, DTG and DTA curves of pure sodium carbonate are to be seen. Two peaks (350 and 480°) can be observed in the DTA curve, indicating two endothermal transformations

which, however, are not connected with weight changes. These are, therefore, inversion points, indicating reversible recrystallisation. The huge endothermic maximum at 840° indicates the melting of the sodium carbonate (m.p. according to the literature is 850°). From the DTG and TG curves it can be seen that the weight decrease begins above 800°, and reaches its highest rate at 850°. Above this temperature the rate of weight-change decreases. After melting the rate of weight-change decreases because carbon dioxide can be removed from the viscose melt only slowly, so the latter will be saturated with carbon dioxide and the rate of decomposition decreases. The acid strength of sodium, which is a weak cation acid, increases with increase of temperature,

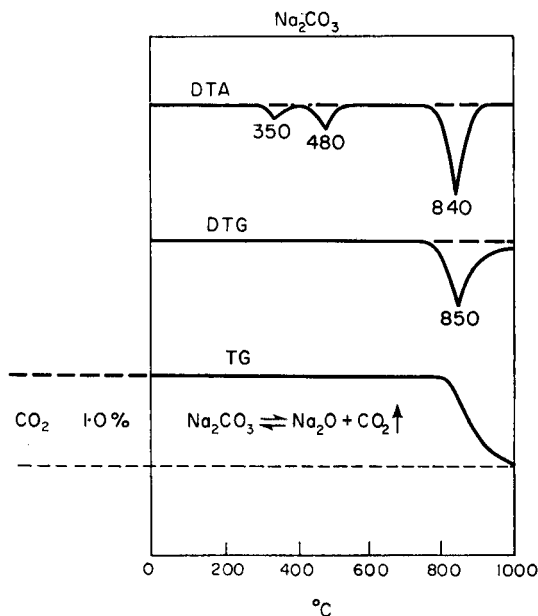


FIG. 5.

and reaches the acid strength of carbon dioxide above 800°. The weight loss is caused by the departure of carbon dioxide. Sodium oxide remains in the melt and so the oxygen ion activity increases steadily. Up to 1000° the carbon dioxide loss is about 1%.

In the experiments made with potassium carbonate formation of potassium oxide and departure of carbon dioxide were also perceivable. It could also be established from the curves that potassium being a weaker cation acid than sodium (because of its smaller ionic potential), the endothermic DTA peak, indicating melting, reaches its maximum only at higher temperatures (890°). The weight loss, measurable up to 1000° was about one third of that of sodium carbonate, which shows also the weaker cation acid character of the potassium ion. In practical silicate analyses it is well known that the fusion ability of potassium carbonate is worse than that of sodium carbonate, thus further proving our theories.

In Fig. 6 curves of a mixture of 4:1 moles of sodium carbonate and aluminium oxide are to be seen. The reaction starts above 680° and reaches its maximal rate at 850°. The area under the DTA curve shows that both the melting and the reaction heat are endothermic. According to calculations from the weight changes (using the TG and DTG curves), the formation of sodium meta-aluminate (NaAlO_2) is finished at 920°. The

reaction, however, does not stop at this stage, but goes on further to the formation of sodium ortho-aluminate. With such an excess of fusion agent aluminium oxide becomes completely fused. Further experiments have shown that in a mixture of 2:1 mole ratio, the fusion of aluminium oxide is only 97% complete and at a 1:1 mole ratio only 90%. In practice we suggest that the fusion of aluminium oxide should be made with the 4:1 mole ratio. With a mixture of sodium carbonate and sodium tetraborate the fusion of corundum can also be achieved; the temperature of the melt must, however, be raised in this case up to at least 850°.

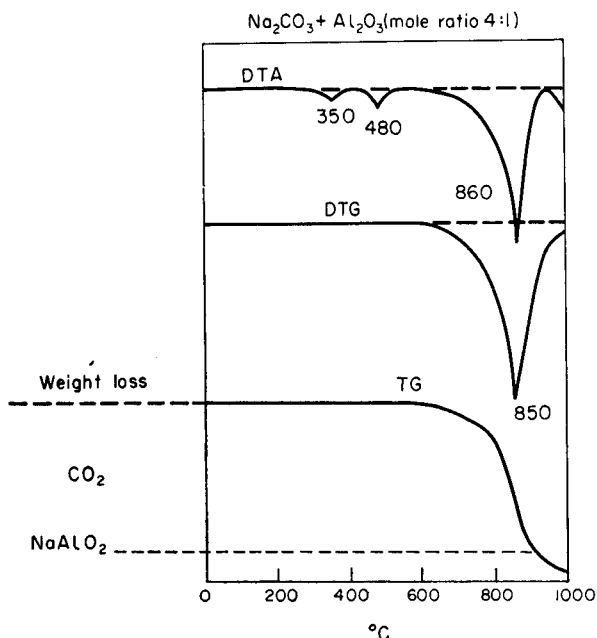


FIG. 6.

In Fig. 7 thermoanalytical curves of a 2:1 mole ratio mixture of sodium carbonate and silicon dioxide are to be seen. Reaction took place above 500°, still in the solid state, and after a maximal rate at 660° it became slower. On the granular surface of the solid silicon dioxide glass formation begins at much lower temperatures than the melting point of sodium carbonate. Maximal rate of glass formation is indicated by the DTA and DTG peaks at 660°. After a time, however, the path of diffusion becomes long because of the thick layer of glass on the surfaces, and therefore the rate of reaction decreases. At the melting of sodium carbonate (855°) the glass becomes depolymerised, and the silicate formed approaches the composition of sodium metasilicate. Depolymerisation increases with increase of temperature in the direction of sodium ortho-silicate formation. Carbon dioxide, liberated in the reaction, is slowly removed from the homogeneous melt, so the oxygen ion activity is decreased and the reaction becomes slower. Because of the decrease of viscosity, at about 930° the reaction becomes more rapid and the fusion becomes complete.

It can be perceived that because silicon is a stronger acid cation than aluminium, the reaction begins at a lower temperature and fusion is complete using a mixture of

2:1 mole ratio, while for the fusion of aluminium oxide at least a mole ratio of 4:1 is needed.

In Fig. 8 thermoanalytical curves of a sodium carbonate-barium sulphate mixture of 4:1 mole ratio are to be seen. Here TG and DTB curves show only small changes; the total weight loss is about 3%. The minimum at 740° on the DTA curve indicates where the fusion reaction took place. The reaction begins at 700°, and it has a maximal

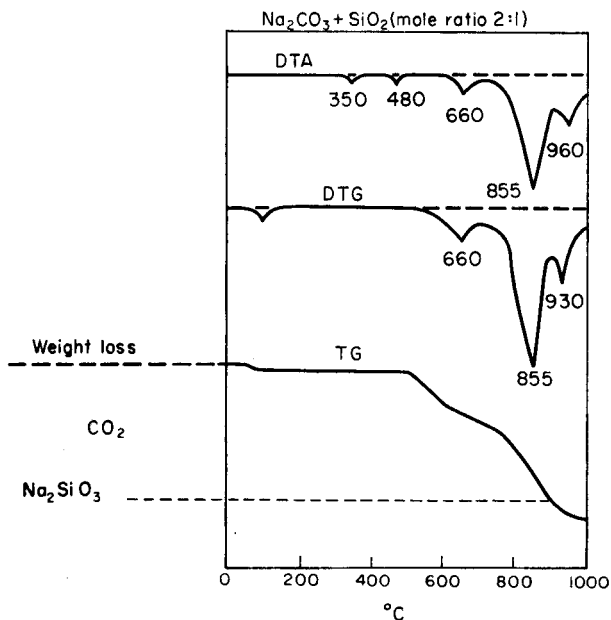


FIG. 7.

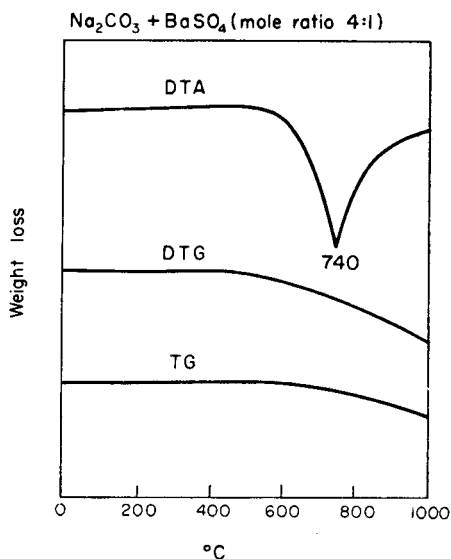


FIG. 8.

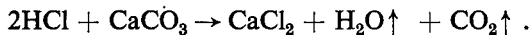
rate at 740° (DTA curve). The reaction begins in the solid phase and sodium sulphate, which is formed, decreases the melting point of sodium carbonate from 850° to about 740°. Fusion was, however, incomplete in these circumstances.

Among high temperature reactions, the Lawrence Smith fusion, used in the determination of the alkali metal content of silicates, has great importance. Silicates are heated with a mixture of calcium carbonate and ammonium chloride, being converted to calcium silicate, other metals to oxide and alkali metals to chloride. The method can be used both for acid-soluble and acid-infusible silicates.

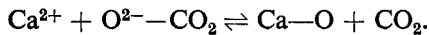
At the ignition the basic strength of the chloride ions of ammonium chloride increases to such an extent that the proton is removed from the ammonium ion and hydrogen chloride is formed:



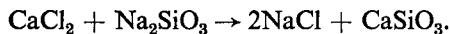
The proton, being present in hydrogen chloride, reacts as an acid cation with the strongly basic carbonate ion and calcium chloride is formed:



On further heating the acid strength of the calcium ion increases to such an extent that oxygen ion is removed from the carbonate ion (counter polarisation) and calcium oxide is formed:



Calcium oxide depolymerises the silicate and a monomer, sodium silicate, is formed. Silicate anion exchanges the slightly acidic sodium ions for the stronger acidic calcium ions:



On leaching the melt with water, sodium chloride is dissolved, while the calcium silicate, having covalent-type bonds, remains undissolved. Recently a mixture of calcium oxide and calcium chloride has also been used, this having the advantage that the temperature can be raised more rapidly. Stevens suggests the use of crystallised barium chloride instead of ammonium chloride, which has the further advantage over calcium oxide that sulphate (alunite) present in the silicate does not influence the alkali metal determination, because it remains undissolved in the form of barium sulphate after leaching.

We have investigated thoroughly the mechanism of the Smith fusion, using a felspar-type eruptive rock, potassium trachyte, for this work. The rock contains 9.3% of potassium oxide and 60.9% of silicon dioxide, of which 12% is present as free silicon dioxide. The rock was ignited at 1000° before the measurements.

In Fig. 9 a derivatogram of a mixture of 10% potassium trachyte, 10% ammonium chloride and 80% calcium carbonate can be seen. The DTA peak at 195° indicates a change of modification. The DTG peak at 350°, as well as the DTA peak at 375°, indicates the sublimation of ammonium chloride and the formation of calcium chloride. The endothermal DTA peak at 810° shows the beginning of the fusion, while the peak at 915° indicates the decomposition of calcium carbonate. Using a heating rate of 10°/min the recovery of alkali metal was 75%. The enthalpy change from the fusion reaction can hardly be perceived because the decomposition of calcium carbonate overlaps this process.

In Fig. 10 the derivatogram of a mixture of 40% trachyte, 40% calcium oxide and 20% crystallised calcium chloride can be seen. The crystal water of calcium chloride

is removed at 180°. The peak at 540° is characteristic for the decomposition of calcium hydroxide formed from calcium oxide, while at 620° calcium hydroxychloride [Ca(OH)Cl] decomposes. The peak at 785° indicates the fusion reaction.

The role of calcium chloride and calcium oxide in this system was investigated. Calcium oxide alone yielded a 0% alkali metal recovery, using a heating rate of 10°/min up to 1000°. The alkali metal output from a mixture of 50% trachyte and 50% calcium

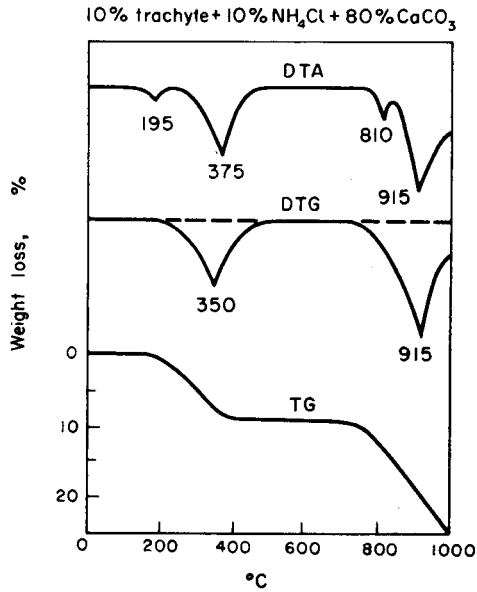


FIG. 9.

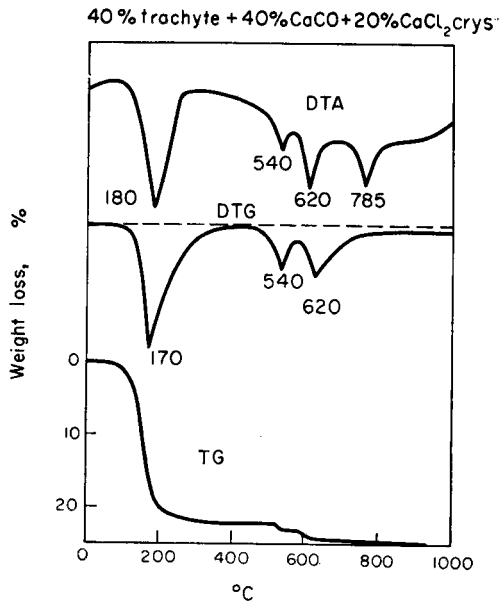


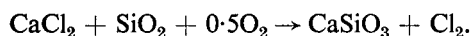
FIG. 10.

chloride was 57%. After adding 5% calcium oxide to the former mixture, the alkali metal recovery increased to 82%. Increasing the amount of calcium oxide to 50%, the alkali output became 96%.

Calcium chloride alone is also usable for the fusion, but the time required becomes very long. Furthermore, calcium chloride also reacts with the free silicon dioxide content of the silicates, and the following two reactions may take place, depending on whether there is water in the system or not. In the presence of water a hydrolytic reaction occurs:

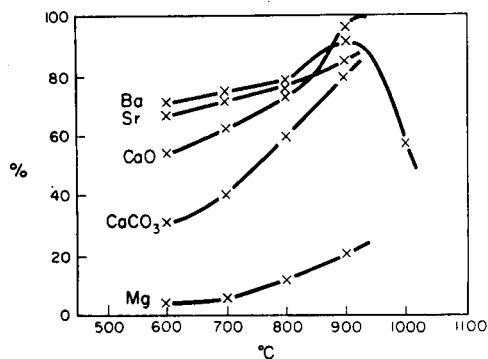


and in the presence of atmospheric oxygen the following reaction takes place:



In an inert atmosphere (argon) the two substances do not react, but calcium chloride begins to volatilise at about 1000°.

Calcium oxide has a double role in the fusion. The first one is that it reacts with the free silicon dioxide of the silicates and so prevents the reactions mentioned before. The second and more important role of calcium oxide is to carry out the depolymerisation of silicates and so the reaction between calcium chloride and silicates of smaller polymerisation grade (even perhaps monomer alkali metal silicates) can easily occur. At the same time the time required for the fusion becomes also essentially smaller. In our experience there is no need for the large excess of calcium carbonate or calcium



20 % chloride
40 % oxide
40 % potassium trachyte

°C	MgCl ₂ +MgO	CaCl ₂ ⁺ CaCO ₃	CaCl ₂ ⁺ CaO	SrCl ₂ ⁺ SrO	BaCl ₂ ⁺ BaO
600	4.3	30.9	53.9	66.8	70.8
700	5.4	39.9	62.5	71.7	74.3
800	11.5	59.4	73.1	75.8	78.1
900	20.1	79.8	96.9	84.7	91.2
1000	—	—	—	—	58.1

FIG. 11.

oxide recommended by Lawrence Smith in the fusion of trachyte; in most cases a fraction of this is quite sufficient.

In the literature alkaline earths other than calcium chloride and carbonate are also recommended for the fusion. For comparison, we made experiments with mixtures of chlorides and carbonates of magnesium, calcium, strontium and barium. A static method was used, temperatures were changed by 100° between 600 and 900°. In all cases the same experimental circumstances were used.

The results of these investigations are shown in Fig. 11. It can be seen that fusion begins even in the solid phase, and its efficiency becomes better and better near to the melting point. The graph shows well the order of acid strengths of the alkaline earth metal ions: magnesium is the strongest, then comes calcium and strontium, while barium is the weakest.

The curves also give data for the temperature of fusion. It should not be raised over 900°, because alkali metal chloride, formed in the reaction, begins to volatilise at this temperature. The optimal temperature of the fusion is about 850°.

The efficiency of the fusion reaction was investigated as a function of time with a mixture of calcium chloride and calcium oxide at 850°. A complete fusion was reached after 60 min, both in an electric furnace and in a Lawrence Smith crucible. After 60 min the potassium chloride formed volatilises considerably, and so the recovery of alkali decreases.

These experiments show that derivatography is a very useful method for the investigation of high temperature reactions and for clarification of the mechanism of such processes. In future studies we hope to make clear some other types of fusion reaction.

Acknowledgements—The authors express their thanks to György Liptay for carrying out part of the experiments. The merits of development of the derivatograph are those of Ferenc Paulik and Jenő Paulik.

Zusammenfassung—Es wird über derivatographische Untersuchungen von Säure-Basen-Reaktionen bei hohen Temperaturen in fester und geschmolzener Phase berichtet. Es wird gezeigt, dass die Spitzen in der derivierten thermogravimetrischen und differential-thermogravimetrischen Kurve die Stärke der während der Reaktion geformten oder gelösten Bindungen charakterisiert. Die Lewis'sche Theorie wird auf Hochtemperaturreaktionen ausgedehnt. Die Sodaschmelz und der Aufschluss nach Smith-Lawrence werden durch derivatographische und andere analytische Methoden untersucht.

Résumé—Les auteurs étudient les réactions acide-base à haute température dans les solides et les sels fondus par la thermogravimétrie dérivée. Ils montrent que les pics obtenus en thermogravimétrie dérivée (TGD) et en analyse thermique différentielle (ATD) sont caractéristiques de la rupture des liaisons chimiques au cours des réactions. La théorie de Lewis est étendue aux réactions acide-base à haute température. L'attaque par la soude fondue et la fusion de Smith sont étudiées par la thermogravimétrie dérivée et d'autres méthodes analytiques.

REFERENCES

- ¹ L. Erdey, *Periodica Polytechn. Hung.*, 1957, **1**, 91.
- ² L. Erdey, G. Liptay, S. Gál and F. Paulik, *ibid.*, 1961, **5**, 209.
- ³ *Idem, ibid.*, 1961, **5**, 287.
- ⁴ F. Paulik, J. Paulik and L. Erdey, *Z. analyt. Chem.*, 1958, **160**, 321.
- ⁵ *Idem, Bergakademie*, 1960, **12**, 413.
- ⁶ H. Lux, *Z. Elektrochem.*, 1939, **45**, 303.

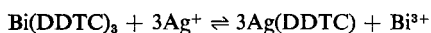
INDIRECT POLAROGRAPHIC DETERMINATION OF SILVER

M. KOPANICA and R. PŘIBIL

Laboratory of Analytical Chemistry, Polarographic Institute
Czechoslovak Academy of Science, Praha 1, Jilská 16, Czechoslovakia

(Received 20 June 1962. Accepted 23 August 1962)

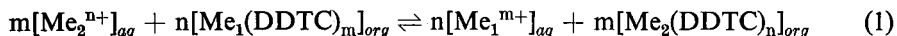
Summary—Conditions for the indirect polarographic determination of silver, based on the substitution reaction of silver ions with bismuth diethyldithiocarbamate dissolved in carbon tetrachloride



are reported. Liberated bismuth^{III} ions can be determined polarographically in the supporting electrolyte containing EDTA. Using this principle a method has been developed for the determination of silver in galenite and in silver alloys.

SILVER, being an electrolytically noble metal, produces no well-developed polarographic waves and the diffusion current of silver ions starts at zero applied e.m.f. Spálenka¹ used this phenomenon for the polarographic determination of silver in bronze and measured the shift of the lead wave above the zero current. In the present paper the substitution reaction of silver ions with bismuth diethyldithiocarbamate is studied as a possible means for the indirect polarographic determination of silver.

According to Bode² bismuth is extracted by diethyldithiocarbamate (DDTC) into carbon tetrachloride in the pH range 5–11, even in the presence of EDTA. The same applies to the extraction of silver. Because the stability constants of these carbamates differ considerably, substitution of bismuth ions by silver can occur. Eckert³ gives the sequence in the order of increasing stability for a series of carbamates of various metals as: Mn–As, Zn–Sn, Fe^{III}–Cd–Pb–Bi–Ni, Co–Cu–Ag–Hg. According to this series it is evident that, for example, mercury ions in aqueous solution displace Ag⁺, Cu²⁺, etc., from their DDTC complexes in an organic solvent. In this way Vašák and Šedivec⁴ determined mercury; similarly, Přibil *et al.*⁵ determined cobalt and Eckert⁶ manganese. The equilibrium used by these authors is illustrated by the equation:



where Me₂ is a metal, the complex of which with DDTC is more stable than that of the metal Me₁, and *org* and *aq* are the organic and water phases, respectively.

EXPERIMENTAL

Reagents

0.01 and 0.005M silver nitrate solutions: Prepared by dissolving metallic silver in nitric acid (1:1) and standardised gravimetrically.

5% bismuth diethyldithiocarbamate in carbon tetrachloride: Prepared by precipitation of bismuth from alkaline solution containing EDTA with a 1% solution of diethyldithiocarbamate in carbon tetrachloride. The formed Bi(DDTC)₃ complex was washed by shaking with an alkaline solution of bismuth-EDTA complex to remove the free DDTC, then with the ammoniacal buffer solution and

finally with water. The water extract of the solution prepared in this way did not produce a polarographic wave of the bismuth^{III} ion nor of free DDTC.

Solutions of other metallic salts were prepared from reagent grade chemicals. The ammoniacal buffer solution was prepared by mixing 200 ml of 0.5M ammonia solution, 200 ml of 0.5M ammonium chloride and 200 ml of 0.5M EDTA, and diluting to 1 litre with water.

Apparatus

Polarographic curves were recorded with a polarograph of type LP55 (Laboratorní přístroje, Prague, Czechoslovakia) with a polarographic cell used in conjunction with a saturated calomel electrode.

pH was measured with an electronic pH meter, Multoscop V (Laboratorní přístroje).

DISCUSSION

Displacement of bismuth^{III} ions from Bi(DDTC)₃ is based on the reaction given in (1).

A 0.01M aqueous solution of silver nitrate was prepared so that it was 0.1M with respect to both potassium nitrate and EDTA and the pH was adjusted to 5 by addition of aqueous ammonia or hydrochloric acid. Measured amounts of this solution were shaken for 3–5 min with 25 ml of 5% bismuth diethyldithiocarbamate in carbon tetrachloride in a separating funnel. After separation of the two phases, the aqueous layer was boiled for 1 min to remove traces of carbon tetrachloride. After cooling, 20 ml of ammoniacal buffer were added, the solution diluted to 100 ml with water, and the polarographic wave of the displaced bismuth^{III} ions recorded.

These experiments, carried out in the pH range 5–11, have shown that the height of the polarographic wave corresponding to the displaced bismuth^{III} ions remains constant and is in a molar ratio of 1 : 2.94 to the concentration of silver ions originally present in the solution. This ratio agrees quite satisfactorily with the theoretical value of 1 : 3 and therefore it is possible to formulate the substitution reaction as



Also, the experiments have shown that equilibrium (2) is established rapidly and the conditions employed can be used as a basis for the indirect polarographic determination of silver.

Quantitative displacement of bismuth occurs over a wide pH interval, but for analytical use a relatively high pH was selected (ammoniacal buffer), where the bismuth wave is not disturbed by the waves of other metals. In Table I a series of silver determinations is given at pH values of 6 and 9.5 and the results show that the described procedure is suitable and the error of the determination does not exceed that usual error of polarographic analysis.

Influence of other metals on the determination of silver

The selectivity of the indirect procedure described above for the determination of silver depends on the nature of the complexes of other metals with DDTC. According to the sequence of stabilities previously given, it is evident, for example, that Mn, As, Zn, Cd, Pb, Sn and Fe^{III} are not able to influence equilibrium (1), and because the polarographic determination of displaced bismuth^{III} ions is carried out in the presence of EDTA, all of these elements (with the exception of a large concentration of iron) do not interfere in this determination. On the other hand, mercury interferes because, like silver, it displaces bismuth^{III} from Bi(DDTC)₃. Up to a ratio of Cu: Ag = 2:1, substitution of copper for silver does not occur, but copper^{II} ions remain in the aqueous layer and produce a polarographic wave with a more negative half-wave

potential than that of bismuth^{III}. This could be eliminated by the addition of potassium cyanide to the supporting electrolyte. Employing 0.1M EDTA which contains 0.1M potassium cyanide and 10% (v/v) ethanol, bismuth can be determined even in the presence of a one hundred-fold excess of copper.^{7,8} It is, however, impossible to add potassium cyanide before the substitution reaction, because cyanide ions influence equilibrium (2) and considerable displacement of bismuth ions occurs.

TABLE I—DETERMINATION OF SILVER BY DISPLACEMENT OF BISMUTH FROM Bi(DDTC)₃

Ag taken, mg/25 ml	Displacement pH	Ag found, mg/25 ml	Δ, %
0.50	6	0.48	-4
	9.5	0.53	+6
1.00	6	0.95	-5
	9.5	1.03	+3
1.50	6	1.46	-3
	9.5	1.46	-3
2.00	6	2.08	+4
	9.5	2.00	0
2.50	6	2.60	+4
	9.5	2.42	-3

APPLICATION

Experimental results indicated that the procedure could be used for the indirect polarographic determination of silver present in amount from 0.005% upwards and it has been applied to the analysis of silver bronze and galenite.

Determination of silver in materials containing large amounts of copper

Dissolve 1 g of sample (silver bronze) in 10 ml of nitric acid (1:1) and evaporate the solution to a small volume. Dilute to 100 ml with water, neutralise with ammonia solution (1:1) and acidify once more by adding 5 drops of nitric acid (1:1). Add dil. hydrochloric acid to precipitate silver chloride quantitatively, then stand for about 0.5 hr. Filter and wash in the usual way. Dissolve the precipitate on the filter with 10 ml of ammonia solution (1:1), wash the filter-paper with 25 ml of the ammoniacal buffer and add to the resulting solution 0.5 g of ammonium chloride and 10 ml of 1M EDTA. Dilute to about 100 ml with water. Shake for 3 min with 50 ml of 5% bismuth diethyldithiocarbamate in carbon tetrachloride. After separation of the two phases, boil the aqueous layer for 1 min, then transfer it to a 100-ml volumetric flask and dilute to the mark with water. After removing oxygen with nitrogen, record the polarographic curve of bismuth from -0.2 to -1.0 V (saturated calomel electrode).

Determination of silver in galenite

Dissolve 1 g of sample in 25 ml of nitric acid (1:1), evaporate the solution to about 5 ml and, after cooling, dilute to 50 ml with water. Add 10 ml of 1M EDTA, neutralise with ammonia solution (1:1) to phenolphthalein indicator and add 10 ml of a solution 1M with respect to ammonia and 1M with respect to ammonium chloride. Shake 3 min with 50 ml of 5% bismuth diethyldithiocarbamate

in carbon tetrachloride. After separation of the two phases, boil the aqueous phase for about 1 min, transfer to a 100-ml volumetric flask, add 10 ml of 1M potassium cyanide, 10 ml of ethanol and finally dilute to the mark with water. Record the bismuth wave as described above.

The procedures described have been used for samples of bronze with 3.40% of silver, and for galenites which contained 75–85% of lead, and up to 0.1% of copper and silver in the range 0.35–0.55%. Results of these analyses are summarised in Table II, and the corresponding polarographic curves are shown in Fig. 1.

TABLE II—INDIRECT POLAROGRAPHIC DETERMINATION OF SILVER IN VARIOUS MATERIALS

Sample	Ag present, %	Ag found, %	Δ , %
Galenite 1	0.52	0.49	-6
	0.52	0.56	+7
Galenite 2	0.35	0.35	0
	0.35	0.33	-6
Silver bronze	3.40	3.31	-2.5
	3.40	3.45	+1.5

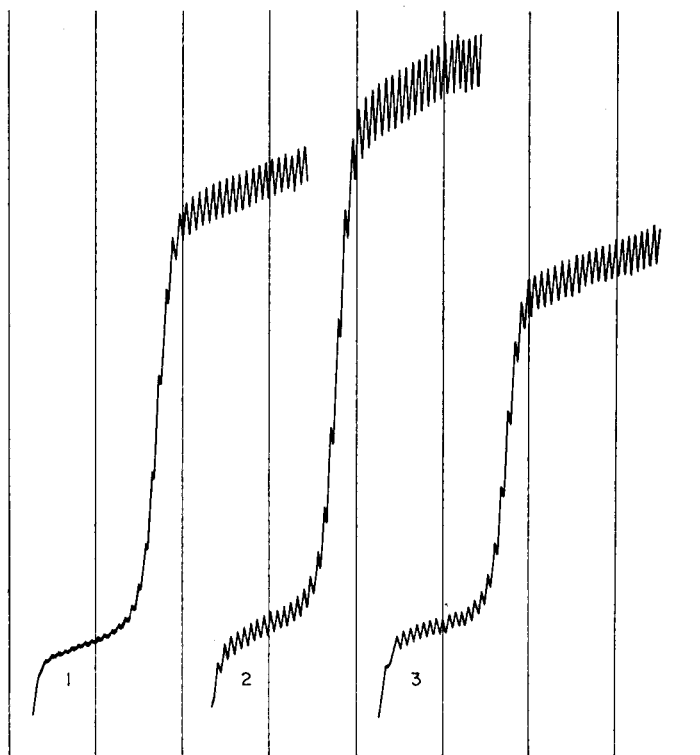
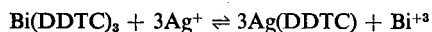


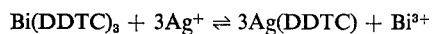
FIG. 1.—Determination of Ag in galenite:
 (1) sample 1 with silver content of 0.35%, sensitivity 1/7;
 (2) the same, sensitivity 1/5;
 (3) standard solution corresponding to 0.27% of silver.

Zusammenfassung—Bedingungen für die indirekte polarographische Bestimmung von Silber wurden gefunden, die auf einer Verdrängungsreaktion von Silber und Wismut-diäthylthiocarbamate in Tetrachlorkohlenstoff beruht. Das chemische Gleichgewicht kann wie folgt beschrieben werden



Das freigesetzte Wismut wird polarographisch in einer ÄDTE enthaltenden Grundlösung bestimmt. Mit der Methode wird Silber in Galena und Silberlegierungen ermittelt.

Résumé—Les auteurs ont mis au point le dosage polarographique indirect de l'argent, fondé sur la réaction d'échange entre les ions argent et le diéthylthiocarbamate de bismuth dissous dans le tétrachlorure de carbone. La réaction d'échange est:



Les ions Bi^{3+} libérés peuvent être dosés par polarographie dans un électrolyte support contenant de l'E.D.T.A. La méthode a permis le dosage de l'argent dans la gallène et différents alliages.

REFERENCES

- ¹ M. Spálenka, *Proceedings of First International Polarography Congress, Prague, 1951, Part III, 1952*, p. 433.
- ² H. Bode, *Z. analyt. Chem.*, 1954, **143**, 182.
- ³ G. Eckert, *ibid.*, 1957, **155**, 23.
- ⁴ V. Vašák and V. Šedivec, *Chem. listy*, 1951, **45**, 437.
- ⁵ R. Příbil, J. Jeník and M. Kobrová, *Coll. Czech. Chem. Comm.*, 1952, **19**, 470.
- ⁶ G. Eckert, *Z. analyt. Chem.*, 1955, **148**, 14.
- ⁷ M. Ishibashi, T. Fujinaga and M. Sato, *Bull. Inst. Chem. Research, Kyoto Univ. (Japan)*, 1956, **34**, 10.
- ⁸ G. Conradi and M. Kopanica, in press.

A SPECTROPHOTOMETRIC STUDY OF *p*-NITROSODIPHENYLAMINE AS A REAGENT FOR RHODIUM

JAMES R. STOKELEY and WILLIAM D. JACOBS[®]

Department of Chemistry, University of Georgia, Athens, Georgia, U.S.A.

(Received 22 June 1962. Accepted 21 August 1962)

Summary—The red colour produced by heating excess *p*-nitrosodiphenylamine with rhodium has been studied to determine the optimum conditions for the analytical use of the reagent. The absorbance curve of the coloured complex shows an absorbance maximum at 520 m μ when measured against a reagent blank. The reaction is carried out in a buffered solution at pH 5.4 and is allowed to stand at room temperature for 1 hr for colour development. Beer's law is obeyed over the range investigated, 0.62 to 4.34 ppm, the optimum concentration range being 1.0 to 3.8 ppm. The sensitivity of the reaction is 0.0054 μ g per cm². Samples containing 3.12 ppm of rhodium gave absorbance readings showing average and maximum relative deviations of 0.69 and 1.22%, respectively. Interferences of other platinum metals have been investigated.

INTRODUCTION

YOE and Overholser¹ introduced *p*-nitrosodiphenylamine as a sensitive colorimetric reagent for palladium. Later, in a study of some *p*-nitrosophenylamino derivatives,² they found that *p*-nitrosodimethylaniline and *p*-nitrosodiethylaniline possessed several advantages over *p*-nitrosodiphenylamine as colorimetric reagents for palladium; on the other hand, *p*-nitrosodiphenylamine allowed higher limiting concentrations of copper^{II}, iron^{III} and gold^{III}.

Few satisfactory spectrophotometric methods are available for rhodium. Beamish and McBryde^{3,4} have reviewed several spectrophotometric methods for the determination of rhodium. Sandell⁵ describes methods based upon the use of tin^{II} chloride and tin^{II} iodide. Tin^{II} iodide gives the more sensitive reaction with rhodium, but conditions must be more closely controlled. Jacobs⁶ describes a method using *N,N'*-bis(3-dimethylaminopropyl)dithio-oxamide. The main deficiency of all of these methods is their lack of sensitivity.

Wilson and Jacobs⁷ describe a method based on the cherry-red colour formed when aqueous-alcoholic solutions of rhodium are heated with *p*-nitrosodimethylaniline. Although the colour reaction is very sensitive, close control must be maintained over heating time and volume of solution heated. *p*-Nitrosodiphenylamine, although similar in many respects to its analogue, *p*-nitrosodimethylaniline, is comparatively free from these undesirable characteristics. On the other hand, its sensitivity is approximately one-fourth that of *p*-nitrosodimethylaniline.

EXPERIMENTAL

Apparatus

All absorbance measurements were made with either a Beckman Model DU or DK-2A spectrophotometer using matched silica cells of 1-cm light path. pH measurements were made with a Beckman Model G pH meter equipped with micro glass and micro calomel electrodes.

Reagents

Standard rhodium solution: Two g of rhodium^{III} chloride were dissolved in 500 ml of distilled water containing sufficient hydrochloric acid to give a 1M final solution. The rhodium content was determined by the method previously employed by Wilson and Jacobs.⁸ The standard solution contained 1.95 mg of rhodium per ml.

Working solutions were prepared daily, because, as described by Ayres,⁹ a change in chloride concentration tends to alter the rhodium species present. Obviously, this effect takes place on standing, because it was apparent in working solutions containing 78 μg of rhodium per ml and 0.04M in hydrochloric acid after standing for 1 day.

Reagent solution: *p*-Nitrosodiphenylamine was obtained from Aldrich Chemical Co., Inc. and was further purified by recrystallisation from 25% ethyl alcohol. A solution containing 0.5 mg per ml was prepared by dissolving 250 mg in 500 ml of absolute ethyl alcohol. It was stored in a flask with ground-glass stopper and was stable for at least 4 weeks.

Buffer solutions: Analytical grade reagents were used to prepare 2M solutions of sodium acetate, acetic acid and hydrochloric acid. Buffers of desired pH were prepared by mixing various volumes of either sodium acetate and acetic acid or sodium acetate and hydrochloric acid, all 2M. It was found that 2 ml of these concentrated buffer solutions, when diluted to 25 ml, gave the desired stabilised hydrogen ion concentration. The buffer in the recommended procedure was prepared by mixing 100 ml of 2M sodium acetate with 20 ml of 2M hydrochloric acid.

Solutions of diverse ions: Stock solutions of diverse ions were prepared in various concentrations so that a convenient volume could be used depending upon the extent of interference expected. All were prepared from nitrates and chlorides of the metal, except osmium which was prepared from potassium osmate.

Recommended procedure

Concentrate or dilute the sample such that it contains between 25 and 95 μg of rhodium per ml. Introduce a 1-ml aliquot of this solution into a 25-ml volumetric flask. Add 2 ml of sodium acetate-hydrochloric acid buffer of pH 5.3 and 5 ml of reagent solution. Dilute to the mark immediately with a stock solution of 95% ethyl alcohol. Allow 1 hr at room temperature for colour development and measure the absorbance of the sample at 520 $m\mu$ against a reagent blank which has been treated in a similar manner. Determine the rhodium content from a calibration curve.

RESULTS AND DISCUSSION

Description of rhodium complex

When a buffered, aqueous-alcoholic solution of the reagent, containing rhodium^{III}, is allowed to stand at room temperature, a red complex is slowly formed. The absorbance curve of a 3.12-ppm solution of the rhodium complex measured against a reagent blank and the absorbance curve of the blank measured against 95% ethyl alcohol are shown in Fig. 1. Considerable absorbance by the blank is evident at the absorbance maximum of the complex (520 $m\mu$); thus, all absorbance measurements were made using a reagent blank.

Effect of standing time

On heating in a boiling water bath, the rhodium complex forms within 1 min but rapidly decolourises to give brown-red solutions with reduced absorbance. Best results are obtained by allowing a buffered, aqueous-alcoholic solution of rhodium and the reagent to stand for 60 min at room temperature before measurement of the absorbance.

The absorbance of a sample containing 3.12 ppm of rhodium, 2 ml of buffer, 5 ml of reagent, and sufficient 95% ethyl alcohol to give a total volume of 25 ml was read after successive intervals of time from mixing. The results are shown in Fig. 2. The absorbance gradually increases and becomes constant 45 min after mixing. It remains constant for 30 min, then slowly decreases. The decrease in absorbance is associated with the formation of a brownish colour in the solution.

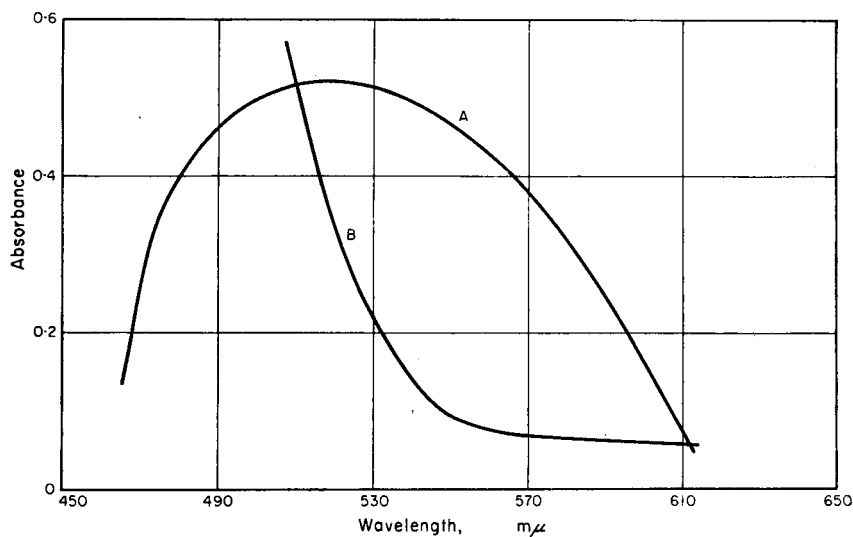


FIG. 1.—Absorbance curves for rhodium complex and reagent:
(A) 3.12 ppm of rhodium
(B) Reagent, $1.01 \times 10^{-3}M$

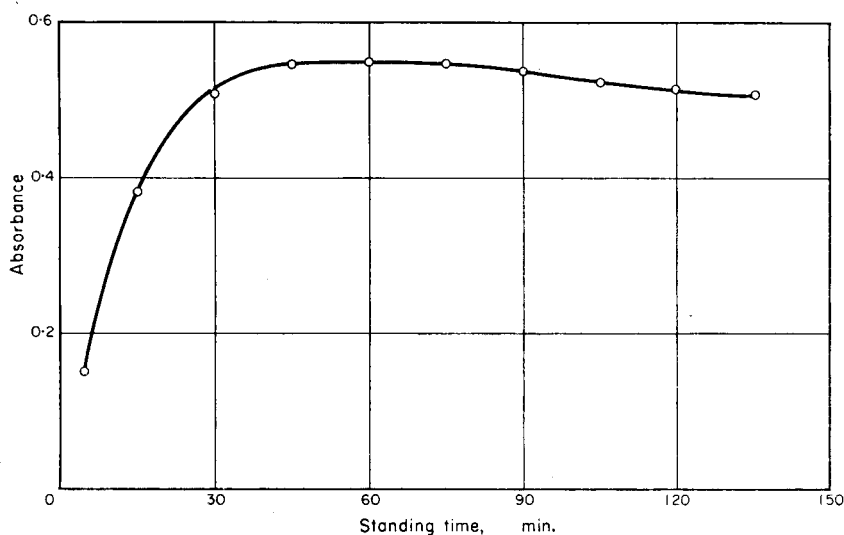


FIG. 2.—Effect of standing time on rhodium complex
(rhodium concentration, 3.12 ppm).

Effect of pH and buffer

No colour is formed in solutions of low pH even after standing 2 hr. In solutions of high pH the colour forms at once but discolouration becomes apparent immediately. Clear, red solutions of maximum absorbance are formed after standing 60 min with a sodium acetate-hydrochloric acid buffer of pH 5.3 or a sodium acetate-acetic acid buffer of pH 5.4. The variation of absorbance with buffer pH and the effect of the

buffer system used are shown in Fig. 3. Both buffer systems show approximately the same maximum absorbance, but, because the absorbance is less dependent on pH in the sodium acetate-hydrochloric acid system, this system is recommended.

Rather than affect the maximum absorbance, the pH serves to alter the rate of formation of the complex. An increase in pH is associated with increased rate of formation. Also, increased rate of formation is associated with rapid discoloration.

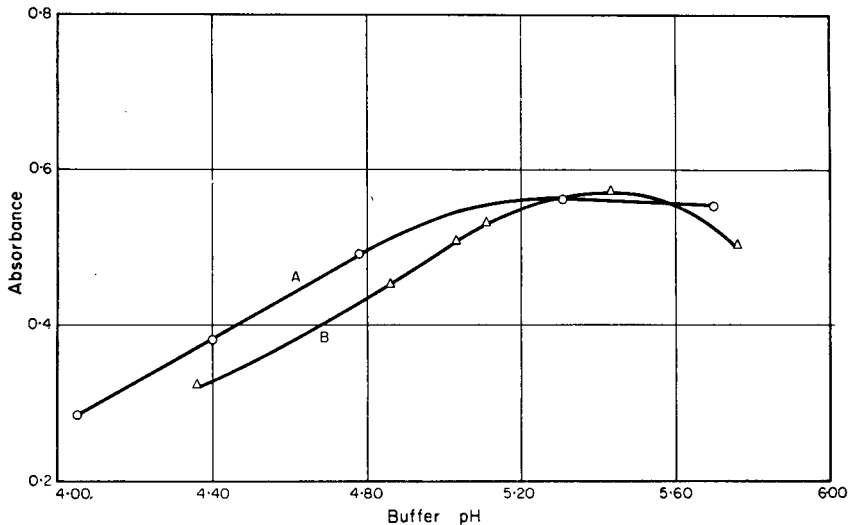


FIG. 3.—Effect of pH and buffer system:
(A) Sodium acetate-hydrochloric acid buffer
(B) Sodium acetate-acetic acid buffer

Effect of volume of water

The rate of colour formation is altered by the volume of water present in the solution. By increasing the volume of water, the rate of formation of the complex decreases.

The absorbance of solutions containing 3.74 ppm of rhodium (1-ml aqueous aliquot), 2 ml of buffer solution, 5 ml of reagent, varying volumes of water, and sufficient 95% ethyl alcohol to give a total volume of 25 ml was read after standing for 60 min at room temperature. The effect of the added volume of water on the absorbance is shown in Table I.

TABLE I—EFFECT ON ABSORBANCE OF VOLUME OF WATER ADDED

Volume of water added, <i>ml</i>	Absorbance (520 $m\mu$)
0	0.628
1.00	0.572
2.00	0.522
3.00	0.478
5.00	0.369
7.00	0.281

All solutions contained 3.64 ppm of rhodium

Effect of temperature

In addition to pH and volume of water, temperature affects the rate of formation of the complex. It was determined that by varying the temperature from 23 to 28°, an error of less than 3% is produced in the absorbance of a solution 3.12 ppm in rhodium. If a greater variation in room temperature is expected, a constant temperature bath is recommended.

Reagent concentration

A large molar excess of reagent over rhodium was found necessary to produce solutions of maximum colour intensity. However, too great an excess produces appreciable absorbance by the blank at the wavelength of maximum absorbance of the complex. As a compromise between sensitivity and absorbance by the blank at the wavelength of maximum absorbance of the complex, 2.5 mg of reagent per 25 ml of solution was employed.

Adherence to Beer's law

A series of 1-ml aliquots containing varying quantities of rhodium, 2 ml of buffer, 5 ml of 0.5 mg per ml reagent solution, and sufficient 95% ethyl alcohol to make a total volume of 25 ml was allowed to stand at room temperature for 1 hr. The absorbance of each sample was measured at 520 m μ against a reagent blank. These data show a linear relationship between concentration and absorbance over the concentration range investigated, 0.62 to 4.34 ppm of rhodium.

Sensitivity and precision

The sensitivity of the reaction as expressed by the notation of Sandell¹⁰ is 0.0054 μ g per cm².

The range of most accurate spectrophotometric measurements is 1.0 to 3.8 ppm.¹¹

When controlled according to optimum conditions, solutions containing 3.12 ppm of rhodium developed colours which gave maximum and average relative deviations of 1.22 and 0.69%, respectively.

Effect of diverse ions

Various ions were selected for study of their influence on the colour reaction. The metals tested were: iron^{III}, nickel^{II}, cobalt^{II}, copper^{II}, chromium^{III}, ruthenium^{III}, palladium^{II}, osmium^{VI}, iridium^{IV}, platinum^{IV} and gold^{III}. Anions tested were: sulphate, nitrate, bromide and iodide. Diverse ions were added individually to solutions containing 3.12 ppm of rhodium, and the colour was developed. Tolerance limits for the various foreign ions were taken as those concentrations which cause absorbance errors not exceeding 3%. The results are summarised in Table II.

Because all of the metal ions tested, except palladium^{II} and ruthenium^{III}, interfere by decreasing the absorbance, attempts were made to reduce the interference by masking the diverse ions with ethylenediaminetetra-acetic acid and by increasing the reagent concentration. Both attempts were unsuccessful.

CONCLUSIONS

p-Nitrosodiphenylamine has been found to be superior in some respects to *p*-nitrosodimethylaniline as a spectrophotometric reagent for microgram quantities of

TABLE II—EFFECT OF DIVERSE IONS

Diverse ion added	Concn. for 3% relative error, ppm	% Relative to Rh
Fe ^{III}	0.10	3.2
Co ^{II}	1.80	58
Ni ^{II}	2.52	81
Cu ^{II}	0.84	27
Ru ^{III}	0.20	6.4
Pd ^{II}	0.014	0.45
Os ^{VI}	0.24	7.7
Ir ^{IV}	0.72	23
Pt ^{IV}	0.88	28
Au ^{III}	1.75	56
Cr ^{III}	3.64	117
Sulphate	330	
Nitrate	10 ^a	
Bromide	10 ^a	
Iodide	250	

All solutions contained 3.12 ppm of rhodium

rhodium. Conditions for the development of the complex do not have to be controlled as rigorously in the *p*-nitrosodiphenylamine procedure as is required in the use of *p*-nitrosodimethylaniline. The sensitivity of the present procedure is about one-fourth that of the method using *p*-nitrosodimethylaniline. The two procedures are approximately equal with respect to quantities of diverse ions which can be tolerated.

Zusammenfassung—Wenn Rhodium mit überschüssigem *p*-Nitrosophenylamin erhitzt wird, entsteht eine rote Färbung. Die optimalen Bedingungen für diese Reaktion wurden im Hinblick auf eine analytische Verwertung ermittelt. Wenn gegen eine Reagensblindlösung gemessen, zeigt die Probe bei 520 *mμ* ein Absorptionsmaximum. Die Reaktion wird in einer Pufferlösung von pH 5.4 ausgeführt und 1 Stunde ist als Stehzeit vorgesehen um ein Maximum der Farbtintensität zu erzielen. Im untersuchten Bereich, 0.62 bis 4.34 ppm Rhodium, ist Beer's Gesetz erfüllt. Der optimale Konzentrationsbereich ist 1–3.8 ppm. Die Empfindlichkeit der Reaktion beträgt 0.0054 μg per cm^2 . Proben mit 3.12 ppm Rhodium ergaben Absorptionablesungen mit einer mittleren und maximalen Abweichung von 0.69 bzw. 1.22%. Die Störungen durch andere Platinmetalle wurden untersucht.

Résumé—Les autres ont étudié le complexe rouge formé en chauffant un excès de *p*-nitroso diphenylamine avec du rhodium. Ce complexe présente un maximum d'absorption à 520 *mμ*. La réaction est effectuée en solution tamponnée à pH 5,4. La coloration se développe en une heure à la température ordinaire. La loi de BEER est suivie de 0,62 à 4,34 ppm de rhodium. Le domaine de concentration optimal est compris entre 1,0 et 3,8 ppm. La sensibilité de la réaction est de 0,0054 μg par ml. L'erreur moyenne au cours du dosage de 3,12 ppm de rhodium a été de 0,69%, l'erreur maximale de 1,22%. L'influence des autres métaux de la mine du platine est étudiée.

REFERENCES

- ¹ J. H. Yoe and L. G. Overholser, *J. Amer. Chem. Soc.*, 1939, **61**, 2058.
- ² *Idem, ibid.*, 1941, **63**, 3224.
- ³ F. E. Beamish and W. A. E. McBryde, *Analyt. Chim. Acta*, 1953, **9**, 349.
- ⁴ *Idem, ibid.*, 1958, **18**, 551.
- ⁵ E. B. Sandell, *Colorimetric Determination of Traces of Metals*. Interscience Publishers, New York, 3rd Ed., 1959, p. 769.
- ⁶ W. D. Jacobs, *Analyt. Chem.*, 1960, **32**, 514.
- ⁷ R. B. Wilson and W. D. Jacobs, *ibid.*, 1961, **33**, 1652.
- ⁸ *Idem, ibid.*, p. 1652.
- ⁹ G. H. Ayres, *ibid.*, 1953, **25**, 1622.
- ¹⁰ E. B. Sandell, *op. cit.*, p. 83.
- ¹¹ *Idem, op. cit.*, p. 97.

DIFFERENTIAL COULOMETRIC ANALYSIS

A HIGH-PRECISION TECHNIQUE AND ITS APPLICATION TO THE DETERMINATION OF DICHROMATE BY CONSTANT-CURRENT GENERATION OF IRON^{II} ION

R. G. MONK and G. C. GOODE

Atomic Weapons Research Establishment, U.K.A.E.A., Aldermaston, Berks., England

(Received 13 July 1962. Accepted 9 August 1962)

Summary—The application of the differential method of working to coulometric analysis is discussed. Experiments are described on the differential constant-current coulometric titration of potassium dichromate with iron^{II} ion to establish the validity and precision of the technique. Using "Primary Volumetric Standard" potassium dichromate as standard, "Analytical" and "Laboratory Reagent" grades of material were assayed and a relative standard deviation of 0.006% was obtained

THE use of a differential technique for increasing the precision of a determination by an instrumental method is now well-established practice in the field of spectrophotometry and has recently been applied to polarography.¹ Briefly, the principle is that the instrument is used to determine the small difference in the particular physical property being measured between the sample and an accurately known standard. Thus the percentage error on the total quantity being determined is very much less than that of the instrumental measurement.

There are practical limits to the extent to which the overall error may be reduced in this manner, such limits depending on the instruments and techniques used. However, a relative standard deviation of 0.03% has been obtained in the differential spectrophotometric determination of uranium² compared with the 1–2% normally observed in the measurement of absorbance with a spectrophotometer. It is reasonable to suppose that even greater precision than this could be attained by the use of a differential technique with an instrumental method which is itself of high inherent accuracy. For example, if a method having a standard deviation of 0.1% were used to determine a difference of 1% between a sample and standard, the overall standard deviation would be only 0.001%; this, of course, assumes that other sources of error, such as weighing, can be kept below this level, and in practice these may be expected to contribute significantly to the total error.

Coulometry, whether operated under conditions of controlled potential or constant current, is an example of a highly accurate analytical technique which should be well suited to differential working. In either case, differential operation simply requires two cells connected in series, one containing the standard and the other a slightly larger weight of sample. After the exact completion of the electrolytic reaction with the standard, it is then necessary to measure the further quantity of electricity needed to complete the reaction with the sample.

The methods of operation of the two types of coulometry in the differential mode

would be expected to differ slightly. In controlled potential operation, the working electrode of the cell containing the standard would be first controlled, and electrolysis would be continued until the current fell to an appropriate low background value. At this stage, the control would be transferred to the working electrode of the sample cell, the coulometer being switched into the circuit, and electrolysis would be continued until the current again fell to background level.

In a differential coulometric titration most of the electrolysis could be carried out at a relatively high current which would not need to be precisely measured or controlled (it must, of course, not exceed the maximum current density corresponding to 100% current efficiency). During this time the indicator electrode potential of the cell containing the standard would be followed until fairly near the end-point; at this stage the large current would be switched off, and electrolysis would be continued to the end-point using a smaller, but accurately measured, constant current. The observation of the indicator electrode potential would then be transferred to the sample cell, and the electrolysis would be timed accurately to the second end-point.

To establish the principle of differential coulometry we have carried out experiments on the determination of dichromate by titration with electrolytically generated iron^{II} ion at constant current, a system which is well known to be highly accurate and simple to carry out. Potassium dichromate supplied as a primary volumetric standard was used in preliminary experiments to evaluate the precision of the procedure, and this material was then used as a standard for assaying two other batches, one described as of "Analytical Reagent" quality and the other as "Laboratory Reagent".

The experiments were performed with relatively small amounts of material, and it was possible to arrange matters so that the differential quantity of electricity measured was 0–300 millicoulombs, which could be determined to an accuracy of about 0.2% from the product of time and current. For this purpose the current used was less than 1 mA and an elaborate constant current electronic unit was therefore unnecessary, the simple device of a high voltage battery in series with a high resistance being adequate for the purpose.

EXPERIMENTAL

Apparatus

The two identical electrolysis cells were 40 ml in capacity and similar in design to those described by Cooke and Furman.³ The main electrodes consisted of a 60 × 120 mm cathode of 48-mesh platinum gauze and a 50 × 5 mm anode of 30-SWG platinum sheet; the cathode was bent into cylindrical form and enclosed a 15-mm diameter Corning 7930 Vycor porous glass tube, closed at its bottom end and containing a 5% aqueous solution of sodium sulphate into which the anode dipped. Each cell was fitted with a 4-mm glass tube drawn out into a jet for passage of nitrogen through the solution and with platinum and tungsten indicator electrodes, each consisting of about 3 mm of 18-SWG wire sealed into glass.

The constant current source, which delivered about 800 μ A, consisted of a 120-volt dry battery connected in series with a resistance of 150,000 ohms, and a 300-ohm \pm 0.1% resistance. The precise value of the current was determined by measuring the voltage drop across the 300-ohm resistance by means of a Pye portable potentiometer. During a determination involving passage of 800 μ A for up to 15 min, the current did not vary by more than 0.2%.

A Harwell-type 1350A Timing Unit was used to measure the time of electrolysis and to pass current through the cells by means of a relay-operated switch. With this unit the electrolysis current could be switched on or off for any required period of time or, by operation of another switch, current could be switched on for a pre-selected interval of 0.1, 1, 10, 120 sec or 20 min. In either case, the total time of operation was integrated by the unit and indicated on Dekatron tubes. The accuracy of the 1350-A unit is that of the mains frequency, which is always within 0.2%, and generally very much better than this.

The current of 100 mA used during most of the electrolysis was supplied by an Integrated Current

Source of the type developed by Smythe.⁴ This was used because it happened to be available, but a much less precisely controlled source would have served as well.

The potential across the indicator electrodes was measured with an Electronic Instruments Ltd. valve millivoltmeter which could be connected to either of the two cells by means of a double-pole, double-throw switch. A similar switch was used to connect the cells with either of the two current sources.

Reagents

0.6M iron^{III} solution: A solution was prepared containing 290 g of ferric alum, 140 ml of concentrated sulphuric acid and 40 ml of 85% phosphoric acid per litre. The iron^{III} content of this solution, determined coulometrically, was found to be $3 \times 10^{-5}M$.

Potassium dichromate solutions: Potassium dichromate, P.V.S. Grade, supplied by Hopkin and Williams Ltd., was used as the standard with which to compare samples of two other grades of material designated as "Analytical Reagent" (A.R.) and "Laboratory Reagent" (L.R.). Each sample was finely crushed in an agate mortar and dried for 1 hr at 140–150° before use. Standard solutions of each sample, containing approximately 12 mg of $K_2Cr_2O_7$ per g of solution, were prepared by dissolving about 2 g of the salt in water and diluting to about 150 ml. Potassium dichromate was weighed to 0.00001 g in stoppered glass weighing bottles, and the solutions to 0.0001 g in 200-ml stoppered polythene bottles. All vessels and solutions were conditioned in the balance case for 15 mins before weighing.

Procedure

The conditions used for the coulometric titration procedure were essentially those described by Cooke and Furman,³ care being taken, however, to ensure that reagent concentrations were the same in both cells; this is desirable to minimise errors caused by possible traces of oxidising or reducing impurities in the reagents. Twenty-five ml of 0.6M iron^{III} solution were pipetted into each cell, and weighed amounts of potassium dichromate solutions were also added from small polythene ampoules. The portions of dichromate contained 25–35 mg of $K_2Cr_2O_7$, a slightly larger amount being added to the sample cell than to the standard, but the difference not exceeding 0.2 mg. Weighings were made to 0.00001 g.

The magnetic stirrers were started, and nitrogen was bubbled through both solutions for 10 mins. The cells were then connected in series, the 100-mA supply was switched on, and electrolysis was allowed to proceed until the potential across the indicator electrodes of the cell containing the standard indicated approach of the end-point. At this stage the 100-mA current was replaced by the 800- μ A supply and the remaining dichromate in the standard was titrated by use of the timing unit, the end-point being determined in the usual way by plotting indicator electrode potential against time. The millivoltmeter was then switched over to read the indicator electrode potential of the sample cell, and the titration was continued to the second end-point.

RESULTS

Table I shows results obtained with the P.V.S. potassium dichromate in each cell; these results

TABLE I.—DIFFERENTIAL COULOMETRIC TITRATIONS WITH P.V.S. POTASSIUM DICHROMATE IN EACH CELL.

Cell 1	Wt. of $K_2Cr_2O_7$, mg		Diff. found	Error		
	Cell 2	Diff.		mg	% on diff.	% on whole
31.8018	31.8589	0.0571	0.0556	-0.0015	-2.6	-0.005
26.0717	26.1738	0.1021	0.1034	+0.0013	+1.3	+0.005
26.8650	27.0051	0.1401	0.1403	+0.0002	+0.1	+0.001
24.0915	24.2266	0.1351	0.1349	-0.0002	-0.1	-0.001
31.4975	31.6493	0.1518	0.1509	-0.0009	-0.6	-0.003

Relative standard deviation calculated on difference = 1.1%

Relative standard deviation calculated on whole = 0.004%

are summarised in the first line of Table II, which also shows the results in which the A.R. and L.R. samples were compared with the P.V.S. material.

DISCUSSION

The above results clearly establish the value of differential coulometry as a high precision analytical method. Using quite simple instrumentation, the relative standard deviation obtained for the differential titration of dichromate with electrolytically generated iron^{II} ion was only 0.006% and the method has enabled us to distinguish between very highly pure grades of potassium dichromate; further, all these measurements have been made with as little as 20–40 mg of material. It was noted above that there are generally practical limits to the improvement in precision attainable by using

TABLE II. DIFFERENTIAL COULOMETRIC TITRATIONS OF P.V.S., A.R. AND L.R. POTASSIUM DICHROMATE AGAINST P.V.S. MATERIAL

Sample	Series	No of determinations	% $K_2Cr_2O_7$		
			Mean	Std. dev.	Std. dev. of mean
P.V.S.	—	5	99.999	0.004	0.002
A.R.	A	3	100.009	0.007	0.004
A.R.	B	6	100.010	0.006	0.002
A.R.	All results	9	100.010	0.006	0.002
L.R.		5	99.964	0.006	0.003

Series A and B refer to two sets of determinations in which different solutions of both P.V.S. and A.R. potassium dichromate were used.

the differential technique. In the present instance, the relative standard deviation of 0.006% obtained corresponds to 1.1% calculated on the differential amount of potassium dichromate (0.05–0.15 mg) determined, as against 0.2% for the direct coulometric titration of dichromate at this level. This loss in precision is probably attributable to a number of errors which are normally negligible, such as weighing, but which begin to be effective when measurements are made to the third decimal place. In this connection, errors arising from differential titration of iron^{II} ion in the iron^{III} solution because of pipetting errors, cannot exceed 0.0002% of $K_2Cr_2O_7$.

The results obtained for the A.R. and L.R. samples of potassium dichromate are of interest in showing how very easily this material may be obtained with a high degree of purity, even the Laboratory Reagent being well up to Analytical Reagent standard. The figure of 100.010% for the A.R. dichromate may seem somewhat curious but it is suggested that the most likely explanation lies in the existence of polychromates. Both potassium trichromate, $K_2Cr_3O_{10}$, and tetrachromate, $K_2Cr_4O_{13}$, have been obtained by crystallisation of strongly acid solutions of potassium dichromate⁵ and it seems reasonable to suppose that the crystallisation of potassium dichromate could lead to incorporation of a slight excess of CrO_3 in the lattice if the acidity of the solution were higher than theoretical for $K_2Cr_2O_7$.

The present paper is concerned with the application of the differential principle to a constant-current coulometric titration, and we now plan to extend the work to controlled-potential coulometry. However, it seems to us that, as well as having high precision applications, differential coulometry might prove useful with systems in which generation of titrant falls short of 100%. Differential coulometric titrations of reasonable accuracy might thus become feasible for systems involving the generation of powerful oxidants and reductants which are accompanied by simultaneous evolution of oxygen or hydrogen, and which are unsuitable for normal coulometry; obvious examples are the generation of Ag^{2+} and Cr^{2+} .

Zusammenfassung—Die Anwendung einer Differentialmethode in coulometrischen Analysen wird besprochen. Experimente werden beschrieben zu differential coulometrischer Titration unter konstantem Strom für Dichromat mit Ferroeisen um die Brauchbarkeit der Methode sowie ihre Präzision zu zeigen. Unter Verwendung von urtiterreinem Kaliumbichromat wurden chemischreines und p.a. Material analysiert und eine Standardabweichung von 0.006% erhalten.

Résumé—L'application d'une méthode différentielle à la coulométrie est discutée. Le titrage coulométrique à intensité constante du bichromate de potassium par le Fer [II] est étudié afin d'établir la validité et la précision de la méthode. En utilisant du bichromate de potassium de pureté garantie comme étalon, et des réactifs de pureté analytique, les auteurs ont obtenu une précision de 0,006%.

REFERENCES

- ¹ H. I. Shalgosky and J. Watling, *Analyt. Chim. Acta*, 1962, **26**, 66.
- ² A. Bacon and G. W. C. Milner, *Analyst*, 1956, **81**, 456.
- ³ W. D. Cooke and N. H. Furman, *Analyt. Chem.*, 1950, **22**, 896.
- ⁴ L. E. Smythe, *Analyst*, 1957, **82**, 228.
- ⁵ J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*. Longmans, London, 1931. Vol. XI, p. 349.

ANALYTICAL APPLICATIONS OF THE FLAME EMISSION SPECTRA OF LEAD AND TITANIUM*

C. L. CHAKRABARTI†, R. J. MAGEE and C. L. WILSON
Department of Chemistry,

The Queen's University, Belfast, N. Ireland

(Received 17 July 1962. Accepted 1 August 1962)

Summary—The flame emission spectra of lead and titanium, weak emitters in an oxy-hydrogen flame, have been studied with a view to their analytical applications. Interference effects, especially on the titanium emission band at $\lambda 518\text{ m}\mu$, and methods for eliminating or reducing them, have been investigated. Methods for determining lead and titanium in their respective alloys, by the use of a standard addition technique, have been developed. These methods have been tested on suitable alloys; the results have a reproducibility of $\pm 4\text{--}5\%$ (coefficient of variation). The advantages and the limitations observed in this study have a general bearing on the application of flame photometry to other elements.

INTRODUCTION

THE elements of the Fourth Group of the Periodic Table are either weak emitters or are non-emitters in an oxygen-fuel flame. Of these elements only lead^{1,2} exhibits any emission lines, while titanium gives only a series of completely overlapping oxide bands in the mantle of an oxygen-fuel flame.

The lead emission line at $\lambda 405.8\text{ m}\mu$ has been successfully applied to the determination of tetra-ethyl lead in gasoline by flame photometry. This lead line is subject to spectral interference from manganese and potassium, but the interference can be eliminated by using a monochromator with adequate resolution and a very narrow slit-width. Also, this interference can be avoided by using the lead line at $\lambda 368.3\text{ m}\mu$.

The determination of lead by flame photometry has not received much attention because of the very low emission sensitivities of lead lines. However, as mentioned in an earlier study,⁵ the lead line at $\lambda 405.8\text{ m}\mu$ has been found to be suitable for the flame photometric determination of lead. The first part of this paper indicates the accuracy and the precision that may be obtained in the determination of lead in alloys by flame photometry. The second part deals with titanium.

EXPERIMENTAL

Apparatus

A Hilger H700 Uvispek Photo-electric Spectrophotometer, fitted with a Hilger H868 Flame Photometer Attachment, was used in the studies both of lead and of titanium.

Reagents

All reagents were of analytical grade.

I—LEAD

Flame spectrum

Fig. 1 shows the flame spectrum of lead in which the following experimental conditions were maintained: lead, 1000 ppm; a variable slit-width giving a bandwidth of about $1\text{ m}\mu$ throughout the wavelength region covered; pressures of hydrogen and oxygen at, respectively, 20 lb and 30 lb per in². The emission intensities were

* Presented at the Joint Meeting of the Scottish and North of England Sections of the Society for Analytical Chemistry, Queen's University of Belfast, N. Ireland, 28–29 June, 1962.

† Present address: Coates Chemical Laboratories, College of Chemistry and Physics, Louisiana, State University, Baton Rouge, 3, La., U.S.A.

measured on the galvanometer scale which was suitably modified for this purpose. The spectrum so obtained (by plotting the galvanometer scale readings) was found to be better than that taken with a recorder with a 0.5-mv full-scale deflection.

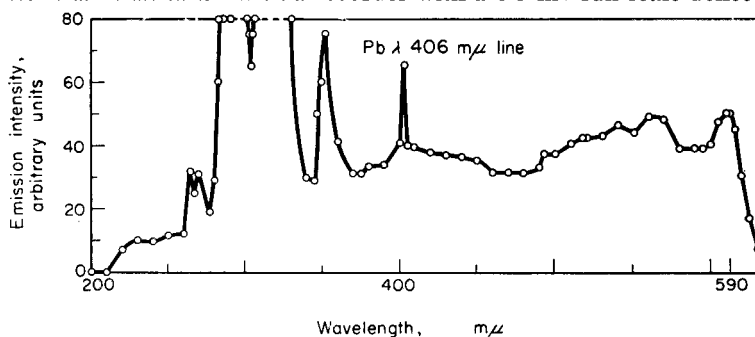


FIG. 1—Flame spectrum of lead.

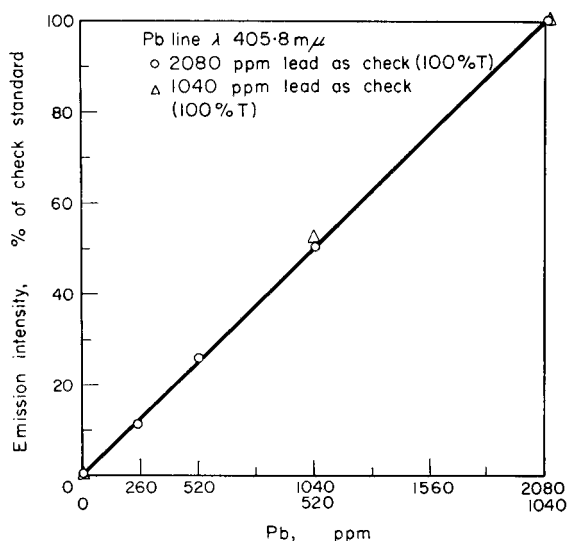


FIG. 2—Calibration curve of lead emission.

The characteristic feature of this spectrum is the lead line at $\lambda 405.8 \text{ m}\mu$. The other lead lines at $\lambda 283.3$, 287.3 , 364.0 and $368.4 \text{ m}\mu$ are overshadowed by stronger bands from the superimposed flame background. All other bands are from flame background, the most prominent of which are the OH $\lambda 306.4 \text{ m}\mu$ system, the Schumann-Runge O_2 emission system in the $\lambda 310\text{--}437 \text{ m}\mu$ region and the C_2 Swan bands in the $\lambda 437\text{--}653 \text{ m}\mu$ region (only up to $\lambda 610 \text{ m}\mu$ has been shown in the spectrum).

Calibration curve

By plotting the emission intensity of a series of standard lead solutions (expressed as the percentage of a check standard containing the highest concentration of lead selected for this study) as a function of the lead concentration, a linear curve was obtained for the range investigated, *viz.*, 260–2080 ppm of lead. This curve is shown in Fig. 2. Because the object of this study was to investigate the suitability of the flame

photometric technique for the determination of lead in lead alloys, concentrations of lead outside the above range were not investigated.

Selection of concentration limits

Because of the low emission sensitivities of the lead lines, a high concentration of lead is required in the test solution. For the $\lambda 405.8 \text{ m}\mu$ line, Dean¹ reports an emission sensitivity of 14 ppm of lead per unit percentage transmittance, which indicates that the check (100% transmittance standard) should contain at least 1400 ppm of lead.

In the absolute method of flame photometry, solutions containing known concentrations of the test element are compared with the unknown, and the concentration of the latter is determined in terms of the standard. In this method 100% transmittance is set for the highest concentration of lead to be studied and the lead content in the unknown is calculated from the relationship:

$$\text{ppm of lead (unknown)} = \%T \times 10^{-2} \text{ ppm of lead (check)} \quad (1)$$

When this method is applied, the concentration of lead in the unknown should preferably be very slightly less than that in the check standard solution. Apart from minimising any effects from self-absorption, this condition also minimises the percentage error in the final result introduced by an error in the measurement of transmittance. For example, curve A in Fig. 3 represents the possible percentage error that may be

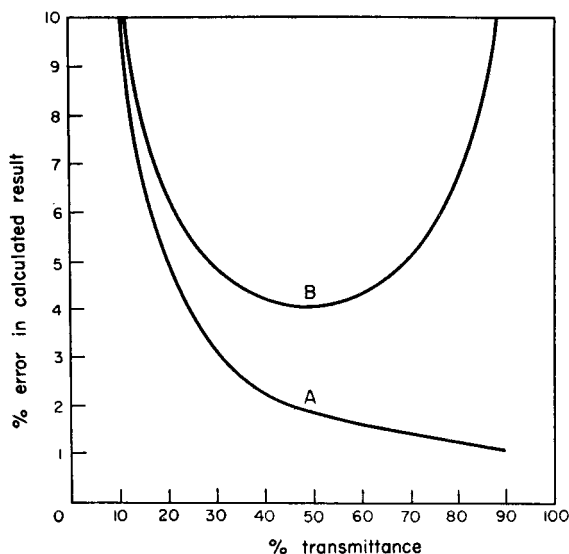


FIG. 3—Percentage error introduced into calculated lead content of sample by a 1% error in transmittance reading:

(A)—Assay measured directly against a standard lead solution.

(B)—Assay measured against a reference solution prepared by the method of internal standard addition.

introduced in the final results with direct reading of transmittance, assuming that there is a 1% error in the reading of transmittance. It is found from this curve that the concentration of lead in the unknown solution should be large enough to yield a reading of at least 40% transmittance, which with a minimum concentration of 1400 ppm of lead in the check standard, corresponds to 550 ppm of lead in the test solution.

If the test solution is prepared by dissolving 1 g of alloy and diluting to 100 ml, this 550 ppm of lead corresponds to 5.5% of lead in the alloy. This method, therefore, appears to be suitable mainly for alloys containing an appreciable amount of lead, *i.e.*, >1%.

In the analysis of metal alloys, difficulty arises in preparing standard check solutions of similar composition to the test solution. In these circumstances, in order to eliminate the effect of unknown interferences in the test solutions, the standard addition method was applied. The application of the standard addition method requires the calibration curve to be essentially linear. In this method the emission of the test solution is compared with that of an aliquot of the test solution to which a known amount of a standard lead solution is added. Because the concentration-transmittance graph is linear, the unknown concentration of lead within the range of the linear relationship can be calculated from the equation below:

$$\frac{x(v_1 + v_2)}{v_1x + v_2y} = \%T \times 10^{-2} \quad (2)$$

where x = concentration of lead in the unknown solution,

y = concentration of lead in the added standard solution,

v_1 = volume of aliquot of the test solution,

v_2 = volume of lead-standard added,

and $\%T$ = transmittance reading.

When this method is used, an error in the transmittance reading is magnified by the calculations involved. In Fig. 3, curve B represents the error in the result that may be introduced by a 1% error in the transmittance reading with the standard addition method. It can be seen from this curve that the transmittance reading should lie preferably between 40% and 60% if the errors are to be kept to a minimum. This corresponds to a minimum of 550 ppm and a maximum of 850 ppm of lead. These limits may be increased to higher values by using check solutions containing higher concentrations of lead but experience has indicated that the maximum concentration in the check solution should be limited to about 2000 ppm of lead. Above this limit the precision is impaired because the scale divisions correspond to larger units of lead concentration.

The optimum conditions for the flame photometric determination of lead with the Hilger Flame Photometer Attachment appears to be the adjustment of the test solution so that it contains 700–1000 ppm of lead, and the adjustment of the check solution (by addition of standard lead solution) so that it contains approximately twice the concentration of lead in the test solution. Studies of the precision have confirmed the suitability of these limits.

Precision

To determine the precision, multiple readings were taken using a standard solution of lead nitrate in distilled water and also test solutions prepared from lead alloys. The precision of the readings was calculated in terms of the standard deviation using the formula:

$$\text{standard deviation} = \sqrt{\frac{\sum x^2}{n - 1}}$$

where x is the deviation from the mean reading and n the number of readings. The following observations were made:

- (1) The best precision was obtained only within the optimum limits set earlier in this paper.
- (2) The precision is greatly improved by considering the mean of three readings, which emphasises that multiple readings, preferably nine for the optimum precision, should be taken with every test solution. Because a single reading takes less than 0.5 min and consumes only a very small volume of liquid, taking multiple readings is not considered to be a disadvantage of this technique.
- (3) If a single reading is taken, the average standard deviation indicates the possibility of errors of the order of $\pm 10\%$ (coefficient of variation) in the calculated lead contents of the sample. On the other hand, if the mean of three readings is taken, and only those samples which satisfy the concentration limits suggested earlier are considered, a precision of $\pm 3-5\%$ (coefficient of variation) is obtained. This precision gives a measure of the instrumental variables, *e.g.*, flame fluctuation, atomising rate, variation in drop size, *etc.*

Accuracy and reproducibility

Multiple samples of a number of alloys containing certified lead contents were analysed by flame photometry. The lead content of each sample was obtained by taking the mean of at least six transmittance readings in equation (2). The results obtained with these individual samples were used to calculate the reproducibility of the whole technique comprising both the sample preparation and the flame photometry proper. The reproducibility with lead was found to be $\pm 4.6\%$ (coefficient of variation). This can be compared with the reproducibility of $\pm 4.5\%$ (coefficient of variation) obtained with titanium, another weak emitter.

The lead content of each alloy was finally calculated by averaging the results obtained with three samples of the alloy. The results are set out in Table I.

TABLE I.—REPRODUCIBILITY AND ACCURACY OF LEAD ANALYSIS

Description of samples	Number of tests	Mean lead content found, %	Standard deviation, %	Coefficient of variation, %	True lead content, %	Error as % of lead content
Solder A: 43% Pb, 56.9% Sn.	9	40.9	± 2.5	6.1	43.0	4.9
Solder B: 60.1% Pb, 39.6% Sn.	12	60.1	± 3.8	6.2	60.1	0.0
White metal A: 3.90% Pb, 84.0% Sn, 7.50% Sb, 4.10% Cu.	4	3.63	± 0.15	4.1	3.90	7.4
White metal B: 84.5% Pb, 5.09% Sn, 10.4% Sb.	3	84.5	± 3.7	4.4	84.5	0.0

DISCUSSION

The main advantages of flame photometry include the relative speed of determination and a minimum of chemical preparation or element separation required before an analysis. Increased speed generally results in some loss in accuracy.

The flame photometric determination of lead possibly provides an extreme case, because the excitation of lead with an oxy-hydrogen flame results in lines of very low intensity. However, it has been established, by this study, that a satisfactory analysis can still be achieved if suitable limits of lead concentration are chosen and multiple readings are taken. The lead determinations are reproducible to $\pm 5\%$ (coefficient of variation). This low reproducibility arises from the instrumental variables inherent in the present flame photometer which give a reproducibility of $\pm 3-5\%$ (coefficient of variation) with standard lead solutions. It is, therefore, emphasised that the results obtained, in this study, represent the accuracy and precision that may be obtained by using the present flame photometer. Increased sensitivity can be obtained by using a photomultiplier attachment, and the precision could be improved by better instrumentation.

An alternative approach to increased accuracy and precision is that recommended by Dean,¹ who suggests the extraction of lead into organic solvents with direct aspiration of the organic phase into the flame. The enhancement of emission sensitivity caused by the organic phase has been clearly demonstrated with gasoline, but for safety reasons organic solvents should only be used with flame photometers fitted with an integral aspirator-burner. The Hilger attachment is fitted with a separate glass spray chamber. Because of the hazard of explosion within the glass spray chamber, the beneficial effect of organic solvents was not investigated in this study.

II—TITANIUM

Various methods have been used for the determination of titanium in metal alloys and other materials^{2,7} but there is no record of the use of flame photometry for its determination. Titanium does not exhibit any emission lines but emits a series of overlapping oxide bands. As mentioned in an earlier study,⁸ low emission intensity bandheads are given at $\lambda 497$, 518 and $715\text{ m}\mu$; the bandhead at $\lambda 518\text{ m}\mu$ has been found to be the most sensitive. However, many other oxide band systems emit radiations in the same spectral region.

Flame spectrum

Fig. 4 shows the flame spectrum of titanium in which the experimental conditions, *etc.*, were as for lead.

The following are the characteristic features of the spectra of titanium:

- (1) A series of completely overlapping bands originating from TiO.
- (2) The TiO bandhead at $\lambda 518\text{ m}\mu$.
- (3) The TiO bandhead at $\lambda 497\text{ m}\mu$, which is less sensitive than that at $\lambda 518\text{ m}\mu$.

All other bands are from flame background, the most prominent of which are the OH3064 Å system, the Schumann-Runge O₂ emission system in the $\lambda 310-437\text{ m}\mu$ region, and the C₂ Swan bands in the $\lambda 437-653\text{ m}\mu$ region (only up to $\lambda 620\text{ m}\mu$ has been shown in the spectrum).

The spectra obtained by plotting the galvanometer-scale readings were better than those taken with a recorder with a 0.5 mv full-scale deflection.

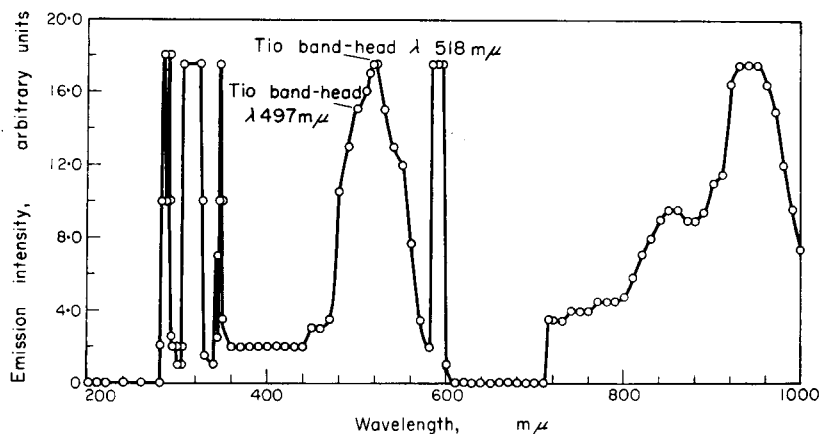


FIG. 4—Flame spectrum of titanium.

Calibration curve

The intensity of emission of a series of standard titanium solutions at $\lambda 518 \text{ m}\mu$ was measured against that of solutions containing from 10 to 2000 ppm of titanium as check standards. The results are shown in Figs. 5 and 6. It can be seen from these

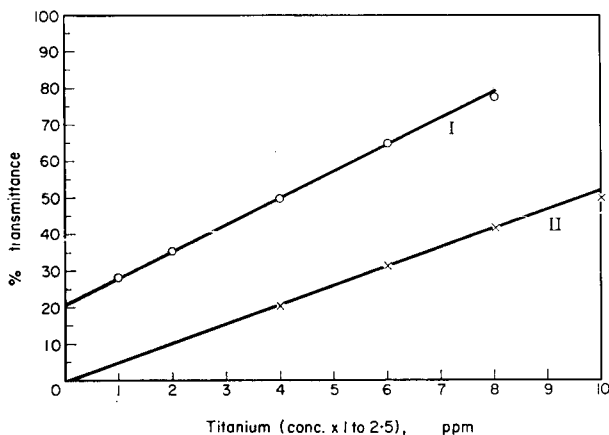


FIG. 5—Calibration curve of titanium emission at $\lambda 518 \text{ m}\mu$:
 (I) 0–10 ppm; check titanium, 10 ppm; slit-width, 1.0 mm.
 (II) 0–25 ppm; check titanium, 50 ppm; slit-width, 0.5 mm.

curves that the relationship between the intensity of emission and the concentration of titanium is linear when a check standard of 200 ppm or less of titanium is used. With higher concentrations of titanium in the test solutions and check standards, the calibration curves become convex in shape because of self-absorption, the convexity increasing with increasing concentration. At 1000 ppm or above, the calibration curve becomes parabolic, and the emission increases as the square root of the concentration.

Accordingly, for flame photometric studies, it is desirable, but not essential, to use a standard check solution containing from 10 to 200 ppm of titanium, and unknown test solutions of lower concentration. In these conditions, a precision in emission

readings (expressed as standard deviation) of $\pm 3.5\%$, corresponding to ± 7 ppm of titanium was obtained. By comparison, the precision obtained in emission readings when a 1000 ppm of titanium solution was used as check standard was $\pm 4.1\%$ corresponding to ± 41 ppm of titanium.

Interferences

Most of the metals which accompany titanium in a hydrous oxide analytical group separation were found to interfere with the flame photometric determination of titanium.

The presence of zirconium and phosphorus had little significant effect on the intensity of emission of a standard titanium solution, but the following elements enhanced titanium emission at $\lambda 518 \text{ m}\mu$, the magnitude of the interference effect decreasing in the order: $\text{Cr} > \text{Al} > \text{Mo} > \text{V} > \text{Fe} > \text{Mg} > \text{Na}$.

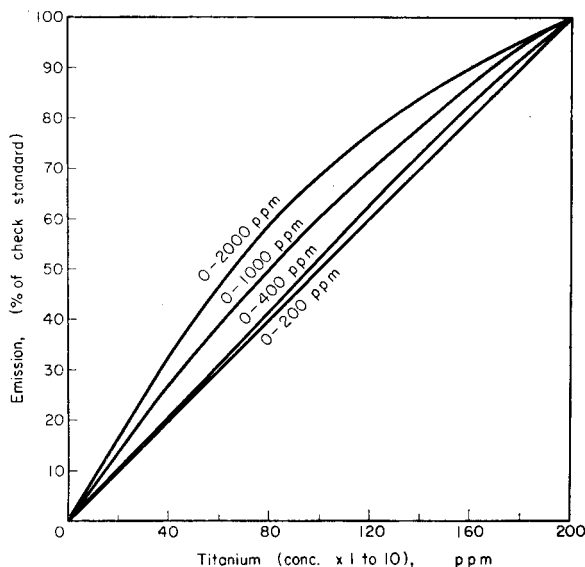


FIG. 6.—Calibration curve of titanium emission for 0-2000 ppm of titanium.

This list was not extended further, because the marked intensity of these interfering emissions demonstrated quite clearly that the flame photometric determination of titanium could be applied only to solutions which were virtually free from other cations. The determination of titanium in steel, alloys, *etc.*, by flame photometry thus requires an efficient preliminary separation of titanium from most other elements.

Because speed and simplicity are important attributes of flame photometric methods of analysis, the separation procedure used to isolate the titanium should also possess these attributes. A variety of methods of separation of titanium have been proposed⁶ but few satisfy the essential requirement of speed. Two suitable methods of separation are presented below.

(1) *Separation of titanium as hydrated titanium oxide.* A method^{9,10} of separation of titanium with ammonia as hydrated titanium oxide from a solution masked with EDTA, with magnesium sulphate acting as an accelerator, has been used in this study. This method has the disadvantage that the reproducibility of the separation is of the

order of $\pm 3.5\%$. For flame photometric determination, it is also necessary to reduce, by reprecipitation, the concentration of impurities in the product initially isolated; the remaining traces of impurities can be compensated by using the standard addition method. For the determination of titanium in titanium alloys, the results had a reproducibility of $\pm 4\%$ (coefficient of variation).

(2) *Separation of titanium by solvent extraction.* Titanium can be separated from many associated elements by forming a chelate with oxine, the titanium oxinate being extracted with chloroform. Because of the pronounced non-selectivity of oxine, most other elements interfere. However, the pH at which oxine complexes with various elements differs sufficiently to permit separation by a very close control of the pH. Further selectivity can be attained by the use of suitable masking agents or a combination of masking agents to inactivate the interfering species; a study of this extraction procedure has been carried out.¹¹ This method of separation has a reproducibility of about $\pm 5\%$ (coefficient of variation).

Flame photometry of titanium

Although titanium in an organic solvent can be aspirated straight into the flame with an integral aspirator-burner, thereby increasing the emission sensitivity of titanium many fold, such a procedure would be hazardous with the present atomiser-burner (with its glass spray chamber because of the possibility of explosion) and was,

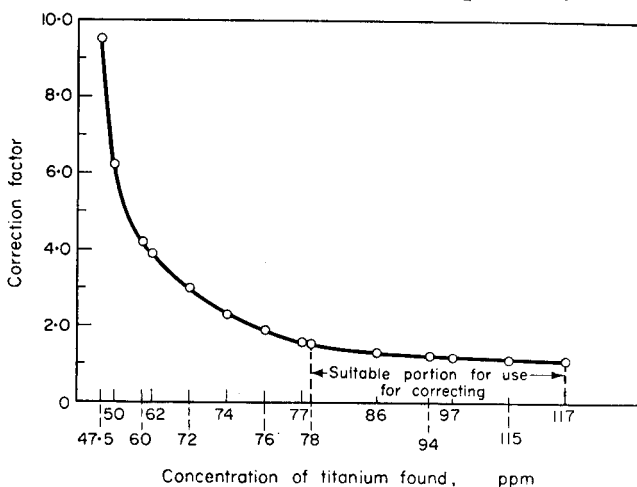


Fig. 7.—Correction curve for flame photometric determination of titanium.

therefore, not attempted. In the present procedure the organic extract containing titanium as the oxinate was washed with distilled water, then titanium was back-stripped from the organic extract with 20 ml of 10% sulphuric acid solution containing 3 ml of hydrogen peroxide (100-volume). Titanium reverted quantitatively into the aqueous phase, hydrogen peroxide facilitating this reversion by forming a very stable complex with titanium in the presence of sulphuric acid. This aqueous solution contained impurities which interfered with the titanium emission, and the standard addition method was therefore used. Even using this method, it was found that the titanium emission was systematically enhanced, but this enhancement could be compensated by a correction curve. Fig. 7 shows the correction curve which is nearly

linear from about 78–117 ppm of titanium (apparent value), corresponding to true titanium contents of about 50–104 ppm, respectively. The range above 117 ppm of titanium (apparent value) was not investigated. However, it appears from the slope of the curve that at higher concentrations of titanium, enhancement of emission from interferences progressively approaches a constant value. In order that the correction factor can be applied with the best results, it is, therefore, necessary to adjust the true titanium contents in the test solution to 50–104 ppm or possibly a higher concentration. The results have a reproducibility of $\pm 5\%$ (coefficient of variation) based on the average of single determinations. The results of titanium analyses are presented in Table II.

TABLE II—REPRODUCIBILITY AND ACCURACY OF TITANIUM ANALYSIS

(A) Titanium Separated as Hydrated Titanium Oxide

Description of samples	True Ti content, %	Number of tests	Single precipitation	Double precipitation	
			Standard addition method mean Ti content found, %	Standard addition method mean Ti content found, %	Calibration curve method mean Ti content found, %
Ferro-titanium (8% Al, 5% Si)	35.3	6	34.3	38.0	37.8
Error as % of Ti contents			-2.8	+7.6	+6.6
Aluminium-titanium alloy	70.1	6	67.5	70.6	66.1
Error as % of Ti contents			-3.7	+0.7	-5.7
Standard deviation of Ti, ppm (considering both alloys together)			± 14.1	± 5.4	± 7.6
Coefficient of variation, % (considering both alloys together)			± 10	± 4	± 6

(B) Titanium Separated by Solvent Extraction

Description of samples	Certified Ti content %	Number of tests	Mean Ti content found %	Standard deviation %	Coefficient of variation %	Error as % of Ti content
B.C.S. No. 235/1, stainless steel, 18.36% Cr, 8.21% Ni	0.36	5	0.34	0.017	± 5	5.6

DISCUSSION

The separation of titanium by precipitation as hydrous oxide gives better accuracy and reproducibility than the solvent extraction separation of titanium. This is because of the extreme dependence of the system involved in the solvent extraction on the pH of the solution and partly on the concentration of masking agents and interferences.

This investigation has shown that it is possible to determine titanium by flame photometry, although limitations inherent in the technique militate against many practical applications. Probably, the most restrictive limitation is the need to isolate titanium in a pure form before atomisation into the flame. Most methods do require a preliminary separation from interferences, but rarely is it necessary to ensure such complete removal of interferences as in the flame method.

A second major consideration is the existence of absorptiometric methods for titanium which are comparable in speed to the flame photometric determination and are far more accurate and reproducible.

The main drawback of the flame photometric technique which is inherent in the present flame photometers (including spectrophotometers) is its poor reproducibility and its unsuitability for use with organic solvents. This has a bearing on its application to any elements. Poor reproducibility arises from instrumental variables, *e.g.*, atomisation rate, drop size, flame stability, *etc.* Reproducibility may be improved by better instrumentation and design, *e.g.*, improvement in atomiser-burner, use of double beam instruments, *etc.* Substitution of an integral type aspirator-burner for the present atomiser-burner with its glass spray chamber, would enable safe use of organic solvents. Such use of organic solvents, by increasing emission sensitivity many fold, would extend the application of this technique to much lower limits of concentration, and also to other elements with very weak emission lines and bands which are not yet determinable by the flame photometric technique.

Acknowledgement—One of the authors (C. L. C.) wishes to thank the Queen's University of Belfast for the research scholarship which enabled him to undertake this research.

Zusammenfassung—Die Emmisionspektren von in Flammen angeregtem Blei und Titan (beide bekannt als schwach emittierend in Wasserstoff-Sauerstoff-Flammen) wurden im Hinblick auf eine analytische Verwendung untersucht. Störungen, besonders für die Titanbande bei 518 m μ und Möglichkeiten zur Ausschaltung oder Minderung wurden geprüft. Methoden zur Bestimmung von Pb und Ti in ihren Legierungen wurden ausgearbeitet. Der Variationskoeffizient der Resultate ist $\pm 4-5\%$. Die Studie zeigt die Vorteile und Beschränkungen der Flammphotometrie im allgemeinen Hinblick auf die Bestimmung auch anderer Metalle.

Résumé—Les spectres de flamme du plomb et du titane, qui sont des émetteurs faibles en flamme oxygène-hydrogène ont été étudiés en vue d'applications analytiques. Les interférences, en particulier la raie d'émission du titane à 518 m μ et les méthodes permettant de les réduire ou de les éliminer ont été étudiées. Des méthodes de dosage du plomb et du titane dans leurs alliages respectifs ont été mises au point. Ces méthodes ont été appliquées au dosage de différents alliages et leur précision et leur reproductibilité ont été déterminées. La reproductibilité est de l'ordre de 4 à 5%. Cette étude met en lumière les avantages et les limitations de la photométrie de flamme.

REFERENCES

- ¹ J. A. Dean, *Flame Photometry*. McGraw-Hill Book Company, Inc., New York and London, 1960, p. 238.
- ² M. Whisman and B. H. Eccleston, *Analyt. Chem.*, 1955, **27**, 1861.
- ³ P. T. Gilbert, *A.S.T.M., Spec. Tech. Publ.* 116, 1951, 77.
- ⁴ G. W. Smith and A. K. Palmley, *Analyt. Chem.*, 1959, **31**, 1798.
- ⁵ C. L. Chakrabarti, R. J. Magee and C. L. Wilson, *Talanta*, 1962, **9**, 145.

- ⁶ W. T. Elwell and D. F. Wood, *Metal Ind.*, 1960, **97**, 23, 51 and 67.
- ⁷ F. Burriel Marti and J. Ramirez-Munoz, *Flame Photometry*. Elsevier Publishing Company, London, 1957, p. 167.
- ⁸ C. L. Chakrabarti, W. F. Pickering and C. L. Wilson, *Talanta*, 1962, **9**, 451.
- ⁹ W. F. Pickering, *Analyt. Chim. Acta*, 1953, **9**, 324.
- ¹⁰ *Idem, ibid.*, 1955, **12**, 572.
- ¹¹ C. L. Chakrabarti, R. J. Magee and C. L. Wilson, *Talanta*, in press.

L'OXALATE DE *p*-DIMETHYLAMINOANILINE DANS LA COLORIMETRIE DES ALDEHYDES ET DES CETO-STEROÏDES

MAURICE PESEZ et JAROSLAV BARTOS
Centre de Recherches Roussel-Uclaf, Paris 7e, France

(Reçu le 17 juillet 1962. Accepté le 30 juillet 1962)

Résumé—L'accès à la *p*-diméthylaminoaniline est facilement réalisé par réduction de la *p*-nitrosodiméthylaniline à l'aide d'un hydroborure alcalin, en présence de cuivre. Le réactif est isolé sous forme d'oxalate, stable. En milieu acétique, les aldéhydes fournissent des colorations qui permettent généralement leur dosage sur quelques dizaines de μg . En méthanol et en présence d'acide perchlorique, les cétostéroïdes conjugués réagissent également et leur colorimétrie est possible sur des prises d'essais inférieures à 100 μg .

LA condensation de la *p*-diméthylaminoaniline sur divers aldéhydes a été signalée dès 1884.^{1,6,7,9} En milieu acide, l'intense coloration des sels obtenus a été mise à profit pour déceler et doser les aldéhydes et plusieurs dérivés carbonylés insaturés²⁻⁴ puis, tout récemment, les cétostéroïdes insaturés conjugués.⁵

On sait que la *p*-diméthylaminoaniline présente une mauvaise conservation, ce qui est une gêne pour son emploi en analyse. On a dès lors proposé de l'utiliser sous forme de complexe d'addition avec le chlorure stanneux, $\text{C}_8\text{H}_{12}\text{N}_2$, H_2SnCl_4 , ou d'oxalate, $2\text{C}_8\text{H}_{12}\text{N}_2$, $\text{C}_2\text{O}_4\text{H}_2$, qui offre, dans les conditions usuelles, une stabilité remarquable. Nous avons précisément montré que, par réduction de la *p*-nitrosodiméthylaniline à l'aide des hydroborures alcalins en présence de cuivre, l'oxalate de *p*-diméthylaminoaniline peut être aisément obtenu sous forme très pure.⁸

L'application du réactif aux aldéhydes

Selon nos essais, ce réactif en solution dans l'acide acétique autorise la colorimétrie de quelques microgrammes d'aldéhydes aromatiques ou hétérocycliques (tableau I).

TABLEAU I.—ALDÉHYDES AROMATIQUES OU HÉTÉROCYCLIQUES

	Maximum d'absorption, $m\mu$	Prise d'essai pour une densité optique de 0,3 (cuve de 1 cm), μg
Aldéhyde <i>o</i> -aminobenzoïque	480	16
Aldéhyde anisique	465	9
Aldéhyde benzoïque	465	19,1
Aldéhyde <i>p</i> -nitrobenzoïque	450	33
Aldéhyde protocatéchique	465	7,4
Aldéhyde salicylique	465	26,8
Aldéhyde <i>p</i> -toluïque	460	12,1
Aldéhyde vératrique	465	10
Furfural	480	9
2-Méthoxy 6-naphtaldéhyde	475	11,5
Pipéronal	465	10
Vanilline	460	9

Les aldéhydes aliphatiques sont aussi réactifs, mais leur structure influe notablement sur la sensibilité (tableau II). En outre, les colorations obtenues sont moins stables et, dans quelques cas, la loi de Beer n'est pas satisfaite.

TABLEAU II.—ALDÉHYDES ALIPHATIQUES

	Maximum d'absorption, <i>mμ</i>	Prise d'essai pour une densité optique de 0,3 (cuve de 1 cm), <i>μg</i>
Aldéhyde acétique	390	11,5
Aldéhyde butyrique	390	25,5
Aldéhyde <i>isobutyrique</i> *	370	109
Aldéhyde caprylique	435	129
Aldéhyde cinnamique	490	5,2
Aldéhyde crotonique*	450	10
Aldéhyde α,α -diméthyl hydroxy- propionique	390	120
Aldéhyde α -éthyl caproïque*	390	40
Aldéhyde glycérique	410	10
Aldéhyde ω -hydroxy valérique	385	1044
Aldéhyde laurique	400	56
Aldéhyde oenanthylique	400	73
Aldéhyde propionique	430	81,5
Aldéhyde <i>isovalérique</i> *	390	25
Chloral (hydrate)	Pas de coloration	—
Citral	445	9
Citronellal	390	276

* La loi de Beer n'est pas satisfaite avec ces composés.

Plusieurs cétones simples réagissent, mais de façon moins intense. C'est ainsi qu'une densité optique de 0,21, en cuve de 1 cm, n'est obtenue dans les conditions décrites qu'avec 700 μg d'acétone ou 235 μg de méthyléthylcétone.

L'application du réactif aux céto-stéroïdes

L'application du réactif aux céto-stéroïdes nous a conduits à des résultats favorables en méthanol, en présence d'acide perchlorique. Des modes opératoires particuliers, suivant la structure étudiée, permettent d'obtenir une sensibilité maximale (tableau III).

Avec les Δ^1 ou Δ^4 3-céto-stéroïdes, le maximum d'absorption de la coloration est situé vers 420 $m\mu$ en pratiquant la réaction à température ordinaire. En milieu plus acide et également à froid, les dérivés $\Delta^{4,6}$ 3-cétoniques montrent un maximum à 450 $m\mu$. Il en est de même avec les $\Delta^{1,4}$ 3-cétones, mais la condensation doit être effectuée à chaud. Ces dernières conditions rendent aussi possible la colorimétrie d'un Δ^5 7-céto-stéroïde, le 3-éthylénécétal de la 17-acétoxy Δ^5 -androstène 7-one, tandis que la 3 β -acétoxy Δ^5 -cholestène 7-one ne réagit pas.

Les substituants sur les cycles B, C et D sont sans influence sur l'intensité des colorations obtenues; mais celles-ci diminuent par contre fortement si une modification est apportée dans le cycle A. Il convient d'ailleurs de noter que la présence de la

double liaison conjuguée au carbonyle est nécessaire, la réaction étant négative avec les 3-céto-stéroïdes à cycle A saturé. Le nor-éthynodrel et la 17-acétoxy 19-nor $\Delta^{5(10)}$ -androstène 3-one ne développent qu'une faible coloration par condensation à froid. On peut toutefois les doser, après un traitement acide qui les isomérisé en Δ^4 3-cétones, avec un rendement voisin de 90 pour cent.

TABLEAU III.—CÉTO-STÉROÏDES

	Maximum d'absorption, <i>mμ</i>	Prise d'essai pour une densité optique de 0,3 (cuve de 1 cm), <i>μg</i>
Δ^1 3-Céto		
-17-Acétoxy Δ^1 -androstène 3-one	420	83
-2-Acétoxy 16 α -méthyl 17 α -hydroxy Δ^1 -pregnène 3, 11, 20-trione	pas de coloration	—
-17 α -Hydroxy 21-acétoxy Δ^1 -pregnène 3, 11, 20-trione	420	120
Δ^4 3-Céto		
- Δ^4 -Cholestène 3-one	420	60
-Cortisone	420	62
-Ethinistérone	420	48
-9 α -Fluoro hydrocortisone	420	61
-2-Hydroxyméthylène testostérone	420	200
-4-Hydroxy 17 α -méthyl testostérone	420	750
-6 α -Méthyl hydrocortisone	420	57
-2 α -Méthyl 11-hydroxy 17-acétoxy Δ^4 -androstène 3-one	420	1900
-Progéstérone	420	58
-Testostérone	420	47
-19-Nor testostérone (benzoate)	420	63
$\Delta^{4,6}$ 3-Céto		
- $\Delta^{4,6}$ -Cholestadiène 3-one	450	50
-17 β -Hydroxy 17 α -méthyl $\Delta^{4,6}$ -androstadiène 3-one	450	43
- Δ^6 -Testostérone (benzoate)	450	60
-11, 17 α , 21-Trihydroxy $\Delta^{4,6}$ -pregnadiène 3, 20-dione	450	48
$\Delta^{1,4}$ 3-Céto		
- $\Delta^{1,4}$ -Androstadiène 3, 17-dione	450	60
- $\Delta^{1,4}$ -Cholestadiène 3-one	450	76
-17 α , 21-Dihydroxy $\Delta^{1,4}$ -pregnadiène 3, 20-dione	450	71
-6 α -Méthyl prednisolone	450	69
-16 α -Méthyl prednisolone	450	65
-Prednisolone	450	62
Δ^5 7-Céto		
-3 β -Acétoxy Δ^5 -cholestène 7-one	pas de coloration	—
-3-Ethylène cétal 17-acétoxy Δ^5 -androstène 7-one	450	83
$\Delta^{5(10)}$ 3-Céto (après isomérisation)		
-17-Acétoxy 19-nor $\Delta^{5(10)}$ -androstène 3-one	420	65
-Nor-éthynodrel	420	60

PARTIE EXPERIMENTALE*

Préparation de l'oxalate de p-diméthylaminoaniline

Dans un ballon de 150 cm³, on dissout, en chauffant légèrement, 2,500 g de *p*-nitrosodiméthylaminoaniline¹⁰, dans 20 cm³ d'éthanol. La solution obtenue est additionnée de 37 cm³ d'eau et de 15 cm³ de solution aqueuse à 2 p. cent en SO₄Cu, 5 H₂O, puis on ajoute goutte à goutte, sous agitation et en refroidissant par intermittences pour éviter un dégagement gazeux trop violent, 2,500 g de borohydride de potassium dans 12 cm³ d'eau. On chauffe ensuite pendant 30 mn au reflux, refroidit, filtre et extrait l'amine par 2 fois 25 cm³ d'éther sulfurique.

Aux solutions étherées réunies, on ajoute 1 g d'acide oxalique en solution dans 12 cm³ d'eau. On agit énergiquement et filtre l'oxalate précipité. Rendement: 1,75 g.

On recristallise par chaud et froid, avec traitement au noir dans 8 volumes d'eau renfermant un poids d'acide oxalique égal à celui de l'oxalate de *p*-diméthylaminoaniline brut. On obtient finalement des aiguilles incolores, F. 200°.

Dosage des aldéhydes aromatiques et hétérocycliques

La prise d'essai, en solution dans 0,5 cm³ d'acide acétique, est additionnée de 2 cm³ d'une solution à 2 p. cent d'oxalate de *p*-diméthylaminoaniline dans l'acide acétique. Après 5 mn de repos à température ambiante à l'obscurité, on ajoute 1,5 cm³ d'acide acétique et effectue la lecture sur spectrophotomètre, à la longueur d'onde du maximum d'absorption, par rapport à un témoin sans aldéhyde.

Dosage des aldéhydes aliphatiques

La prise d'essai, en solution dans 1 cm³ d'acide acétique, est portée à une température comprise entre +5 et +10°, et additionnée de 2 cm³ d'une solution à 2 p. cent d'oxalate de *p*-diméthylaminoaniline dans l'acide acétique, refroidie à la même température que la prise d'essai. On effectue la lecture sur spectrophotomètre immédiatement, par rapport à un témoin sans aldéhyde.

Dosage des céto-stéroïdes

Δ^1 ou Δ^4 3-céto-stéroïdes: La prise d'essai, dissoute dans 0,5 cm³ de méthanol 0,01 N en acide perchlorique (solution méthanolique d'acide perchlorique à 70 p. cent) est additionnée de 1 cm³ de solution à 0,1 p. cent d'oxalate de *p*-diméthylaminoaniline dans le méthanol. On laisse reposer pendant 30 mn à l'obscurité, à température ambiante, puis dilue par 2,5 cm³ de méthanol et effectue la lecture sur spectrophotomètre à 420 m μ par rapport à un témoin sans stéroïde.

$\Delta^{4,8}$ 3-céto-stéroïdes: La prise d'essai est dissoute dans 0,5 cm³ de méthanol 0,02 N en acide perchlorique. On opère ensuite selon la technique proposée pour les Δ^4 3-céto-stéroïdes, et effectue la lecture à 450 m μ .

$\Delta^{1,4}$ 3-céto et Δ^5 7-céto stéroïdes: La prise d'essai, dissoute dans 0,5 cm³ de méthanol 0,02 N en acide perchlorique, est additionnée de 1 cm³ de solution à 0,1 p. cent d'oxalate de *p*-diméthylaminoaniline dans le méthanol. On maintient pendant 1 h à 60° à l'obscurité puis refroidit pendant 5 mn dans un bain d'eau à température ambiante. On ajoute 2,5 cm³ de méthanol, puis effectue la lecture sur spectrophotomètre à 450 m μ par comparaison avec un témoin sans stéroïde.

$\Delta^{5(10)}$ 3-céto-stéroïdes: La prise d'essai, en solution dans 0,5 cm³ de méthanol 0,01 N en acide perchlorique, est maintenue pendant 10 mn à 60°. On refroidit pendant 5 mn dans un bain d'eau à température ambiante, puis procède à la colorimétrie selon la technique proposée pour les Δ^4 3-céto-stéroïdes.

Summary—By reduction of *p*-nitrosodimethylaniline with alkali borohydride in the presence of copper, *p*-dimethylaminoaniline is formed, and can be isolated as the stable oxalate. In acetic acid medium, this reagent produces colours with aldehydes which permit them to be determined in amounts of the order of 10–30 μ g. In methanol, in the presence of perchloric acid, conjugated keto-steroids react in the same way as aldehydes, and can be determined in samples of less than 100 μ g.

Zusammenfassung—Durch Reduktion von *p*-Nitrosodimethylanilin mit Alkaliborhydrid in Gegenwart von Kupfer wird *p*-Dimethylaminoanilin gebildet, welches als Oxalat in stabiler Form isoliert werden kann. Dieses Reagens erzeugt in essigsaurem Medium mit Aldehyden Färbungen, wodurch letztere noch in Mengen von 10–30 μ g bestimmt werden können. Konjugierte Ketosteroide reagieren in Methanol in Gegenwart von Perchlorsäure in gleicher Art wie Aldehyde und können daher in kleineren als 100 μ g- Proben bestimmt werden.

* Avec Mlle. M. Guérard.

BIBLIOGRAPHIE

- ¹ A. Calm, *Ber.*, 1884, **17**, 2938.
- ² S. Hünig et J. Utermann, *ibid.*, 1955, **88**, 1201.
- ³ *Idem*, *ibid.*, 1955, **88**, 1485.
- ⁴ S. Hünig, J. Utermann et G. Erlemann, *ibid.*, 1955, **88**, 708.
- ⁵ R. Hüttenrauch, *Z. physiol. Chem.*, 1961, **326**, 166.
- ⁶ F. J. Moore et R. D. Gale, *J. Amer. Chem. Soc.*, 1908, **30**, 394.
- ⁷ G. Nuth, *Ber.*, 1885, **18**, 573.
- ⁸ M. Pesez et J. F. Burtin, *Bull. Soc. chim., France*, 1959, 1996.
- ⁹ H. Vogtherr, *Ber.*, 1892, **25**, 635.
- ¹⁰ *Organic Syntheses*, 1932, **12**, 30.

SODIUM PEROXIDE AS A FLUX IN REFRACTORY AND MINERAL ANALYSIS

C. B. BELCHER

The Broken Hill Proprietary Co. Ltd., Central Research Laboratories
Shortland, 2N, N.S.W., Australia

(Received 30 July 1962. Accepted 15 August 1962)

Summary—The use of sodium peroxide as a flux in refractory and mineral analysis is reviewed. The rate of attack of sodium peroxide on various types of crucibles is compared and the influence of the impurities introduced into the assay by crucible attack and by sodium peroxide impurity is critically examined. The superior erosion resistance of zirconium crucibles at temperatures exceeding 550° is discussed. It is concluded that many fusion decompositions could be supplanted by sinter decomposition, thereby resulting in a significant reduction in blank levels. Some interferences caused by residual peroxide in extract solutions are also discussed.

Sodium peroxide has long been recognised as a powerful and efficient flux for the decomposition of ferro-silicon, chromite and chrome iron ores, the fusions generally being performed in nickel or iron crucibles at 600°–700°. The last decade has seen the introduction of sintering techniques, zirconium fusion crucibles and increased application to a wide range of minerals. The pertinent information is widely scattered under individual analytical procedures and this review discusses the advances that have taken place.

DECOMPOSITION TECHNIQUES

Cunningham and McNeill¹ described how 1 g of <100-mesh chromite could be completely decomposed by heating with 8 g of sodium peroxide at a dull red heat for 3–5 min. Applications were limited, because the fusions were carried out in iron, nickel or porcelain crucibles, which were appreciably attacked by the molten peroxide. The subsequent extract solutions contained the eroded crucible material and all the trace-to-minor impurities therein. Analyses which could be completed after these fusions were therefore limited to those which were not vitiated by the uncontrollable impurity level introduced. Repeated fusion in the same crucible was not recommended because erosion breakthrough soon took place, and this represented an operator hazard.

Rafter and Seelye² observed that the melts were more readily soluble in water if the sodium peroxide fusions were carried out at lower temperatures. This observation was followed by an extensive investigation of the decomposition properties of sodium peroxide, when it is used as a sintering agent for a 7-min period at 480° ± 20°. This study showed that fusions (>500°) were often unnecessary, that an impressive list of minerals could be completely decomposed and that platinum ware could be used for sinters (<500°).

Rafter³ recommended that samples should be ground to pass <240-mesh, that the sample weight should be in the range 0.2–1.0 g, and that the weight of sodium peroxide should be 1.2–3.0 g. Using these conditions, gas evolution volumes and exothermic temperature rises in the sintered mass were measured over a temperature range of 50°–500°, using a wide range of minerals. These experiments illustrated that many minerals could be completely decomposed at temperatures as low as 270°. Rafter³ also observed that the erosion loss on iron and nickel crucibles was insignificant at 500°; for a nickel basin a loss of 0.5 mg of nickel per g of sodium peroxide was quoted. The work of Rafter³ provided precise information about the fluxing and sintering properties of sodium peroxide, and indicated that a wide range of minerals could be resolved by sintering in iron, nickel and platinum crucibles with a minimum of erosion losses. Since minimum erosion losses allows controlled blanking, the accurate analysis of minerals for minor and trace elements, and the use of batch techniques in muffle furnaces become possible.

The decomposition of blast furnace slags, raw materials and refractories was reviewed by Harpham,⁴ who confirmed the wide applicability of sodium peroxide as a sintering agent. The use of sodium peroxide as a sintering agent for the decomposition of slags, refractories and iron ores was also proposed by Clarke.⁵

With the better understanding of the powerful decomposition properties of sodium peroxide, studies were made using coarser mineral particles. For example, Dinnin⁶ reported that using a zirconium crucible it was possible to fuse 0.5 g of <30-mesh chrome ore with 5 g of sodium peroxide and obtain complete decomposition in 5 min. Antweiler⁷ argues against the grinding of silicate rocks when minor element analyses are required. In support of the argument, it was shown that using a zirconium crucible, it was possible to obtain complete decomposition of a 5-g piece of rock fragment in 20–25 g of sodium peroxide in 30–60 min.

The importance of thorough mixing^{3,6} of the sample and sodium peroxide has been emphasised. In this regard fine-grained sodium peroxide provides a greater surface area for reaction and grains of sample are more readily mixed and kept suspended. AnalaR or <30-mesh grades have been described as satisfactory.

ZIRCONIUM DECOMPOSITION VESSELS

The most significant development associated with the increased use of sodium peroxide has been the ready availability of zirconium decomposition vessels since 1957. In 1951, Petretic⁸ reported the superior resistance of zirconium metal to molten sodium peroxide, and the results which were presented indicated that the rate of attack decreased as the purity of the zirconium metal increased. Using open flame conditions, zirconium losses of 5 mg per g of sodium peroxide were obtained, and these compared favourably with the equivalent nickel, iron and silver losses of 100–250 mg per g of sodium peroxide. However, the subsequent discussion on costs clearly indicated that large scale use could not be contemplated at that stage. A systematic study of the behaviour of titanium, vanadium and zirconium towards a variety of fusion agents was made by Young and Strachan,⁹ and the noteworthy resistance of zirconium to sodium peroxide was again evident. Further information on the effect of metal purity was provided by Blake and Holbrook,¹⁰ who had used zirconium crucibles milled from bars of unspecified purity from 1952 to 1957. In 1957, crucibles pressed from 0.0035-inch high purity zirconium (0.1% hafnium) sheet were substituted, and these pressed crucibles had superior resistance to erosion by sodium

peroxide, weight losses of 26–44 mg per fusion being indicated. The fusion temperatures and times were not stated. The discussion clearly indicated that with the marketing of high purity zirconium in sheet form, pressed crucibles could be made at a reasonable cost.

The erosion rates of crucibles fabricated from nickel, iron, porcelain and pressed zirconium have been compared.¹⁰ The crucibles were charged with 5 g of sodium peroxide and placed in a muffle furnace for 10 min, the temperature range 500°–800° being studied. A graphical representation of these results is presented in Fig. 1 and the superior resistance of zirconium, especially at the higher temperatures in the range, is evident.

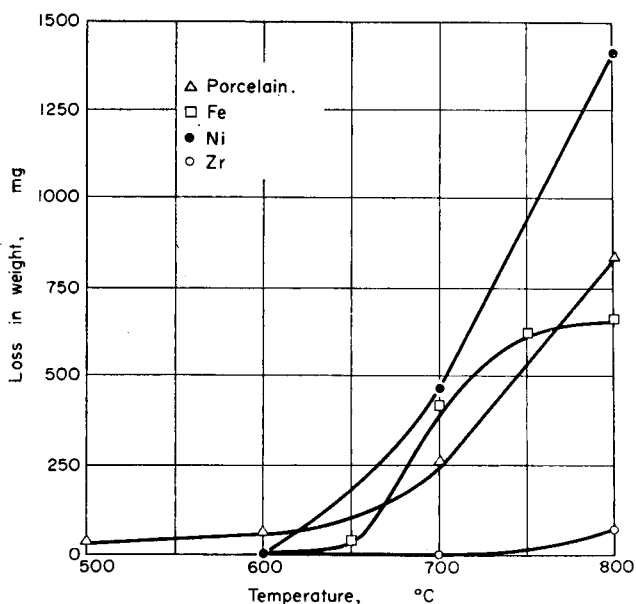


FIG. 1.—Weight loss (mg/5 g of peroxide fusion) against fusion temperature for crucibles of stated materials.

(Reprinted from *Chemist-Analyst*, 1957, 46, 42, by courtesy of J. T. Baker Chemical Company).

Deep-drawn zirconium crucibles fabricated from pure 0.03-inch strip have been marketed for several years, and are available in the size range 25–55 ml at an average cost of \$18. The manufacturers^{11,12} indicate that all crucibles have a bottom internal diameter of 2.5 cm, and a base thickness of 0.076 cm, which is an estimated base volume of 0.38 cm³ (2.5 g). Thus, using the erosion data quoted in Figs. 1 and 2, a crucible subjected to uniform base erosion rates would, before complete destruction, give the theoretical service lives shown in Table I.

TABLE I.—THEORETICAL SERVICE LIVES OF ZIRCONIUM CRUCIBLES WHEN USED AT VARIOUS TEMPERATURES

Temperature, °C	400	450	500	550	600	650	700	750	800
Lives (no. of fusions or sinters)	25000	12500	3000	1000	450	125	80	50	25

THE CHOICE OF A DECOMPOSITION VESSEL

The choice of a decomposition vessel will depend upon the mesh size of the sample, the time and temperature required for sample decomposition and the tolerable blank levels. The crucibles normally considered are zirconium, iron, nickel, platinum, silica, porcelain and silver.

Various workers have advanced procedures for the sodium peroxide decomposition of samples which vary in mesh size from 5-g pieces to <240-mesh. For any given mineral type an increased temperature, or increased time of fusion, or both, is required to obtain complete decomposition of a sample as its mesh size increases.

The erosion rate results of Blake and Holbrook¹⁰ are deficient in the temperature range 400°–650°, because the work was mainly directed to showing the superior resistance of zirconium. However, sodium peroxide is now widely applied in trace analyses, and it is therefore necessary to know the general erosion rates of all potential crucible materials at this lower temperature range. Hence the erosion rates of zirconium, porcelain, platinum, nickel, iron and silver crucibles have been studied¹³ under similar conditions to those used by Blake and Holbrook.¹⁰ The erosion rates obtained are indicated in Fig. 2.

When the crucible material undergoes serious oxidation, as is the case with iron and nickel, the true weight loss figure should be obtained by assay of the sinter or fusion extract. Undoubtedly the losses obtained in various laboratories will vary depending upon the mesh size of the sodium peroxide, the assay value of the sodium peroxide and the exposed surface area of the crucible. The data for platinum loss at 550° are taken from the accident reported by Clarke.⁵ The erosion data shown in Fig. 2 indicate that in general all the crucible materials studied may be used at sintering temperatures up to 500°. Beyond 550° zirconium emerges as the most resistant material, but its use may be precluded because the eroded metal interferes in the subsequent analysis.

Harpham⁴ discussed a modification which allowed the use of crucible materials at higher temperatures than are apparently indicated by the data in Figs. 1 and 2. It was proposed that sodium peroxide fusions could be performed in platinum crucibles which had first been lined by fusing a little sodium carbonate and then allowing the carbonate to solidify in a thin layer on the base and walls of the crucible. The fusion may then be performed at a temperature insufficient to melt the sodium carbonate. Precise temperature and time maxima were not indicated, but the method has been extended to silica¹⁴ ware, and obviously it can be extended to other crucible materials.

The choice of a suitable crucible can be further modified by consideration of the impurity elements in the crucibles. A typical analysis of one manufacturer's¹⁵ zirconium crucibles indicated 99·8% purity and an impurity level as follows: Fe 0·10%, Cr 0·01%, Hf 0·02%, Si 0·01%, Al 0·01%, C 0·02%, no other metallic impurity exceeding 0·005%. A typical analysis of one manufacturer's¹⁶ platinum-iridium crucibles indicates 99·8% minimum purity and trace impurities of gold, other platinum group metals and iron.

Typical analyses for silver,¹⁶ iron,¹⁷ and nickel¹⁷ crucibles indicate respective purity levels of 99·99%, 99·8% and 99·8%. Therefore for all metals mentioned, the maximum impurity level which could be introduced is only 2 μ g per mg of eroded metal; but, of course, in most instances the individual impurity levels introduced can be very much lower than this maximum figure.

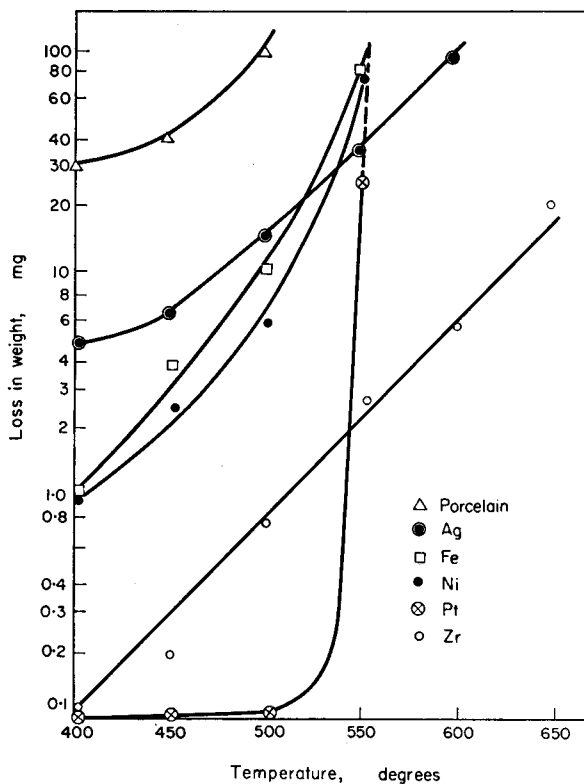


FIG. 2.—Weight loss (mg/5 g of peroxide fusion) against temperature for crucibles of stated material.

A consideration of three chemical manufacturer's¹⁸⁻²⁰ published maximum impurity limits in sodium peroxide would indicate that sodium peroxide is a more serious source of impurity elements. For example, the average of these maximum impurity levels for iron is 0.007%, whilst there is no guarantee for other alkali and alkaline earth or transition elements. Therefore under the conditions used to obtain the data in Figs. 1 and 2 the maximum iron impurity level introduced into the extract solution would be 35 μg .

Dinnin⁶ has referred to the high calcium content of several sources of sodium peroxide, the average value found being 0.04% CaO. Such percentages prevent the determination of minor amounts of calcium after sodium peroxide decomposition, for on the basis of 5 g of sodium peroxide and 0.5 g of sample this represents a blank value of 0.40%. This difficulty with high calcium oxide blank has been confirmed by the present writer.

INTERFERENCE EFFECTS

Residual undecomposed peroxide in solution can cause some difficulties in analysis, for example in the determination of silicon using the photometric methods based on the formation of heteropoly silico-molybdates. Dinnin⁶ has suggested that maximum elimination of hydrogen peroxide can be attained by allowing the extracted slurry to stand for 1 hr. Belcher and Skelton²¹ also encountered this type of interference, but

overcame it by the addition of potassium permanganate, the manganese and potassium having no effect upon the subsequent determinations.

Dinnin⁶ found that the Cr_2O_3 results obtained were 1% low when the sample was fused with sodium peroxide in a zirconium crucible. The samples were extracted, made acid, and boiled with potassium permanganate for 2 min. Anibal,²² however, has explained that zirconium forms a stable peroxy compound in alkaline solution and therefore when the solution is acidified, the peroxide reduces some of the Cr^{VI} . It is therefore recommended that the chromium be re-oxidised using the ammonium persulphate-silver nitrate reaction.

CONCLUSIONS

The increasing importance of sodium peroxide as a flux in refractory and mineral analyses has been considered. It is shown that sintering at a maximum temperature of 500° is suitable in many instances and that a wide choice of decomposition vessels is available if the decomposition temperatures are maintained below 550° . Zirconium crucibles exhibit outstanding erosion resistance at temperatures in excess of 550° . Sodium peroxide decompositions can now be used for many trace to minor analyses, but in this regard there is a need for the production of higher purity sodium peroxide possessing lower maximum impurity levels.

Acknowledgements—Appreciation is expressed to W. F. Pickering for helpful discussion, to H. M. Knagge for experimental assistance and to the Director of Research, The Broken Hill Pty. Co., Ltd. for permission to publish.

Zusammenfassung—Es wird die Verwendung von Natriumsuperoxyd als Flussmittel in der Analyse von feuerfesten Materialien und Mineralien besprochen. Die Angriffsgeschwindigkeiten von Natriumsuperoxyd auf verschiedene Tiegelmateriale werden verglichen; der Einfluss von Verunreinigungen die durch die Korrosion des Tiegels und durch das Natriumsuperoxyd selbst in die Probe eingeführt werden, wird einer kritischen Betrachtung unterzogen. Die besonders hohe Widerstandsfähigkeit von Zirkoniumtiegeln gegen Erosion bei Temperaturen über 550° wird besprochen. Es wird die Schlussfolgerung gezogen, dass zahlreiche Schmelzaufschliessungen mit Vorteil durch Versinterungszersetzung ersetzt werden können, wobei eine bedeutende Verminderung im Ausmass der Blindwerte erzielt wird. Einige Störungen, die durch die Anwesenheit von Superoxydresten in den Auszügen verursacht werden, werden ebenfalls diskutiert.

Résumé—On revit l'utilisation de peroxyde de sodium comme fondant dans l'analyse réfractaire et minérale. La vitesse d'attaque par le peroxyde de sodium sur les divers types de creusets est comparée et on fait un examen critique de l'influence d'impuretés introduites dans l'essai par l'attaque au creuset et par l'impureté du peroxyde de sodium. La résistance supérieure à l'érosion des creusets de zirconium aux températures qui dépassent 550° , est discutée. On conclut qu'on pourrait supplanter beaucoup de décompositions de fusion par la décomposition d'aggloméré, de quelle manière on aboutit à une diminution importante de niveaux blancs. De plus, quelques interférences occasionnées par le peroxyde résiduel dans des solutions d'extrait sont discutées.

REFERENCES

- ¹ T. R. Cunningham and T. R. McNeill, *Ind. Eng. Chem., Analyt.*, 1929, **1**, 70.
- ² T. A. Rafter and F. T. Seelye, *Nature*, 1950, **165**, 317.
- ³ T. A. Rafter, *Analyst*, 1950, **75**, 485.
- ⁴ E. W. Harpham, *Metallurgia*, 1955, **52**, 45.

- ⁵ W. E. Clarke, *B.C.I.R.A. Journal*, 1961, **9**, 185.
- ⁶ J. J. Dinnin, *The Rapid Analysis of Chromite and Chrome Ore. U.S. Geol. Surv. Bulletin* 1084B, 1959.
- ⁷ J. C. Antweiler, *U.S. Geol. Surv. Professional Paper*, 138, B322, 1961.
- ⁸ G. J. Petretic, *Analyt. Chem.*, 1951, **23**, 1183.
- ⁹ R. S. Young and K. G. A. Strachan, *Chem. and Ind.*, 1953, 154.
- ¹⁰ H. E. Blake and W. F. Holbrook, *Chemist-Analyst*, 1957, **46**, 42.
- ¹¹ Zirconium Fusion Crucibles, Oremet Metallurgical Corporation, Albany, Oregon, U.S.A.
- ¹² Anon., *The Laboratory*, 1960, **28**, 151.
- ¹³ R. B. Belcher, Unpublished results.
- ¹⁴ *Iron in Ores, Slags and Refractories*. Brit. Stand. 1121, Part 33, 1955.
- ¹⁵ Private communication, Oremet Metallurgical Corporation, Albany, Oregon, U.S.A.
- ¹⁶ Private communication, Garrett, Davidson and Matthey, Sydney, Australia.
- ¹⁷ *Scientific Apparatus and Reagents*. Arthur H. Thomas Company, Philadelphia, U.S.A. 61st Edition, 1961.
- ¹⁸ *Notes on Laboratory Chemicals*. E. Merck, Darmstadt, Germany, 1961.
- ¹⁹ *Laboratory Chemicals Catalogue*. The British Drug Houses Ltd., Poole, England, 1961.
- ²⁰ *Specification Catalog No. 58*. J. T. Baker Chemical Company, Phillipsburg, U.S.A.
- ²¹ C. B. Belcher and L. B. Skelton, *Analyt. Chim. Acta*, 1960, **22**, 567.
- ²² R. P. Anibal, *Analyt. Chem.*, 1960, **32**, 293.

THERMAL NEUTRON-ACTIVATION ANALYSIS OF TITANIUM USING 5.8-MINUTE TITANIUM-51 AND RAPID RADIOCHEMICAL SEPARATIONS

CHONG KUK KIM* and W. WAYNE MEINKE

Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.

(Received 16 August 1962. Accepted 7 September 1962)

Summary—A nuclear reactor has been used to determine trace amounts of titanium by neutron-activation analysis in a variety of samples. A 10-min radiochemical separation procedure coupled with gamma-ray spectrometry permitted measurement of 5.8-min titanium-51. With a neutron flux of about 10^{12} neutrons.cm⁻².sec⁻¹ the practical lower limit of detection was about 6×10^{-7} g of titanium.

INTRODUCTION

TRACE quantities of many elements have been analysed by neutron-activation analysis but little work has been reported to date on titanium. This lack of interest is undoubtedly related to the fact that only one radioactive isotope, 5.8-min ⁵¹Ti, is formed by the (n, γ) reaction on the titanium isotopes. Reports have been published^{1,2} on a low sensitivity determination of titanium by the (n, p) reaction using fast neutrons to produce long-lived scandium isotopes, but little work has been done with the short-lived ⁵¹Ti.

The calculated sensitivity for production of this short-lived isotope indicates³ that the (n, γ) activation of titanium does not produce the ultra high sensitivity possible with elements such as silver and vanadium, but nonetheless submicrogram quantities of titanium can easily be determined. Although colorimetric methods are reported⁴ which also approach this level of sensitivity, serious interferences from other elements in the sample often arise. Similarly, corrections for "reagent blanks" become quite appreciable at these levels.

The nuclear characteristics of the titanium (n, γ) activation give little promise for non-destructive analysis of samples using only scintillation spectrometry. On the other hand, rapid radiochemical procedures can be designed to separate titanium from other activated contaminants and thus permit the analysis of this element on a time scale of a few min.

This study is one of several^{5,6} which have been made with the facilities of the Ford Nuclear Reactor at the University of Michigan to explore the use of short-lived radioisotopes in activation analysis. These rapid activation and measurement facilities have been coupled with rapid radiochemical separations to determine titanium (by 5.8-min ⁵¹Ti) in a variety of samples.

EXPERIMENTAL

Apparatus

Powdered samples sealed in pharmaceutical-type gelatin capsules were irradiated in nylon snap-type "rabbits" in the pneumatic tube system of the Ford Nuclear Reactor of the University of Michigan. This system permits irradiations at thermal neutron fluxes of about 10^{12} neutrons/cm²/sec¹ (at

* Present address: Atomic Energy Research Institute, Seoul, Korea.

full power of 1 MW) and delivery to a hood within 3 sec after the end of irradiation. Samples were then worked up chemically and were measured by a $3'' \times 3''$ NaI(Tl) crystal coupled to a 100-channel pulse-height analyser with duplicate memories. This equipment has been described in detail elsewhere.⁷⁻¹⁰

Preparation of samples

A number of typical samples were analysed to test the general applicability of the radiochemical separation procedure. Biological ash samples had been prepared by igniting dried marine organisms in a quartz crucible at a temperature below 550°.¹¹ There was no prior preparation for the tobacco and leaf samples. Rock samples and some meteorite samples were ground to a fine powder by an extremely clean agate mortar and pestle. The G-1 and W-1 samples were obtained in powdered form from the U.S. Geological Survey.

The weighed samples were placed in a gelatin capsule and surrounded with clean tissue. These were then irradiated in the "rabbit" together with a weighed gold monitoring foil for a period of 15 min at full power. Care was taken that foil and sample were placed in reproducible positions relative to the reactor core because in our reactor facility neutron fluxes can vary by as much as 30% from one side of the rabbit to the other.⁷

*Radiochemical separations**

Rocks, minerals and meteorites. During the irradiation, carrier solution containing 0.80 mg of titanium (prepared by dissolution of titanium oxide in concentrated sulphuric acid and diluting) was evaporated to dryness in a nickel crucible and 4-5 g of sodium peroxide added. About 0.1 g of finely-ground irradiated sample (still in gelatin capsule) was then added, the lid placed tightly on the crucible, and the mixture fused for 1 min. The outside of the crucible was then cooled by dipping into a beaker of cold water and the melt made to solidify in a thin readily dissolved coating by manipulation of the crucible.

The melt was dissolved in water, the solution boiled, and the resulting precipitate centrifuged in a 50-ml cone. This precipitate, which includes all of the titanium, was acidified with either hydrochloric acid or with sulphuric acid, iron carrier added and the solution made alkaline with ammonia to precipitate the iron and titanium. This was also centrifuged and the supernate drawn off. To the residue were added, successively, 20 ml of 4M sulphuric acid, 10 ml of 6% (by weight) aqueous cupferron, and 10 ml of isopropyl ether. The mixture was shaken vigorously and the quadrivalent titanium extracted into the organic layer. At this point a crushed ice bath must be used to keep the liquids cool or the cupferron will be destroyed and the extraction will become ineffective. The aqueous layer was drawn off and discarded. When copper, vanadium, molybdenum and tungsten are present in large amounts in the irradiated sample, they can be eliminated by washing the ether with 20 ml of cooled 5M sodium hydroxide. Ten ml of the ether is then re-washed twice with 4M sulphuric acid and transferred to a marked tube for measurement with the gamma-ray spectrometer.

The entire procedure can be completed in about 10 min with an average recovery of about 70% for the titanium.

Biological samples. For botanical and biological samples it was usually sufficient to leach the sample in a 250-ml beaker with concentrated nitric acid containing the titanium carrier. The mixture was heated nearly to dryness, then 2 ml of 72% perchloric acid added, and the sample fumed to eliminate the last of the organic matter and most of the iodine. Concentrated hydrochloric acid was added and the solution clarified by heating. Iron carrier was then added and the solution made alkaline with sodium hydroxide to precipitate $\text{Fe}(\text{OH})_3$ and TiO_2 . The precipitate was centrifuged and the supernate drawn off. The precipitate was then dissolved in sulphuric acid and the cupferron extraction applied as above.

The hydroxide precipitation can be eliminated if the sample does not contain a large amount of any one inorganic matrix species. Iodine is a rather significant problem in handling marine organisms, however, and the hydroxide precipitation does give some decontamination from this element. A preliminary carbon tetrachloride extraction step could also be used at this point to eliminate much of the iodine, but it must be repeated at least twice to be effective. Fuming expels much of the iodine, but it also can cause considerable contamination on the inside of the hoods.

Fusion with Na_2O_2 , $\text{Na}_2\text{S}_2\text{O}_7$, NaHSO_3 , or KHF_2 in a platinum crucible can be substituted for the acid leach above if desired. The melt is then dissolved in concentrated sulphuric acid and water.

Activity determination

The gamma-ray spectrum for ^{51}Ti shows several peaks of which the 0.323-Mev peak is by far the

* Other information on radiochemical procedures for titanium is available in the monograph *The Radiochemistry of Titanium*.¹²

most prominent (Fig. 1). Spectra were obtained in the energy range of about 0–0.5 Mev as shown in Fig. 2 and the amount of ^{51}Ti determined from the area under the 0.323-Mev photopeak. Background and interfering Compton radiations from other activities remaining in the sample were eliminated by extrapolation of the base line from both sides of the photo peak. A total photopeak area of 100 cpm was considered to be the practical limit of detection.

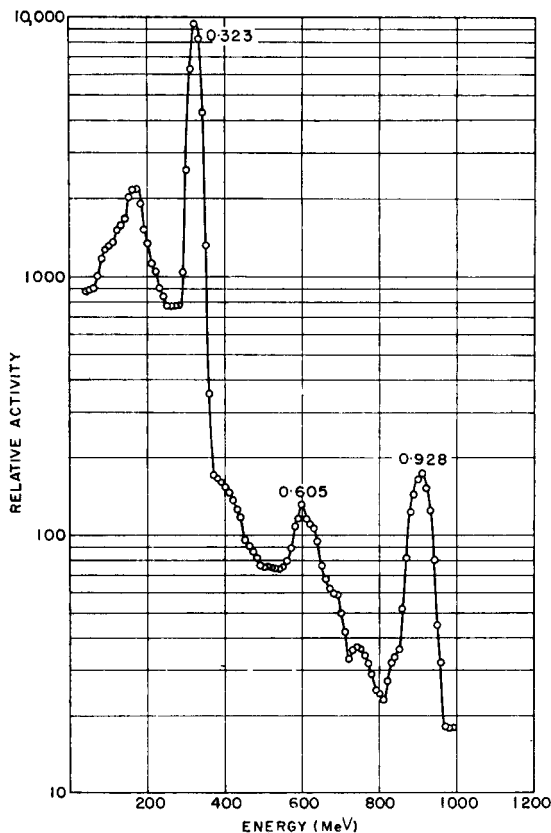


FIG. 1—Gamma-ray spectrum of 5.8-min ^{51}Ti [$3'' \times 3''$ NaI(Tl) crystal; source distance, 0.5 cm].

Monitoring procedures

Gold foils weighing between 0.1 and 0.2 mg were taped to the inside of the cap of the "rabbit". Following irradiation, the foils were set aside for 2 days for decay, then counted in a gamma scintillation well counter. All irradiations were normalised to a neutron flux of 1×10^{12} neutrons. $\text{cm}^{-2}.\text{sec}^{-1}$ by comparison with other measurements made with calibrated gold foils.

Chemical yield determination

The weight of titanium in the counting sample was obtained colorimetrically using the yellow colour of pertitanate. The ether counting sample was evaporated to dryness, 5 ml of concentrated nitric acid added and the solution again heated to near dryness. Five ml of 72% perchloric acid were then added and fumed off until the colour from the sample had completely disappeared. After the sample had cooled, 10 ml of 10% sulphuric acid were added along with 5 ml of 3% hydrogen peroxide to form the pertitanate colour. The total volume of the solution was made up to 50 ml in a volumetric flask. Samples without added titanium carrier were used for reagent blanks.

DISCUSSION

The gamma ray spectrum of ^{51}Ti (Fig. 1) shows three photopeaks of 0.32, 0.60, and 0.93 Mev. The two higher energy peaks, however, are hardly detectable in practical samples containing less than 10^{-4} g of titanium as shown in Fig. 2.

Since the 0.32-Mev photopeak is the only one available for detection of the element by gamma spectrometry, considerable interference is encountered from the Compton scatter of higher energy peaks of contaminating materials. Thus non-destructive analyses would be very difficult or impossible for most samples, and good radiochemical separations are very important for activation analysis of this element.

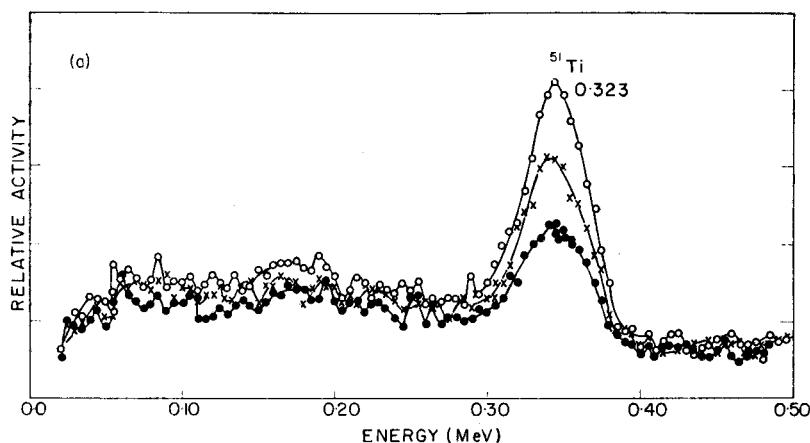
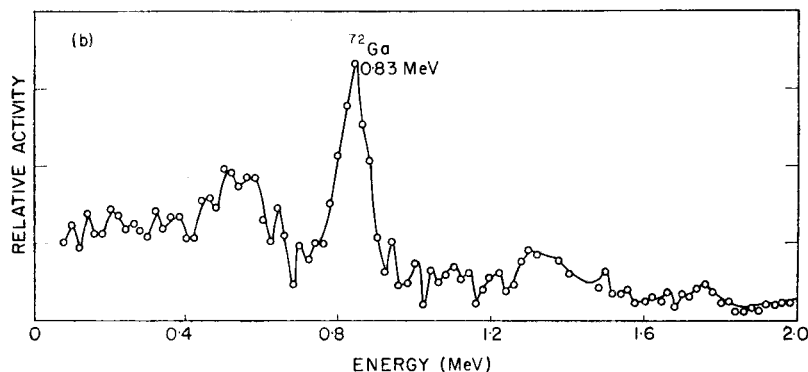


FIG. 2.—Gamma-ray spectra of titanium fraction separated from marine biological ash sample:
(A) Spectra taken at 3-min intervals.



(B) ^{72}Ga contamination after short-lived ^{51}Ti has decayed out.

In addition to providing satisfactory decontamination, the separation must be completed before the activity of the 5.8-min ^{51}Ti has decayed out. A number of procedures were tested in this study and are summarised in the monograph on *The Radiochemistry of Titanium*.¹² An extraction with tri-octyl phosphine oxide (TOPO) in hexane gave somewhat more selectivity than the cupferron procedure, but it took a prohibitive 17–20 min. Oxine extractions were found unsatisfactory because this reagent is selective only at a specific pH level, and additional time was spent adjusting the pH of the solution.

The radiochemical separations outlined above proved to be the most applicable. Depending upon the type of sample, some of the steps in the separation can be omitted. For example, unless a large amount of vanadium is contained in the sample, the sodium hydroxide backwash is unnecessary because most of the vanadium is eliminated as

sodium vanadate (dissolved in water when the sodium peroxide melt is treated with water and centrifuged). However, if there is a large amount of vanadium in the sample, a trace of vanadium precipitating with the titanium will interfere with the colorimetric determination of the titanium carrier. The sodium hydroxide backwashing eliminates vanadium very well, but it also reduces the chemical recovery of titanium appreciably.

The temperature should be kept low (about 10°) preceding the sodium hydroxide

TABLE I.—ACTIVATION ANALYSIS FOR TITANIUM IN A MARINE ORGANISM [ASHES OF *Pandalus* sp. (PRAWN SOFT PARTS) COLLECTED NEAR JAPAN¹¹]

Sample	Amount irradiated, g	Yield of radiochemical separation, %	Ti found, g	Level of Ti in sample, ppm
1	0.2088	71	8.5×10^{-6}	40.3
2	0.2365	73	9.8×10^{-6}	41.3
3	0.2772	65	1.15×10^{-5}	41.4
4	0.2842	68	1.16×10^{-5}	40.4
5	0.2944	66	1.26×10^{-5}	42.6
6	0.3208	69	1.17×10^{-5}	36.4
				Average 40.4 ± 2.2*

* Error is "standard deviation"

backwashing and the aqueous layer should be removed immediately after the shaking to prevent decomposition of the cupferron reagent. The iron precipitation step is often not necessary unless considerable copper is present in the sample. Copper is a rather serious contaminant if it precipitates with titanium because it has a 0.51-Mev annihilation peak near the 0.32-Mev titanium peak. The sodium hydroxide backwash step also eliminates copper.

Isopropyl ether is superior to chloroform as the solvent in the cupferron extraction because the two separated layers appear immediately. Where possible, two sulphuric acid washes should be used to eliminate mechanical contamination accompanying the solvent extraction. Care must also be taken to separate cleanly and completely the aqueous layer from the ether layer.

In its simplest form of one cupferron extraction and a double sulphuric acid wash, this procedure can be completed in 8 min on a sample such as an aluminium alloy with a yield of about 92%.

Calibration curves were taken under several conditions of measurement of the ⁵¹Ti gamma rays. In the standard procedure the 10 ml of ether extractant were counted directly in a 1-in. × 6-in. tube because of the limited time of separation (9 min). When the tube was brought close to the crystal, counting geometries of 20–22% were obtained. Somewhat higher sensitivities can be obtained if the sample is transformed into a dry layer for measurement near the crystal. The ether can be evaporated on the bottom of a 150-ml beaker which is then attached to the crystal; or the sample can actually be precipitated on a Whatman No. 42 filter paper which is then measured on the top shelf. These latter techniques gave counting geometries of about 40% but were time consuming, and thus the simple counting of the ether solution was adopted as the standard procedure. By this technique a photopeak area of 100 cpm is obtained with about 0.6 μg of titanium.

Results obtained from the activation analysis of marine organisms are summarised in Table I and give a general indication of the precision obtainable with this method. Successive spectra similar to those of Fig. 2 were obtained with these samples. Results obtained with small amounts of three types of standard samples are given in Table II. An additional number of analyses are summarised in Table III.

TABLE II—ACTIVATION ANALYSIS OF ROCKS AND ALLOY FOR TITANIUM

Sample	Amount irradiated, g	Yield of radiochemical separation, %	Ti found, g	Level of Ti in sample, %	Values reported
G-1					
(U.S. Geol. Surv.)					
1	0.0334	65	4.46×10^{-6}	0.134	0.140-0.207 ¹³
2	0.0194	65	2.52×10^{-6}	0.131	0.140-0.207 ¹³
				Average 0.133	
W-1					
(U.S. Geol. Surv.)					
1	0.0291	66	1.54×10^{-4}	0.529	0.510-0.864 ¹³
2	0.0286	84	1.64×10^{-4}	0.573	0.510-0.864 ¹³
3	0.0282	66	1.0×10^{-4}	0.532	0.510-0.864 ¹³
				Average 0.54	
Ferrochromium Alloy					
(U.S. Nat. Bur. Stand. 64)					
1	0.0778	70	2.0×10^{-5}	0.0367	0.034
2	0.200	60	4.5×10^{-5}	0.0380	0.034
3	0.0480	68	1.05×10^{-5}	0.0320	0.034
				Average 0.036	

TABLE III—ACTIVATION ANALYSIS OF OTHER TYPES OF SAMPLES FOR TITANIUM*

Sample	Level of Ti in sample, ppm
Ginkgo leaf	$84 \pm 5\%$
Cigarette tobacco	$250 \pm 2\%$
Agate from Utah	$44 \pm 7\%$
Holbrook meteorite	$467 \pm 5\%$
Johnstone meteorite	$505 \pm 5\%$

* In each case these results represent averages of three or more determinations. Errors are standard deviation.

The primary advantage of this type of analysis for titanium is that no correction for reagent blank is necessary because only the titanium which was originally irradiated with the sample will be activated and measured in the analysis.

Acknowledgements—This work was supported in part by the U.S. Atomic Energy Commission. Thanks are due to Professor H. J. Gomberg, C. W. Ricker, and the staff of the Ford Nuclear Reactor for their help in making the irradiations. Part of the stay of one of us (C. K. K.) was supported by a training grant from the Government of Korea.

Zusammenfassung—Ein Kernreaktor wurde zur Bestimmung von Spuren Titans mittels Neutronenaktivierungsanalyse herangezogen. Eine 10-Minuten-Trennungsmethode in Verbindung mit Gammastrahlenspektrometrie erlaubte die Messung des 5.8-Minuten Ti-51. Mit einem Neutronenfluss von $10^{12} \text{ n cm}^{-2} \text{ Sec}^{-1}$ ist die praktische Erfassungsgrenze etwa $6 \times 10^{-7} \text{ g Titan}$.

Résumé—Un réacteur nucléaire a été utilisé pour le dosage de traces de titane par activation dans un certain nombre d'échantillons. Une séparation radiochimique rapide ne demandant que 10 minutes, associée à la spectrométrie gamma a permis le dosage du Ti 51 de 5,8 minutes de période. Avec un flux de neutrons de 10^{12} neutrons par cm^2 et par seconde la limite de détection est de l'ordre de $6 \cdot 10^{-7}$ grammes de titane.

REFERENCES

- ¹ W. A. Brooksbank, Jr., G. W. Leddicotte and J. A. Dean, *Analyt. Chem.* 1958, **30**, 1785.
- ² W. A. Brooksbank, Jr., U.S. Atomic Energy Commission Report ORNL-2226, 1956.
- ³ W. W. Meinke, *Analyt. Chem.*, 1959, **31**, 792
- ⁴ E. B. Sandell, *Colorimetric Determination of Traces of Metals*, Interscience Publishers, N.Y., 1959.
- ⁵ D. G. Kaiser and W. W. Meinke, *Talanta*, 1960, **3**, 255.
- ⁶ J. L. Brownlee, Jr., U.S. Atomic Energy Commission Report TIS-6311 (Ph.D. Thesis), June, 1960.
- ⁷ W. W. Meinke, *Nucleonics*, 1959, **17**, No. 9, 86.
- ⁸ *Idem*, U.S. Atomic Energy Commission Report AECU-3641, November, 1957.
- ⁹ *Idem*, U.S. Atomic Energy Commission Report AECU-3887, November, 1958.
- ¹⁰ R. S. Maddock and W. W. Meinke, U.S. Atomic Energy Commission Report AECU-4438, November, 1959.
- ¹¹ R. Fukai and W. W. Meinke, *Limnology and Oceanography*, 1962, **7**, 186.
- ¹² C. K. Kim, Nuclear Science Series Report NAS-NS-3034, *The Radiochemistry of Titanium*, National Research Council, Washington 25, D.C., March, 1961.
- ¹³ M. Fleischer and R. E. Stevens, *Geochim. Cosmochim. Acta*, 1962, **26**, 525.

CATION-EXCHANGE SEPARATION OF BIVALENT METAL IONS FROM RARE EARTHS*

JAMES S. FRITZ and BARBARA B. GARRALDA
Institute for Atomic Research and Department of Chemistry
Iowa State University, Ames, Iowa, U.S.A.

(Received 30 July 1962. Accepted 27 August 1962.)

Summary—The bivalent metal ions of calcium, magnesium, nickel and strontium are eluted from a cation-exchange column with 1.5*M* nitric acid and separated from trivalent rare earths, aluminium and yttrium. Prior sequential elution of other metal ions with hydrochloric acid in acetone-water or with dilute hydrofluoric acid does not interfere with the present separation method.

INTRODUCTION

SEVERAL excellent ion-exchange methods for the separation of metal ions into groups have been developed in the last few years. Many elements are taken up by anion-exchange columns from aqueous or nonaqueous hydrochloric acid^{7,9} or from hydrofluoric acid solutions.^{2,10} Likewise, many metal cations can be eluted from a cation-exchange column with dilute aqueous hydrobromic acid,⁴ hydrofluoric acid,⁵ hydrogen peroxide,³ or hydrochloric acid in acetone-water solution.⁸ In these separations, aluminium^{III}, chromium^{III}, rare earths^{III}, yttrium^{III}, alkaline earths^{II}, magnesium^{II} and nickel^{II} may remain as a group, because they pass through an anion-exchange column and are not eluted from a cation-exchange column by the methods listed above.

Fritz and Karraker⁶ separated metal cations of different charge type by elution from an ethylenediammonium-form cation-exchange column. For sequential separations, elution of metal ions with a volatile acid from a hydrogen-form cation-exchange column is advantageous. Strelow¹¹ eluted beryllium^{II} from a cation-exchange column with 1.0*M* hydrochloric or 1.2*M* nitric acid and thus separated it from aluminium, iron, rare earths and yttrium. Edge and Ahrens¹ concentrated rare earths from silicate rock samples by prior elution of the bulk of other metal ions with 3.0*M* hydrochloric acid.

In the present work, a scheme is presented for the ion-exchange separation of calcium^{II}, strontium^{II}, magnesium^{II} and nickel^{II} from the trivalent ions, aluminium^{III}, rare earths^{III} and yttrium^{III}. These bivalent metal ions are eluted as a group from a hydrogen-form cation-exchange column using 1.5*M* nitric acid as the eluent. Following this separation, the trivalent metal ions are stripped from the column and titrated with EDTA.

EXPERIMENTAL

Ion-exchange column

Conventional glass ion-exchange columns (I.D. 1.2 cm) were filled to a bed height of 16 cm with a slurry of water and resin. Eluent was added to the column from a cylindrical separatory funnel which was inserted in the top of the column through a one-holed rubber stopper. This method allowed dropwise addition of eluent so that the top of the resin bed was not disturbed.

* Contribution No. 1191. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

Ion-exchange resin

Dowex 50W X8, 100–200 mesh, hydrogen-form cation-exchange resin was used. Before use, the resin was cleaned by back-washing to remove the fine particles. The resin was then washed with 10% ammonium citrate (pH 3.0–3.5), with 3.0M hydrochloric acid, and finally with water until a negative chloride test was obtained with silver nitrate. The resin was then air-dried.

Procedure for separation

An aliquot of 0.05M solution of the nitrate or perchlorate salts of the metal ions containing the desired amount of metal was diluted to 25 ml with water and added to the column. The metal ion was then eluted at a flow-rate of 2 ml/min. In single ion elutions, 10-ml fractions were collected and tested for presence of the metal ion. In the separation of mixtures, a single, large fraction was used, of a volume slightly larger than the amount needed for complete removal of the ion. If subsequent ions were removed with a different eluent, the column was rinsed with 20 ml of water between elutions.

When a nonaqueous medium was used for elution of some mixture components, the solution of metal salts was evaporated to a volume of 1–2 ml. Concentrated nitric acid was added during evaporation to prevent hydrolysis. Before loading this mixture on the column, the column was equilibrated by passing 15 ml of 60% acetone-0.1M hydrochloric acid through at maximum flow rate. After transferring the mixture quantitatively to the column, the flow-rate was adjusted to approximately 0.5 ml/min for all nonaqueous separations.

Analysis

After elution, the collected fractions were evaporated nearly to dryness and analysed for the metal by titration with 0.05M EDTA.⁴

RESULTS

A study was made of the elution of individual metal ions from a 16- × 1.2-cm column with hydrochloric and nitric acids. The best eluent appears to be 1.5M nitric acid (see Tables I and II). With lower concentrations, the elution is too slow; 2.0M

TABLE I.—ELUTION OF INDIVIDUAL METAL IONS FROM A CATION-EXCHANGE COLUMN (1.2 × 16 CM) WITH NITRIC ACID

Ion	Nitric acid eluent, M	Break-through, ml		
		0.25 mmole	0.5 mmole	1.0 mmole
Al ^{III}	1.5	>300	>300	130
	2.0	150	—	—
Cr ^{III}	1.5	120	—	—
	2.0	130	—	—
Dy ^{III}	1.5	>500	>300	220
	2.0	130	—	—
Lu ^{III}	1.5	>500	>300	—
	2.0	130	—	—
Y ^{III}	1.5	>500	>350	240
	2.0	170	—	—
Yb ^{III}	1.5	>500	>350	—
	2.0	130	—	—

TABLE II.—ELUTION OF 0.25 MMOLE OF INDIVIDUAL METAL IONS WITH 1.5M NITRIC ACID (COLUMN 1.2 × 16 CM)

Ion	Break-through, ml	Elution complete, ml
Ca ^{II}	60	160
Mg ^{II}	70	130
Ni ^{II}	70	130
Sr ^{II}	40	170

nitric acid causes some of the rare earth elements to break through too early. Hydrochloric acid, 1.5–2.0*M*, is promising for the separation of bivalent metal ions from rare earths and yttrium but aluminium breaks through very early.

Chromium^{III} splits into two bands upon elution with 1.5*M* nitric acid. One band is eluted and the other remains on the column. The first chromium^{III} appears in the effluent in the 120- to 130-ml fraction. Chromium^{III} is an interference in the proposed separation.

The effect of load was next studied. The normal 0.25-mmole load used for single ion elutions was increased to 1 mmole. This increase had no effect on the volume of 1.5*M* nitric acid required for elution of bivalent metal ions. However, increasing the load of the trivalent metal ion caused it to break through earlier. Fig. 1 shows the

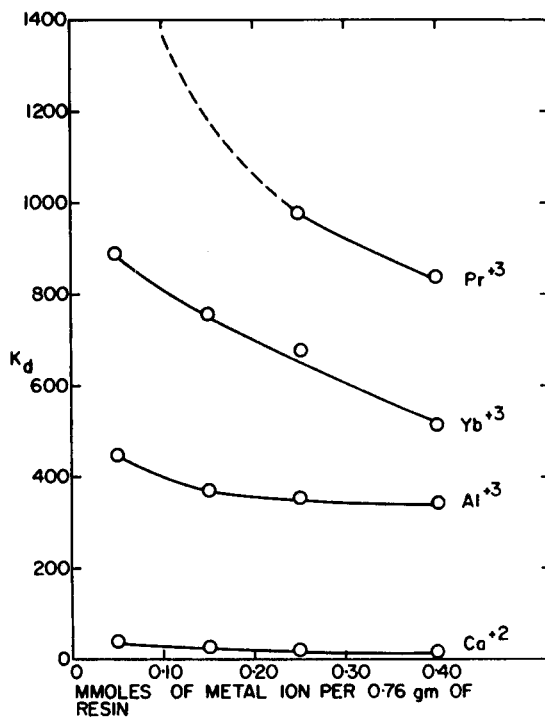


FIG. 1.

significant decrease in the distribution coefficients of trivalent metal ions with increasing load. It appears that 1 mmole is the maximum load for a trivalent metal ion with a column of the dimensions used. The load recommended for separation of mixtures is 0.5 mmole or less of total trivalent metal ion and 0.5 mmole or less of total bivalent metal ion. Larger loads can, of course, be employed with columns of larger dimensions.

Mixtures containing 0.25 or 0.5 mmole of a bivalent metal ion and 0.25 or 0.5 mmole of the trivalent metal ion were added to a cation-exchange column in dilute acid, and the bivalent metal ion was eluted with 200 ml of 1.5*M* nitric acid. Then the trivalent metal ion was stripped from the column with 200 ml of 3.0*M* nitric acid. Each fraction was evaporated to remove excess acid, and the metal ion present was

titrated with EDTA. The following two-component mixtures were all separated successfully:

Ca^{II} from Al^{III}, Dy^{III}, Lu^{III}, Nd^{III}, and Yb^{III}

Mg^{II} from Al^{III}, Dy^{III}, Lu^{III}, Nd^{III}, Y^{III}, and Yb^{III}

Ni^{II} from Al^{III}, Dy^{III}, Lu^{III}, Nd^{III}, Y^{III}, and Yb^{III}

Sr^{II} from Al^{III}, Dy^{III}, Lu^{III}, Nd^{III}, Y^{III}, and Yb^{III}

Mixtures containing 1.00 mmole of yttrium^{III} and 0.10 mmole of nickel^{II} or magnesium^{II} were separated successfully. A mixture of 1.0 mmole of magnesium^{II} plus 0.25 mmole of lutetium^{III}, and a mixture of 0.25 mmole of strontium^{II} plus

TABLE III.—SEPARATIONS ON A 16- × 1.2-CM CATION-EXCHANGE COLUMN

Ion mixtures	Load, mmoles	Eluent	EDTA Titrations		
			Theory, ml	Actual, ml	Diff., ml
Bi ^{III}	0.10	35 ml 60% Acetone—0.1M HCl	2.05	2.04	-0.01
Cd ^{II}	0.10	30 ml 40% Acetone—0.5M HCl	2.05	2.05	±0.00
Zn ^{II}	0.10	25 ml 60% Acetone—0.5M HCl	2.02	2.02	±0.00
		(20 ml 70% Acetone—0.5M HCl			
Fe ^{III}	0.10	20 ml 80% Acetone—0.5M HCl	2.04	2.05	+0.01
Cu ^{II}	0.10	35 ml 80% Acetone—0.5M HCl	2.06	2.06	±0.00
VO ^{II}	0.10	70 ml 0.3% H ₂ O ₂ —0.01M HClO ₄	2.03	2.03	±0.00
Mn ^{II}	0.10	50 ml 92% Acetone—1.0M HCl	2.05	2.04	-0.01
Al ^{III}	0.10	200 ml 0.1M HF	2.05	2.04	-0.01
Ni ^{II}	0.10	200 ml 1.5M HNO ₃	2.07	2.08	-0.01
Y ^{III}	0.10	250 ml 2.0M HNO ₃	2.04	2.04	±0.00
Hg ^{II}	0.25	120 ml 0.12M HBr	4.98	4.99	+0.01
Bi ^{III}	0.25	60 ml 0.5M HBr	5.06	5.07	+0.01
Cd ^{II}	0.25	150 ml 0.1M HF	5.11	5.10	-0.01
Fe ^{III}	0.25	200 ml 1.0M HF	5.13	5.11	-0.02
Ni ^{II}	0.25	200 ml 1.5M HNO ₃	5.04	5.05	+0.01
Y ^{III}	0.25	250 ml 2.0M HNO ₃	5.02	5.03	+0.01

1.0 mmole of dysprosium^{III} were also separated quantitatively. Analysis of all results obtained (65 individual determinations) shows an average recovery of 100.0% with a standard deviation of 0.2%.

It is interesting to know whether prior separations performed on the same column with other eluting agents would effect the separation of bi- and trivalent metal ions with 1.5M nitric acid. To check this, a mixture containing six different metal ions was resolved completely by sequential elutions with 0.12M hydrobromic acid, 0.5M hydrobromic acid, 0.1M hydrochloric acid, 1.0M hydrochloric acid, and 1.5M nitric acid. Another more complicated mixture was separated by sequential elutions with various concentrations of hydrochloric acid in acetone, 0.3% hydrogen peroxide-0.01M perchloric acid, 0.1M hydrofluoric acid, and 1.5M nitric acid. The results given in Table III show excellent recovery of all of the sample components. Thus it appears that these prior elutions have a negligible effect on the separations using 1.5M nitric acid as the eluent.

Zusammenfassung—Die zweiwertigen Kationen von Calcium, Magnesium, Nickel und Strontium werden mit 1.5 m Salpetersäure aus einer Kationenaustauschersäule eluiert und so von dreiwertigen seltenen Erden, Aluminium und Yttrium getrennt. Vorhergehende Eluierungen anderer Metalle mit Salsäure in wässrigem Aceton oder mit verdünnter Flussäure haben auf die obige Trennung keinen Einfluss.

Résumé—Les cations divalents du calcium, du magnésium, du nickel et du strontium sont élués après fixation sur une colonne d'échangeur de cations par de l'acide nitrique 1,5 M et sont ainsi séparés des terres rares, de l'aluminium et de l'yttrium. L'éluition préliminaire d'autres cations métalliques par une solution d'acide chlorhydrique dans un mélange eau-acétone ou par de l'acide fluorhydrique dilué ne gêne pas la séparation considérée.

REFERENCES

- ¹ R. A. Edge and L. H. Ahrens, *Analyt. Chim. Acta*, 1962, **26**, 355.
- ² J. P. Faris, *Analyt. Chem.*, 1960, **32**, 520.
- ³ J. S. Fritz and Janet E. Abbink, *ibid.*, 1962, **34**, 1080.
- ⁴ J. S. Fritz and Barbara B. Garralda, *ibid.*, 1962, **34**, 102.
- ⁵ J. S. Fritz, Barbara B. Garralda and Shirley K. Karraker, *ibid.*, 1961, **33**, 882.
- ⁶ J. S. Fritz and Shirley K. Karraker, *ibid.*, 1959, **31**, 921.
- ⁷ J. S. Fritz and D. J. Pietrzyk, *Talanta*, 1961, **8**, 143.
- ⁸ J. S. Fritz and T. Rettig, *Analyt. Chem.*, 1962, **34**, 1562.
- ⁹ K. A. Kraus and F. Nelson, *Symposium on Ion Exchange and Chromatography in Analytical Chemistry*. Amer. Soc. Testing Materials, Philadelphia, 1956, pp. 27-57.
- ¹⁰ F. Nelson, R. M. Rush, and K. A. Kraus, *J. Amer. Chem. Soc.*, 1960, **82**, 339.
- ¹¹ F. W. E. Strelow, *Analyt. Chem.*, 1961, **33**, 542.

PHOTOMETRIC TITRATION OF ALKYL ALUMINIUM COMPOUNDS

COE W. WADELIN

Research Division, The Goodyear Tire & Rubber Company, Akron 16, Ohio, U.S.A.

(Received 31 July 1962. Accepted 3 October 1962)

Summary—The end-point in the titration of alkyl aluminium compounds with isoquinoline can be detected photometrically. This enables their determination in the presence of oxygenated impurities with a standard deviation of 0.02 mmole per g. The method has been applied to trialkyl aluminium compounds and dialkyl aluminium hydrides in which the alkyl groups ranged from methyl to hexyl.

TRIALKYL aluminium compounds and dialkyl aluminium hydrides catalyse the polymerisation of olefins.¹ These compounds react readily with oxygen, water, and other oxygenated compounds to form dialkyl aluminium alkoxides, dialkyl aluminium hydroxides, and other oxygenated impurities which do not have catalytic activity.

In a study of the catalysis of the dimerisation of propylene by tripropyl aluminium² it was desirable to determine the active components of both fresh and recovered catalysts.

This same problem was solved by Bonitz,³ who observed that isoquinoline forms complexes with trialkyl aluminium compounds and dialkyl aluminium hydrides, but not with dialkyl aluminium alkoxides or dialkyl aluminium hydroxides.

As both trialkyl aluminium compounds and dialkyl aluminium hydrides are catalysts for the dimerisation of propylene and form isoquinoline complexes, while their oxygenated derivatives are neither catalysts nor complex formers, it seems that isoquinoline titration is well suited for this analysis. The sum of the catalytically active compounds is determined and reported as millimoles of active catalyst per g.

Trialkyl aluminium compounds form 1:1 complexes with isoquinoline which are yellow in colour. Dialkyl aluminium hydrides form 1:1 complexes which are colourless, and red complexes containing 2 moles of isoquinoline per mole of dialkyl aluminium hydride. These reactions take place regardless of the size of the alkyl groups. The rate is inversely proportional to the size of the alkyl groups. When a trialkyl aluminium compound and a dialkyl aluminium hydride are present together, and isoquinoline is added, each compound complexes an equimolar amount of isoquinoline before the dialkyl aluminium hydride begins to complex a second mole of isoquinoline. Bonitz took advantage of this order of stability to titrate mixtures of trialkyl aluminium compounds and dialkyl aluminium hydrides, taking the first appearance of the red colour as the end-point at which 1 mole of isoquinoline had been added per mole of active aluminium compound. As equilibrium is established slowly, the colour forms and then fades as the titration proceeds, making it difficult to detect the end-point precisely. Therefore, he discarded visual detection of the end-point in favour of conductometric and potentiometric methods. The use of the appearance of the red colour to detect the end-point has been re-investigated using a photometer to make detection of the colorimetric end-point more precise.

EXPERIMENTAL

Apparatus

Spectrophotometer: Beckman Model B, fitted with cell compartment and cover for photometric titration, (Figs. 1, 2 and 3.)^{4,5} The cell compartment cover was designed so that it could be removed for sample injection without removing the burette.

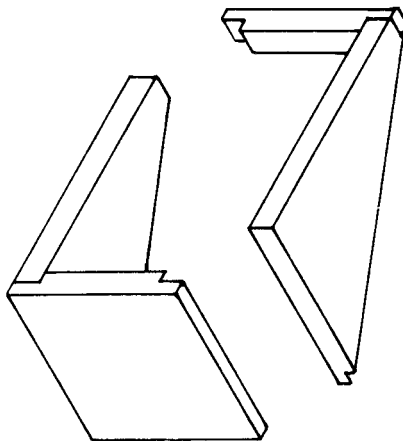


FIG. 2.—Cell compartment for photometric titrations in Beckman Model B spectrophotometer.

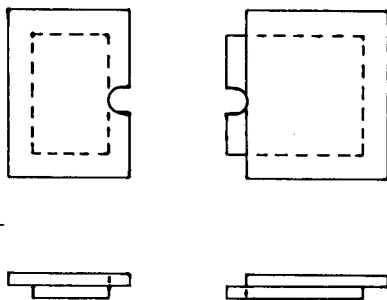


FIG. 3.—Cell compartment cover.

Burette: 10 ml, with attached reservoir, Teflon stopcock, and provision for blanketing with inert gas. Cat. No. JB-6715X, Scientific Apparatus Co., Bloomfield, N.J.

Syringes: Luer Lok, 1-ml, Cat. No. 1YTL, Becton, Dickinson, and Co., Rutherford, N.J. Dry in an oven at 105° before using.

Syringe needles: Huber point, 26 gauge, $\frac{3}{8}$ inch, Becton, Dickinson, and Co.

Syringe needle, modified: Silver solder an 18-gauge, $1\frac{1}{2}$ inch, Huber point syringe needle to a 3-inch length of $\frac{1}{16}$ inch stainless steel tubing.

Rubber serum caps: $\frac{1}{2}$ -inch diameter, Cat. No. 14-126, Fisher Scientific Co., 717 Forbes St., Pittsburgh 19, Pa., and $\frac{7}{8}$ -inch diameter, Cat. No. 13-8855, Chemical Rubber Co., 2310 Superior Avenue, Cleveland 14, Ohio

Bottles: 4-ounce, small mouth, screw cap.

Attach a pressure reducing valve and a manifold with three outlets to a nitrogen cylinder. To one outlet from the manifold attach a 3-inch length of $\frac{3}{16}$ -inch rubber tubing. Close the end with a $\frac{7}{8}$ -inch serum cap. Connect a piece of rubber tubing to another outlet and attach it to a tee. Connect the second arm of the tee to the burette reservoir and the remaining arm to a mineral oil bubbler. Keep nitrogen passing through the bubbler at about 1 bubble per sec.

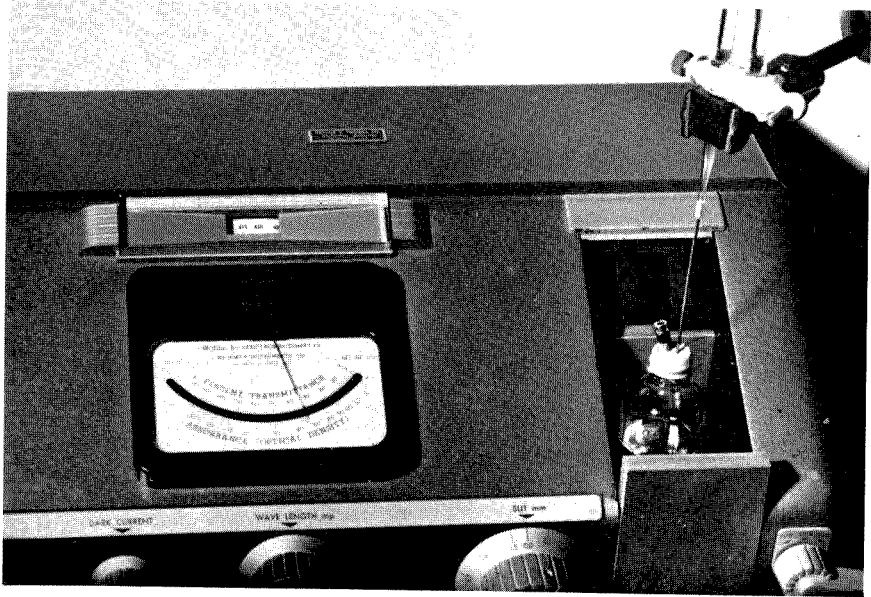


FIG. 1.—Titration assembly

Attach the modified syringe needle to the burette by means of a $\frac{1}{8}$ -inch length of plastic tubing. Butt the end of the steel tubing against the burette tip so that contact of the titrant with the plastic tubing is minimised.

Reagents

Isoquinoline: Distil reagent from Matheson, Coleman, and Bell or Eastman Kodak.

Toluene: Distil, collecting the middle 80%, and store over calcium hydride.

Nitrogen: Lamp grade from General Electric Co., 1331 Chardon Road, Euclid, Ohio or prepurified from Air Reduction Co., 1210 W. 69th Street, Cleveland 2, Ohio

Isoquinoline in toluene: 0.25M. Transfer 400 ml of dry toluene to an oven-dried 16-ounce bottle. Bubble nitrogen through it *via* a fritted glass gas dispersion tube for 15 min. Add 13 g of isoquinoline. Flush the reservoir of the burette with nitrogen for 15 min and transfer the titrant to the reservoir. Admit no gas but nitrogen from then on.

Perchloric acid in acetic acid: 0.25N. Dissolve 11 ml of 70% perchloric acid in 500 ml of acetic acid.

Methyl violet indicator: Dissolve 20 mg of methyl violet in 10 ml of acetic acid.

Dialkyl aluminium hydride: This should contain at least 0.1 mole of hydride per mole of aluminium. The hydride content need not be accurately known. 37% Diethyl aluminium hydride in triethyl aluminium from Ethyl Corp. or di-isobutyl aluminium hydride from Texas Alkyls, Inc., are satisfactory.

Standardisation

Standardise the perchloric acid solution against potassium hydrogen phthalate dissolved in acetic acid, titrating to the methyl violet visual end-point. Standardise the isoquinoline solution, after it has been placed in the burette, by titrating an aliquot of it with perchloric acid solution to the methyl violet visual end-point.

Recommended procedure

Place a representative sample in a bottle with a puncture seal cap. Turn the spectrophotometer on at least 30 min before titrations are to begin. Once a titration has begun, no further check on slit width can be made. Therefore, the spectrophotometer must be well warmed up to minimise drift.

Place 40 ml of dry toluene and a magnetic stirring bar in a 4-ounce bottle. Bubble nitrogen through the toluene *via* a gas dispersion tube for 5 min and close the bottle with a rubber serum cap. Mount the bottle on the beaker platform and insert the modified syringe needle in the serum cap. Insert a 26-gauge needle in the serum cap to serve as a vent. Centre the bottle in the light beam of the spectrophotometer.

Set the pressure regulator on the nitrogen cylinder at 10 psi. Place a 26-gauge needle on a 1-ml syringe, remove the plunger, insert the needle in the serum cap on the nitrogen manifold, and flush the syringe for 1 min. Replace the plunger, set it at 0.1 ml, and withdraw the needle from the serum cap. Withdraw 0.1 ml of the dialkyl aluminium hydride reagent into the syringe. Work the plunger in and out until all the nitrogen bubbles are transferred to the reagent bottle. The nitrogen replaces the liquid withdrawn maintaining a pressure of 1 atm in the reagent bottle. Success in transferring alkyl aluminium compounds without fuming at the needle tip depends on having the liquid in the syringe completely free of bubbles. Inject the dialkyl aluminium hydride into the 4-ounce bottle. Withdraw the needle and cap it with a rubber stopper.

Start the stirrer and adjust it so that the stirring vortex is not drawn down into the light beam. Set the wavelength of the spectrophotometer at 460 m μ , place the cell compartment cover in position, and adjust the slit until an absorbance of 0.0 is indicated. Titrate with isoquinoline solution until the absorbance is steady at 0.5 for at least 2 min.

Select a sample that will contain 1–2 mmole of active aluminium. Flush a syringe with nitrogen, fill it with sample, and insert the needle into a rubber stopper. Weigh the filled syringe, inject the sample into the 4-ounce bottle, recap the syringe needle with the rubber stopper, and reweigh the syringe.

Re-adjust the slit until the absorbance is 0.0. This is necessary because the yellow colour of the trialkyl aluminium-isoquinoline complex absorbs slightly at 460 m μ . Titrate until the absorbance is again steady at 0.5 for at least 2 min.

Continue to add and titrate other samples in the same bottle until the volume of solution in the bottle is about 90 ml.

Clean the syringes and needles by rinsing them with toluene, 1N sulphuric acid, water and acetone. Immerse the needles in 1N sulphuric acid, then rinse with water and acetone. Draw air through them to dry them.

Calculation

$$\text{Activity, mmole per g} = \frac{\text{ml} \times M}{W}$$

where

ml = ml of isoquinoline solution used to titrate the sample.

M = molarity of the isoquinoline solution.

W = g of sample,

DISCUSSION

The spectra of the tri-*n*-propyl aluminium-isoquinoline complex and the 1:2 di-isobutyl aluminium hydride-isoquinoline complex are shown in Fig. 4.

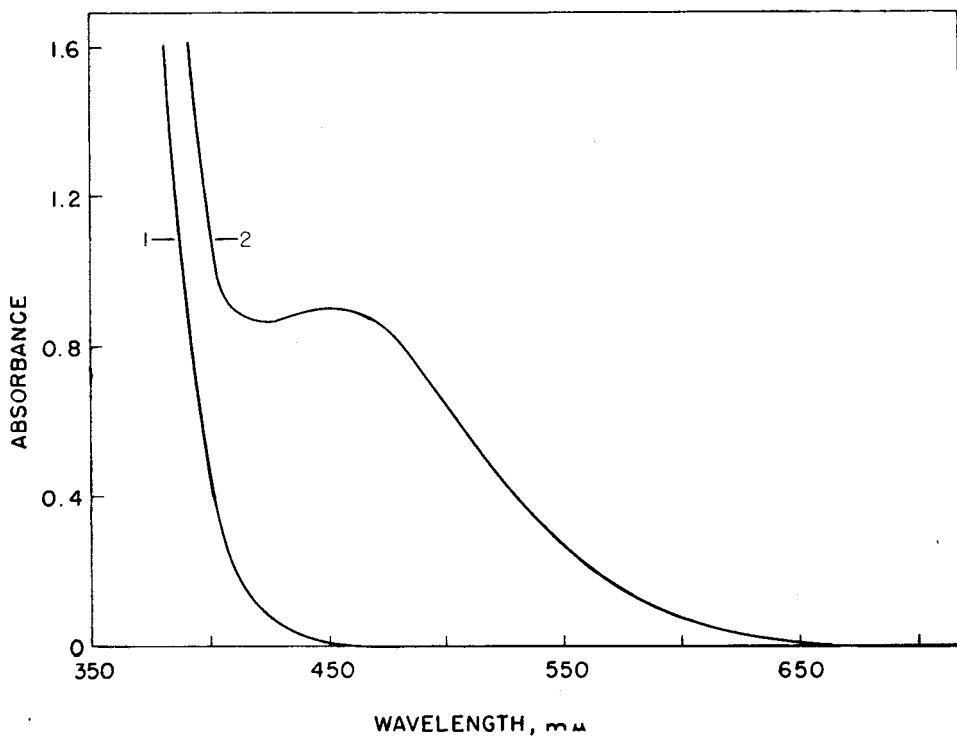


FIG. 4.—Spectra in toluene:

1—Tri-*n*-propyl aluminium-isoquinoline complex, 0.0046*M*.

2—Di-isobutyl aluminium-isoquinoline complex (1:2), 0.0045*M*

Measurements for the photometric titration are made at 460 $m\mu$. This is the wavelength used to measure the dialkyl aluminium hydride content of trialkyl aluminium compounds.⁶ The molar absorptivities of all 1:2 dialkyl aluminium hydride-isoquinoline complexes are the same, regardless of the size of the alkyl groups. The absorption in the visible region is entirely due to changes in the isoquinoline molecule.⁷

The dialkyl aluminium hydride which is added to the titration cell before the sample serves to consume the last traces of water and oxygen in the solvent and cell, and also to ensure the presence of enough dialkyl aluminium hydride to indicate the end-point.

The selection of 0.5 absorbance for the end-point allows fairly rapid titration without fear of overrunning the end-point. About 0.15 ml of titrant beyond the equivalence point is required to reach an absorbance of 0.5, but this is cancelled out by carrying the preliminary titration to the same level.

The concentrations of impurities which react with alkyl aluminium compounds are reduced to 10^{-3} mole per litre by purifying the toluene as described.⁸ As this is only 0.4% relative to the 0.25 molarity of the isoquinoline, it is sufficiently accurate to standardise the titrant on the basis of the isoquinoline content alone. This is conveniently done by titration with perchloric acid in acetic acid.

RESULTS

The method was applied to alkyl aluminium compounds in which the alkyl groups ranged from methyl to hexyl. Undiluted alkyl aluminium compounds as well as hydrocarbon solutions were analysed. When samples of triethyl aluminium and trimethyl aluminium with stated purities of 98% minimum were analysed, purities of 97.2% and 96.8%, respectively, were found.

Nine samples were analysed by isoquinoline titration and also by the method of Ziegler and Gellert⁹ in which ammonia is the reagent. These samples were suspected of containing dialkyl aluminium alkoxide or dialkyl aluminium hydride. The results are shown in Table I.

TABLE I.—COMPARISON OF ISOQUINOLINE AND AMMONIA METHODS

Compound	Activity, <i>mmole/g</i> *	
	Isoquinoline method	Ammonia method
Tri- <i>n</i> -propyl aluminium	6.00	6.02
	5.96	5.92
	6.58	6.57
	6.41	6.37
	6.30	6.34
	5.67	5.81
	5.47	5.81
Tri-isobutyl aluminium	4.85	4.80
Tri-isohexyl aluminium	3.52	3.44

* Each result is the average of duplicate determinations.

Twenty-eight samples were analysed in duplicate to find the standard deviation, which is 0.02 mmole per g.

Acknowledgements—The author wishes to thank R. A. Dove, who performed the analyses by the ammonia method, and J. A. Mitchen of Ethyl Corp., who supplied the high purity triethyl aluminium and trimethyl aluminium.

Zusammenfassung—Bei der Titration von Aluminium-Alkyl Verbindungen mit Isochinolin kann man den Endpunkt photometrisch bestimmen. Das ermöglicht die Bestimmung der Aluminium-Verbindungen in Anwesenheit von Sauerstoff-enhaltenden Verunreinigungen, mit einer Standardabweichung von 0.02 Millimol pro Gramm. Die Methode wurde zur Bestimmung von Aluminium-Trialkylen und Aluminium-Dialkylhydriden verwendet, mit Alkylgruppen von Methyl- bis einschliesslich Hexyl- vorlagen.

Résumé—Lors du titrage des dérivés hydrocarbonés de l'aluminium par l'isoquinoléine, le virage peut être reconnu par spectrophotométrie. Ceci permet leur dosage en présence d'impuretés oxygénées avec un écart moyen de 0.02 millimoles par gramme. La méthode a été appliquée aux composés du type $Al(R)_3$ et $AlH(R)_2$ dans lesquels R désigne un radical hydrocarboné du méthyle à l'hexyle.

REFERENCES

- ¹ K. Ziegler and H. G. Gellert, *U.S. Pat.* 2695327, 23 November, 1954.
- ² V. J. Anhorn, K. J. Frech, C. S. Schaffel and D. Brown, *Chem. Eng. Progress*, 1961, **57**, No. 5, 43.
- ³ E. Bonitz, *Ber.*, 1955, **88**, 742.
- ⁴ J. S. Fritz and D. J. Pietrzyk, *Analyt. Chem.*, 1959, **31**, 1157.
- ⁵ R. F. Goddu and D. N. Hume, *ibid.*, 1954, **26**, 1740.
- ⁶ J. H. Mitchen, *ibid.*, 1961, **33**, 1331.
- ⁷ W. P. Neumann, *Ann.*, 1960, **629**, 23.
- ⁸ T. G. Mungall and J. H. Mitchen, *Analyt. Chem.*, 1961, **33**, 1330.
- ⁹ K. Ziegler and H. G. Gellert, *Ann.*, 1960, **629**, 20.

Contribution No. 278 from the Research Division, Goodyear Tire & Rubber Co., Akron 16, Ohio. Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 6 March, 1962.

DETERMINATION OF SMALL AMOUNTS OF CALCIUM IN THE PRESENCE OF LARGE AMOUNTS OF ALKALI METAL SALTS BY AMPEROMETRIC CHELATOMETRY

M. L. RICHARDSON

John and E. Sturge Ltd., Lifford Chemical Works, Kings Norton
Birmingham 30, England

(Received 28 August 1962. Accepted 12 September 1962)

Summary—A rapid polarographic procedure for the determination of 0–50 ppm of calcium in alkali metal salts is described. It is selective and highly sensitive, with only strontium and barium causing interference to any marked degree. A cathode ray polarograph is used to measure the zinc peak current in a potassium chloride/hydroxide/zincate base electrolyte solution; a standard EDTA solution is added to the test solution; and the peak current of the zinc remains sensibly constant until all of the calcium has reacted, after which the peak current decreases as the zinc reacts with the EDTA. The end-point is found by extrapolation of the current-titration curves.

INTRODUCTION

THE determination of 0–50 ppm of calcium in the presence of large amounts of alkali metal salts by chelatometric titration, using dyestuff indicators is not feasible because of breakdown of the indicator reaction.

The use of fluorescein complexan (Calcein)^{1–6} is an advantage for the macro determination of calcium in potassium salts by titration with the bi-potassium salt of EDTA, but when the potassium to calcium ratio exceeds 250, poor results are obtained because of breakdown of the indicator reaction.²²

Using azo-dyestuff indicators the end-points are invariably poor, although Acid Alizarin Black SN^{7,8,9} has been found to give the best results, particularly if 1,2-cyclohexanediaminetetra-acetic acid is used as the chelating agent in place of EDTA. Methods involving simple flame photometric instruments are not applicable because difficulties are met with from interference by sulphate, phosphate and certain organic anions.^{10,11}

In view of these difficulties the use of the amperometric titration^{12–18} procedure of Laitinen and Sympson was investigated with the view of increasing the sensitivity of their procedure using the K.1000 Cathode Ray Polarograph.

Laitinen and Sympson's paper¹⁶ describes a titration procedure using the Sargent Manual Polarograph Model III and an H-cell of 100-ml capacity in the titration arm. Their titration cell is fitted with calomel and dropping mercury electrodes; a potential of -1.700 V is maintained across a mixture of 50 ml of the solution containing >2 mg of calcium and 10 ml of 0.01M potassium zincate indicator. Standard 0.05M EDTA is run in from a 5-ml burette and the solution then requires deoxygenating for at least 2 min after each increment of reagent. The end-point is found by extrapolation of the current-titration curves. Laitinen and Sympson¹⁶ also evaluate from a study of dissociation constants that practically all of the zinc will be in the form of zincate ion at

the equivalence point in the hydroxide solution and they also indicate that the zincate will be converted to the EDTA complex when only a slight excess of EDTA is present.

The procedure of Laitinen and Sympton¹⁶ was found to be insufficiently sensitive for the determination of 0–50 ppm of calcium in alkali metal salts, but by using the proposed procedure it was found that the sensitivity could be increased by at least twenty-fold over the earlier procedure. In addition, the proposed procedure has the advantage of using the standard 5-ml capacity polarographic cells as supplied with the K.1000 Cathode Ray Polarograph and, furthermore, because the titrant is added by means of a 0.01-ml micro pipette bubbling for only a few sec with nitrogen is required against the 2 min previously recommended.

EXPERIMENTAL

Base electrolyte

A base electrolyte suitable for both the formation of the zincate ion and the reaction of EDTA with calcium and zinc was chosen as the most suitable from consideration of Laitinen and Sympton's studies of the dissociation constants.

An electrolyte containing potassium hydroxide was chosen, because an electrolyte containing ammonia would cause magnesium to be simultaneously titrated.

A concentration of $8.8 \times 10^{-5} M$ zinc in the sample solution prior to titration was found to be satisfactory and was used throughout the work. This concentration of zinc was chosen because it gives a convenient diffusion current for measurement and at the same time is sufficiently sensitive to serve as indicator.

Polarograph

The K.1000 Cathode Ray Polarograph produces peaked polarograms¹⁹ of the type shown in Figs. 1 and 2, and is eminently suitable for this type of work because the polarograms are reproduced every 7 sec. The instrument settings used are as described under *Method*.

Determination of calcium

(a) *In the presence of carbonates and hydroxides of potassium and sodium.* It was found that 1–50 μg of calcium could be determined in carbonates and hydroxides of potassium and sodium, provided that

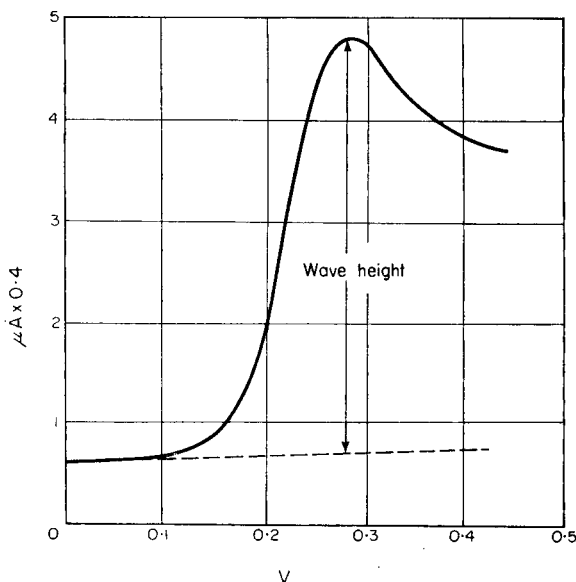


FIG. 1—Typical polarogram at commencement of titration, showing interpretation of wave height.

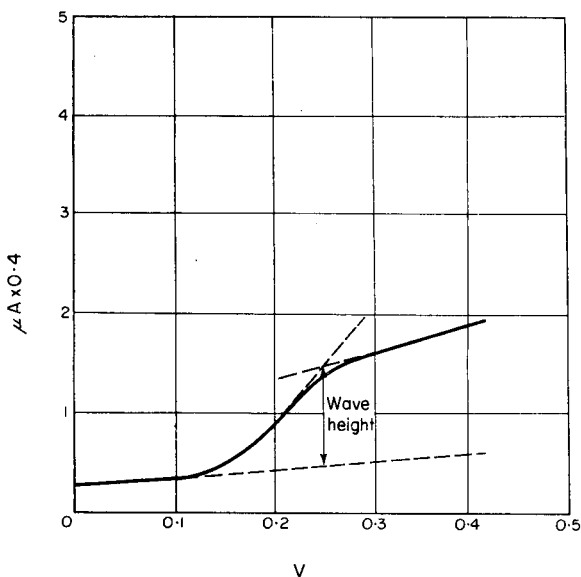


FIG. 2—Typical polarogram at end of titration, showing interpretation of wave height.

the sample was first acidified with hydrochloric acid and the carbon dioxide expelled by boiling. The resulting solutions were then treated as described under *Method*. Failure to remove the carbon dioxide leads to:

- (i) The formation of poorly shaped waves;
- (ii) Low results, because any calcium in the form of carbonate is not taken into solution.

(b) *In the presence of citrate and tartrate.* Attempts to carry out the determination in the presence of citrate and tartrate were not successful, because of the competitive chelating action of the organic ions. Calcium can, however, be determined in mixtures containing citrate and tartrate or other organic matter, providing that the sample is dry ashed and acidified prior to treating with base electrolyte.

Titration curve

A typical titration curve is shown in Fig. 3, and Figs. 1 and 2 show typical polarograms. The equivalence point, found by extrapolation, indicates the quantity of 0.01M EDTA required to form a chelate with all of the calcium.

Interferences

No interference with the calcium titration was found when the ions included in Table I were added to a sample of potassium hydrogen carbonate previously found to contain 22 ppm of calcium.

The samples were treated as described under *Method*.

Interference was, however, found on adding 0.5 g of citrate or tartrate ion to 1 g of potassium hydrogen carbonate as described above, in that a gradually, but consistently sloping titration curve was obtained indicating that competitive chelation was occurring. The effect was less marked with tartrate than citrate.

Recoveries

Varying amounts of calcium were added to the zincate base electrolyte containing added potassium chloride equivalent to the amount of potassium hydrogen carbonate usually taken for a determination and the recoveries are shown in Table II.

Repeats on samples gave a mean percentage error of $\pm 3\%$ on samples containing 10–50 ppm of calcium and $\pm 5\%$ on samples containing 1–10 ppm of calcium.

Method

Calcium is determined by amperometric chelatometry, being titrated with EDTA at pH 12 in the presence of a zincate indicator ion which is polarographically reducible.

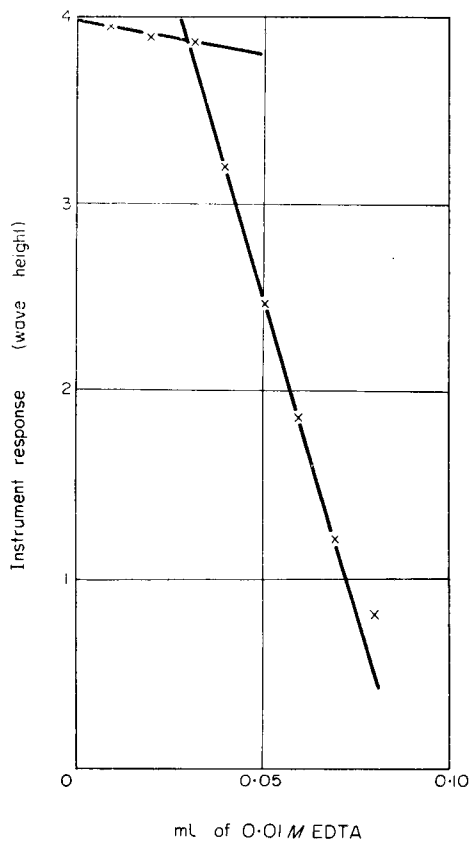


FIG. 3.—Titration curve (titration: 0.030 ml of 0.01M EDTA; blank: 0.003 ml of 0.01M EDTA; calcium content: 22 ppm).

Reagents

All reagents must be of recognised analytical grade.

5N Hydrochloric acid

Zincate base electrolyte: Dissolve 7.1 mg of zinc oxide in 1 ml of 5N hydrochloric acid and 5 ml of water and add to a solution containing 16 g of potassium hydroxide and 14.9 g of potassium chloride. Dilute to 500 ml with distilled water.

0.01M EDTA: Standardised against calcium carbonate, as described by Toribora and Koval.⁴

Apparatus

Polarograph: K.1000 Cathode Ray Polarograph, Southern Analytical Ltd., Camberley, Surrey, England.

Micropipettes: 0.01-ml "E-MIL".

Preparation of sample solutions

(a) **Carbonate and hydroxides of alkali metals.** Transfer a 1 ± 0.01 -g sample to a 30-ml beaker, add 5N hydrochloric acid until the solution is just acid, then boil to expel carbon dioxide. Allow to cool. Transfer to a 10-ml volumetric flask containing 5 ml of zincate base electrolyte solution and dilute to the mark with distilled water.

(b) **Sodium and potassium citrates and potassium sodium tartrate.** Transfer a 1-g sample to a platinum crucible and gently carbonise by carefully heating over a Bunsen flame. Transfer to an electric muffle furnace and heat at 550° for 24 hr. Allow to cool, add 5N hydrochloric acid until the solution is just acid and boil to expel carbon dioxide. Continue as under (a); filter if necessary.

TABLE I

Element added to 1 g of potassium hydrogen carbonate	Amount of element added, μg	Remarks
Aluminium ^{III}	20	No interference
Antimony ^{III}	20	No interference
Bismuth ^{III}	20	No interference
Cadmium ^{II}	20	No interference
Chromium ^{III}	20	Wave height reduced, no interference to titration
Cobalt ^{II}	20	No interference
Iron ^{III}	20	No interference
Lead ^{II}	20	No interference
Magnesium ^{II}	20	No interference
Magnesium ^{II}	40	Wave height slightly reduced, no interference to titration
Manganese ^{II}	20	Wave height reduced, no interference to titration
Molybdenum ^{VI}	20	No interference
Nickel ^{II}	20	No interference
Phosphate	20	No interference
Sulphate	20	No interference
Thallium ^I	20	No interference
Tin ^{II}	20	No interference

TABLE II

Ca added,* μg	No. of determinations	Ca found, μg	Ca recovered, μg	Recovery, %
0	5	1.7 (mean)	—	—
10	1	12.0	10.3	103
10	1	11.6	9.9	99
20	1	21.2	19.5	97.5
20	1	22.4	20.7	103.5
30	1	32.4	30.7	102
30	1	32.4	30.7	102
40	1	42.4	40.7	102
40	1	42.4	40.7	102

* To 10-ml volume.

Instrument settings

Cathodic reduction
 Reference electrode Hg pool
 Start potential—1.05 V
 Scale factor 0.4
 Direct current
 Y shift 13.2

Procedure

Transfer a 5-ml aliquot of the sample solution to a polarographic cell containing mercury and deoxygenate with nitrogen for 3 min. Record the height of the polarogram. The wave height (instrument response) is obtained by measuring the perpendicular distance between the peak height and the tangent to the sloping base line (see Fig. 1 and reference 19). Add 0.01M EDTA in 0.01-ml increments from a micropipette and measure the height of the wave after each addition. The additions up to that at which the polarogram remains sensibly constant should be recorded (*i.e.*, the point at which

all of the calcium has been chelated). Plot a graph relating wave height to titration (ml of EDTA). The point of intersection of the two lines drawn through the respective sets of points gives the equivalence point of the titration (see Fig. 4).

Blank determination

Transfer 5 ml of zincate base electrolyte to a 10-ml volumetric flask, dilute to the mark with distilled water, then proceed as above.

CONCLUSIONS

The method is more rapid and sensitive than the method of Laitinen and Sympton and uses standard polarographic glassware. The sensitivity of the method is high, enabling 1 ppm of calcium to be detected, and is more sensitive than any other chelometric method for calcium in the presence of much alkali metal salt. The procedure is not highly selective, however, as strontium and barium will be titrated along with the calcium, but interferences from many elements and radicals are negligible. The method could be made more sensitive if required by decreasing the quantity of zinc in the zincate base electrolyte, but the polarographic waves are then of an inferior nature; a slope corrector^{20,21} would, however, make this difficulty less apparent.

Acknowledgement—I thank the Directors of John & E. Sturge Ltd. for permission to publish this paper.

Zusammenfassung—Eine Methode zur raschen, polarographischen Bestimmung von 0–50 ppm Calcium in Alkalimetallsalzen wird beschrieben. Das Verfahren ist hochempfindlich und selektiv da lediglich Strontium und Barium Störungen von nennenswertem Ausmass verursachen. Ein Kathodenstrahlpolarograph wird verwendet um den Diffusionsstrom von Zink in einer Kaliumchlorid-Hydroxyd-Zinkat-Grundlösung zu messen; ADTE Standardlösung wird zugesetzt und der Diffusionsstrom des Zinks bleibt praktisch konstant bis alles Calcium reagiert hat. Anschliessend sinkt der Diffusionsstrom ab, da Zinkat mit ADTE reagiert. Der Endpunkt wird durch Extrapolation der Stromstärke-Titrationsmittel-Kurve gefunden.

Résumé—L'auteur décrit une méthode de dosage polarographique rapide de 0–50 ppm de calcium dans les sels alcalins. Cette méthode est très sensible et sélective; le strontium et le baryum gênent peu.

Un polarographe oscillographique est utilisé pour mesurer le courant de diffusion du zinc dans un électrolyte support constitué de chlorure de potassium en milieu alcalin (zinc à l'état de zincate). Une solution étalon d'EDTA est ajoutée à la solution à analyser; le courant de diffusion du zinc demeure sensiblement constant tant que tous le calcium n'a pas réagi; puis le courant de diffusion décroît au fur et à mesure de la formation du complexe entre le zinc et l'EDTA.

Le point équivalent est déterminé par extrapolation des courbes représentant le courant de diffusion en fonction de la quantité d'EDTA ajoutée.

REFERENCES

- ¹ R. Přibil, *Analyst*, 1958, **83**, 188.
- ² H. Diehl and J. L. Ellingboe, *Analyt. Chem.*, 1956, **28**, 882.
- ³ D. H. Wilkins, *Talanta*, 1960, **4**, 182.
- ⁴ T. Y. Toribara and L. Koval, *ibid.*, 1961, **7**, 248.
- ⁵ R. L. Olsen, H. Diehl, P. F. Collins and R. B. Ellestad, *ibid.*, 1961, **7**, 187.
- ⁶ J. Körbl, F. Vydra and P. Přibil, *ibid.*, 1958, **1**, 281.
- ⁷ R. Belcher, R. A. Close and T. S. West, *ibid.*, 1958, **1**, 238.
- ⁸ R. A. Close and T. S. West, *Analyt. Chim. Acta*, 1961, **23**, 261.
- ⁹ *Idem*, *ibid.*, 1961, **23**, 370.
- ¹⁰ R. D. Bond and J. T. Hutton, *Analyst*, 1958, **83**, 684.

- ¹¹ R. N. P. Farrow and A. G. Hill, *Talanta*, 1961, **8**, 116.
- ¹² G. W. C. Milner, *The Principles and Applications of Polarography and other Electroanalytical Processes*. Longmans, London, 1958, p. 685.
- ¹³ G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, 1948, **31**, 1029.
- ¹⁴ R. Přibil and E. Vicenora, *Chem. Listy*, 1952, **46**, 535; *Coll. Czech. Chem. Comm.*, 1953, **18**, 308.
- ¹⁵ D. Lydersen, *Z. analyt. Chem.*, 1953, **139**, 327.
- ¹⁶ H. A. Laitinen and R. F. Simpson, *Analyt. Chem.*, 1954, **26**, 556.
- ¹⁷ A. Ringbom and B. W. Wilkman, *Acta. Chem. Scand.*, 1949, **3**, 22.
- ¹⁸ G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, 1951, **34**, 1798.
- ¹⁹ *K.1000 Cathode Ray Polarograph, Equipment Handbook*, Southern Analytical Ltd., Camberley, Surrey, England, 1961.
- ²⁰ R. C. Rooney, private communication.
- ²¹ J. E. Seaborn, *Improvements to the Cathode Ray Polarograph*, A.E.R.E. Report R. 3630.
- ²² M. L. Richardson, unpublished studies.

PRECIPITATION OF METAL 8-HYDROXYQUINOLATES FROM HOMOGENEOUS SOLUTION—VI*

ZINC

J. PAUL JONES, ORVILLE E. HILEMAN, JR. and LOUIS GORDON[®]
Department of Chemistry, Case Institute of Technology
Cleveland 6, Ohio, U.S.A.

(Received 27 August 1962. Accepted 11 September 1962)

Summary—The precipitation of zinc 8-hydroxyquinolate from homogeneous solution with 8-acetoxyquinoline results in a precipitate with superior physical characteristics in comparison with that produced by the conventional method, and furnishes a much better separation of zinc from lead, calcium and magnesium.

INTRODUCTION

PREVIOUS papers in this series have described the use of 8-acetoxyquinoline to precipitate from homogeneous solution 8-hydroxyquinolates of the following metals: thorium,¹ aluminium,² uranium,³ and magnesium.⁴ The present investigation was undertaken to develop a similar method for the precipitation of zinc.

EXPERIMENTAL

Reagents

Zinc: Exactly 2.0011 g of reagent-grade zinc metal (J. T. Baker Co., Phillipsburg, New Jersey) were dissolved in 10 ml of hydrochloric acid and the resulting solution was diluted to 2.000 litres.

8-Acetoxyquinoline: A solution was prepared by dissolving 12 g of PFHS Grade 8-acetoxyquinoline (Burdick and Jackson Laboratories, 1953 S. Harvey St., Muskegon, Mich.) in 100 ml of acetone; 5 ml of this solution contained twice the stoichiometric quantity of reagent needed to precipitate 50 mg of zinc.

8-Hydroxyquinoline: The solution used in the conventional precipitation of zinc was prepared by dissolving 4 g of the reagent (Matheson, Coleman, and Bell Division of the Matheson Company, East Rutherford, New Jersey) in 250 ml of ethyl alcohol.

All other chemicals used were reagent-grade.

Procedure

To 5–50 mg of a nearly neutral solution of zinc in a 250-ml beaker, add 2 ml of glacial acetic acid and dilute to 150 ml. Adjust the pH to 4.5 with filtered ammonium hydroxide (1:1). Add 5 ml of the 8-acetoxyquinoline solution and dilute to a final volume of 175 ml. Cover the beaker with a watch-glass and place on an electric hot-plate regulated to maintain a temperature of approximately 75° for 2 hr. Filter the hot solution through a medium-porosity filter-crucible, transferring and washing the precipitate with about 100 ml of cold water. Dry to constant weight at 130° and weigh as $Zn(C_9H_6ON)_2$; the gravimetric factor for $Zn/Zn(C_9H_6ON)_2$ is 0.1849.

RESULTS AND DISCUSSION

Table I shows that quantitative results may be obtained with 5–50 mg of zinc; larger quantities of zinc were not determined; quantities less than 5 mg gave low results. Filtrates and washings were analysed for zinc both by spectrophotometric and polarographic methods, and in all cases (11 determinations) were found to contain less than 0.09 mg of zinc.

* Part V: See ref. 4.

TABLE I.—PRECIPITATION OF ZINC 8-HYDROXYQUINOLATE

Number	1	2	3	4	5	6	7	8	9	10	11	12	13
Method of precipitation	Conv.	PFHS	PFHS	PFHS	PFHS	PFHS	Conv.	PFHS	Conv.	PFHS	Conv.	PFHS	Conv.
Diverse element taken, mg	none	none	none	none	none	Pb 100	Pb 100	Ca 100	Ca 100	Mg 100	Mg 100	Pb 100 Ca 100 Mg 100	Pb 100 Ca 100 Mg 100
Zinc taken, mg	50.02	50.02	25.01	10.00	5.00	50.02	50.02	50.02	50.02	50.02	50.02	50.02	50.02
Difference, mg	+0.18 +0.21 +0.16	-0.03 +0.05 -0.14 +0.02	+0.11 +0.02 -0.21	+0.09 +0.11 -0.18	+0.17 +0.19 -0.01 -0.10	+0.24	>57 >61	+0.06 -0.10	+0.33 +0.35	+0.12 -0.01	>41 >36	+0.31	>71

Table I also shows that 50 mg of zinc can easily be separated from lead, calcium and magnesium by PFHS but not by conventional precipitation; the separation from copper or manganese was not successful.

The precipitate formed by PFHS was easily filtered whereas that formed by the conventional method was extremely difficult to filter. Photomicrographs showed that the crystals (PFHS) were much larger and more regular in size than those formed by the conventional method.

Thermogravimetric analysis of the precipitate showed 130° to be a satisfactory drying temperature.

Acknowledgement—The authors wish to acknowledge the support in part of the United States Atomic Energy Commission under Contract AT(11-1)-582.

Zusammenfassung—Die Fällung von Zinkoxinat mittels 8-Acetoxychinolin aus homogener Lösung ergibt einen Niederschlag mit besseren physikalischen Eigenschaften im Vergleich zu einem nach üblichen Methoden erhaltenen. Die Trennung des Zinks von Blei, Calcium und Magnesium ist wesentlich verbessert.

Résumé—La précipitation de l'oxinate de zinc en solution homogène par la 8-acétoxyquinoléine donne un précipité de caractéristiques physiques supérieures si on le compare à celui obtenu par la méthode classique et permet une meilleure séparation du plomb, du calcium et du magnésium.

REFERENCES

- ¹ K. Takiyama, E. D. Salesin and L. Gordon, *Talanta*, 1960, **5**, 231.
- ² D. J. Marec, E. D. Salesin and L. Gordon, *ibid.*, 1961, **8**, 293.
- ³ J. Bordner, E. D. Salesin and L. Gordon, *ibid.*, 1961 **8**, 579.
- ⁴ J. T. Corkins, R. F. Pietrzak and L. Gordon, *ibid.*, 1962, **9**, 49.

SHORT COMMUNICATIONS

Organic analysis—XXIX:* A new spraying agent for reducing sugars on paper chromatograms

(Received 2 January 1961. Revised 18 July 1962. Accepted 2 August 1962)

NUMEROUS reagents have been reported for the detection of reducing sugars on paper chromatograms. These include aniline,¹⁻³ *p*-anisidine, dimethylaniline, α -naphthylamine and diphenylamine,⁴ 3,5-dinitrosalicylic acid,⁵ 3,4-dinitrobenzoic acid,⁶ 4,5-dinitroveratrole,⁷ and ammoniacal silver nitrate.⁸ Some of these are useful in routine work. In the authors' laboratory, however, 3,6-dinitrophthalic acid has proved to be a better reagent for the micro-detection of certain reducing sugars on paper. It is highly sensitive, and the reagent solution is stable.

EXPERIMENTAL

Reagents

3,6-Dinitrophthalic acid solution: Dissolve 0.4 g of potassium 3,6-dinitrophthalate (Ishizu Seiyaku Kabushikikaisha) in 100 ml of water, followed by 2.0 g of potassium carbonate (Japan Industrial Standards, 1st Grade).

Aniline hydrogen phthalate, *p*-anisidine, ammoniacal silver nitrate: Prepared according to references 1, 4, 8, respectively.

Sugars: Japanese Industrial Standards, 1st Grade.

Developing solvents: Redistilled and mixed in the ratios quoted below.

Papers: Toyo Roshi No. 51, 2 × 40 cm.

Procedure

Spot 0.005 ml of an aqueous sample solution, containing 0.2 – 10 μ g of the sugar, on paper, and subject to ascending one-dimensional chromatography for 9 hr. Air-dry the paper, and spray with 3,6-dinitrophthalate solution. Again air-dry, and then heat the paper in an oven at 100° for 3 min. The reducing sugar is indicated by a wine-red spot on a faint pink background.

Other colour developing agents are sprayed and treated according to the methods described in the literature.

RESULTS AND DISCUSSION

3,6-Dinitrophthalic acid is first reduced, by reducing sugars in alkaline medium, to 3-nitro-6-hydroxyaminophthalic acid, which is wine-red. This coloured product is in turn reduced to 4,4'-dinitroazophthalic acid, on prolonged treatment in the presence of sodium thiosulphate.⁹ The final orange-red colour of the latter product is so stable that it has been used successfully for the microl determination of reducing sugars.¹⁰ However, for detection on a paper chromatogram the colour of the first product proves to be more sensitive than that of the second. In consequence, it is more satisfactory for this purpose to carry out the reaction rapidly without sodium thiosulphate. The wine-red colour is stable for 30 min, and then gradually changes to orange-red.

Arabinose, ascorbic acid, fructose, galactose, glucosamine, glucose, glucuronolactone, lactose, maltose, rhamnose, ribose and xylose were run on chromatograms which were developed with each of the following solvent systems: (A) *n*-butanol saturated with water, (B) *n*-butanol-ethanol-water (40:10:50), (C) ethyl acetate-pyridine-water (8:2:1), (D) phenol saturated with water. In general, the sensitivity of detection given by the new reagent was equal to that given by aniline hydrogen phthalate or by *p*-anisidine hydrochloride.

Increased sensitivity (as indicated below) was, however, shown for certain sugars after development by the solvent system indicated.

* Part XXVIII: *Chem. Pharm. Bull.*, Tokyo, 1961, 9, 263.

Solvent system	Sugars	Sensitivity, μg
A	Galactose, glucosamine, ribose	0.2
B	Fructose, glucose	0.2
B	Maltose	0.5
C	Fructose, galactose	0.2
D	Lactose, maltose	2.0

The reagent solution is easily prepared, easy to use, and stable for a long time; aniline hydrogen phthalate and *p*-anisidine solutions turn brown in a few days.

Summary—An alkaline solution of 3,6-dinitrophthalic acid proves to be a very stable and sensitive spraying reagent for the detection of reducing sugars on paper chromatograms.

Zusammenfassung—Eine alkalische Lösung von 3,6-Dinitrophthalsäure wurde als beständiges und empfindliches Sprühmittel für reduzierende Zucker auf Papierchromatogrammen gefunden.

Résumé—Une solution alcaline de l'acide 3,6-dinitrophthalique s'est révélée être un agent de pulvérisation très stable et sensible pour les sucres réducteurs sur les chromatogrammes à papier.

Pharmaceutical Institute
Medical Faculty
University of Kyushu
Fukuoka, Japan

TSUTOMU MOMOSE
MASARU NAKAMURA

REFERENCES

- ¹ S. M. Partridge, *Nature*, 1949, **164**, 443.
- ² R. H. Horrocks and G. B. Manning, *Lancet*, 1949, **256**, 1042.
- ³ S. M. Partridge, *Biochem. J.*, 1948, **42**, 238.
- ⁴ *Idem*, *Nature*, 1949, **164**, 443.
- ⁵ A. Jeans, C. S. Wise and R. J. Dimler, *Analyt. Chem.*, 1951, **23**, 415.
- ⁶ F. Weygand and H. Hofman, *Ber.*, 1950, **83**, 405.
- ⁷ A. Bevenue and T. Williams, *J. Chromatog.*, 1959, **2**, 199.
- ⁸ S. M. Partridge, *Biochem. J.*, 1948, **42**, 238.
- ⁹ T. Momose and A. Inaba, *Chem. Pharm. Bull., Tokyo*, 1961, **9**, 263.
- ¹⁰ T. Momose, A. Inaba, Y. Mukai and M. Watanabe, *Talanta*, 1960, **4**, 33; **5**, 275; *Yakugaku Zasshi*, 1961, **81**, 227.

Use of compounds of the type $\text{M}^{\text{II}}\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot x\text{H}_2\text{O}$ in analytical chemistry—I: The determination of potassium in barium titanate

(Received 2 August 1962. Accepted 12 September 1961)

INTRODUCTION

SEVERAL insoluble titanyl compounds of the type $\text{M}^{\text{II}}\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot x\text{H}_2\text{O}$ have been prepared recently.^{1,2} These compounds are formed, for example, by barium, strontium, calcium and lead. As far as we know no analytical use has been considered for these crystalline compounds, although they can be very useful for the separation or removal of titanium from solutions. A simple example of their use is in the determination of potassium in barium titanate single crystals by means of flame photometry, as described in this paper.

The determination of potassium is influenced by the presence of barium and titanium. A method for removal of titanium by hydrolysis has been proposed by Zikánová,³ but this procedure is slow, and can easily lead to erroneous results caused by occlusion. These disadvantages can be overcome, if titanium is separated as $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$. Moreover the second interfering element, barium, is simultaneously removed in the same operation, especially as the solution obtained from the barium titanate single crystals contains barium and titanium in a favourable ratio for the formation of the barium titanyl oxalate compound.

EXPERIMENTAL

The decomposition of the samples is achieved by means of hydrochloric acid.¹ Chloride ions were recommended for the determination of potassium by flame photometry by Zöllner,⁴ but Collins and Polkinhorne⁵ showed in a later study that the light emission decreases with increasing chloride concentration. Our procedure had, therefore, to take this fact into account.

Further the influence of oxalate ions on the emission had to be checked. Table I shows that interference would not be expected under the experimental conditions adopted.

TABLE I. INFLUENCE OF AMMONIUM OXALATE CONCENTRATION ON EMISSION OF POTASSIUM
Concentration of potassium, 3 mg of K/10 ml.

Concentration of ammonium oxalate, %	Decrease of emission, %
0	0
0.125	0
0.25	1
0.5	3
1	6

Note: The concentration of oxalate in the solutions used for analytical purposes is about 0.1%.

In addition, a closer examination of the conditions under which the precipitate is formed had to be carried out. A slight excess of oxalic acid (about 30%) proved to be useful. Precipitation begins at a pH value of 5.0 and even an excess of ammonia with a pH of 10.0 has no influence on the sedimentation rate. A neutral solution or a slight excess of ammonia is convenient for the determination. The precipitate formed in a hot solution is deposited quickly and can be filtered off without difficulty. No adsorption of potassium was observed.

Finally, a suitable reference material for calibrating had to be found. A very pure potassium-free barium titanate powder was used; this was obtained by thermal decomposition of barium titanil oxalate prepared from purified starting materials.¹

All measurements were performed with a Model III Carl Zeiss, Jena flame photometer provided with a K77 interference filter.

Procedure

(1) Place 0.2 g of a finely powdered sample of BaTiO₃ single crystals, weighed with an accuracy of 0.001 g, in a 100-ml volumetric flask previously carefully dried and weighed.

(2) Add 15 ml of concentrated hydrochloric acid, stir, boil for 30-45 sec, dilute with 15 ml of 2% oxalic acid solution, and heat, with constant stirring, nearly to boiling until dissolution is completed.

(3) Evaporate carefully to a volume of about 10 ml. Weigh the solution in the volumetric flask with an accuracy of 0.1 g. All further samples have to be evaporated to the same weight in order to maintain a constant concentration of chloride ions.

(4) Dilute with 50 ml of water, heat to boiling and add drop by drop concentrated ammonia diluted with an equal volume of water until the solution over the precipitate is neutral or has a slight excess of ammonia.

TABLE II. RESULTS OF DETERMINATION OF POTASSIUM IN BaTiO₃ SINGLE CRYSTALS

Sample no.	Potassium, %			average value
	determination no.			
	1.	2.	3.	
1	0.34	0.32	0.31	0.32
2	0.36	0.35	0.33	0.35
3	0.36	0.35	0.36	0.36
4	0.35	0.36	0.37	0.36
5	0.40	0.41	0.39	0.40
6	0.27	0.27	0.26	0.27

(5) Leave the hot solution in contact with the precipitate for 10 min, cool, add water to bring the volume to 100 ml, stir and filter. Use the filtrate directly for the flame photometric determination.

(6) Prepare a calibration curve with solutions made from potassium-free barium titanate with between 0.25 and 1.25 mg of added potassium (as potassium chloride solution containing 50 μg of K in 1 ml.) Maintain the same conditions and use the same reagents as before.

RESULTS

The procedure described above was used for the determination of potassium in a series of BaTiO_3 single-crystal samples. Table II shows the results of three determinations for each sample, and their average values. These results prove that they lie within tolerances of $\pm 7\%$ for the selected amount of samples with a relatively small potassium content. A gravimetric control by means of sodium tetraphenylborate⁶ was carried out. Its result (0.39% of K obtained for sample no. 5) is in very good agreement with the determination by means of flame photometry.

Finally we should like to point out that the method described here can also be used for a solution containing excess of titanium, if a sufficient amount of barium is added.

Summary—The determination of potassium in barium titanate is the first example of the use of insoluble compounds of the type $\text{M}(\text{II})\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot x\text{H}_2\text{O}$ in analytical chemistry. A simultaneous simple separation of barium and titanium is achieved, and no interference of oxalate ions in the determination of potassium by flame photometry is experienced.

Zusammenfassung—Die Bestimmung von Kalium in Bariumtitanat ist das erste Beispiel für eine analytische Anwendung von unlöslichen Verbindungen des Types $\text{M}(\text{II})\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot x \text{ aq}$. Eine einfache Simultanentrennung von Barium und Titan wird erzielt; Störungen der flammenphotometrischen Bestimmung des Kaliums durch das Oxalat wurden nicht beobachtet.

Résumé—Le dosage du potassium dans le titanate de baryum est le premier exemple d'utilisation des composés insoluble du type $\text{M}(\text{II})\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot x\text{H}_2\text{O}$ en chimie analytique. Une séparation simple et simultanée du baryum et du titane est réalisée et les oxalates ne gênent pas dans la détermination du potassium par photométrie de flamme.

*Institute of Physics
Czechoslovak Academy of Sciences
Prague, Czechoslovakia*

H. AREND
J. NOVÁK

REFERENCES

- ¹ W. S. Clabaugh, E. M. Swiggard and R. Gilchrist, *J. Research Nat. Bur. Stand.*, 1956, **56**, 289.
- ² B. V. Strižkov, A. V. Lapickij and L. G. Vlasov, *Zhurn. priklad. Chim.*, 1961, **34**, 673.
- ³ A. Zikánová, *dipl. thesis*, Charles University, Prague, 1961.
- ⁴ H. Zöllner, *Glas-Email-Keremo-Technik*, 1951, **2**, 378.
- ⁵ G. C. Collins and H. Polkinhorne, *Analyst*, 1952, **77**, 430.
- ⁶ R. Přibil, *Komplexony v chemické analýse*. Prague, 1957.

Determination of boron in zirconium and Zircaloy

(Received 1 August 1962. Accepted 12 September 1962)

INTRODUCTION

THE production of nuclear materials containing low alloying amounts of boron in zirconium and Zircaloy requires a precise analysis. The matrix poses the problem of difficult solution without loss of boron. This problem was solved by dissolution in bromine-methanol under reflux. The carminic acid method is used in the determination of boron because, when the variables are carefully controlled,

it gives high precision. Results obtained on standard samples showed high precision as well as full recovery of boron.

EXPERIMENTAL

Apparatus

The following items of special equipment are required:

150-ml quartz beakers*; 200-ml long-neck, round-bottom, quartz flasks with 29/42 standard taper joint, inner; quartz distillation side-arm* with 29/42 standard taper joint, outer; quartz condensers*; free-flow funnel for 50-ml volumetric flasks.

Reagents

Bromine: AR.

Methanol: AR, anhydrous.

10% *Sodium hydroxide*: Dissolve 10 g of sodium hydroxide in 100 ml of water.

Sulphuric acid: 18M, 6M and 3.6M.

0.92% *Carminic acid solution*: Dissolve 1.84 g of carminic acid in 2 litres of 18M sulphuric acid. It is stable for 6 months.

Tin^{II} chloride.

Boron standard solutions: These should contain 10 and 20 μg of boron/ml of 3.6M sulphuric acid.

TABLE I. STANDARD CURVE

Boron, μg	Absorbance	Absorbance minus average blank	Corrected absorbance/ μg of boron
0	0.000*	} 0.002	
	0.005		
	0.003		
	0.000		
40	0.414	0.412	0.01030
	0.422	0.422	0.01050
	0.426	0.426	0.01060
60	0.624	0.622	0.01037
	0.620	0.618	0.01030
	0.622	0.620	0.01033
	0.625	0.623	0.01038
	0.626	0.624	0.01040
	0.642	0.640	0.01067
100	1.049	1.047	0.01047
	1.032	1.032	0.01032
	1.036	1.034	0.01034
Av. COD per microgram of boron =			0.010413

* Reference solution 0.000 by definition.

Procedure

Weigh 1 g or less of zirconium or Zircaloy into a dry, round-bottom flask. Add 30 ml of methanol and 3 ml of bromine and immediately connect to a reflux condenser.¹ If necessary, warm to obtain complete dissolution of the metal. Allow to cool, then wash condenser with 30 ml of methanol. Disconnect flask and destroy excess bromine with 8 g of tin^{II} chloride. If solution does not turn green, add more tin^{II} chloride. Connect flask to the distillation apparatus and heat in a water bath. Collect the first 35–40 ml of distillate in a quartz beaker, containing 10 ml of methanol and 3 ml of 10% sodium hydroxide[†]. Evaporate solution to dryness on a sand bath at 60–80°. Cool and dissolve

* Special quartz apparatus made by Henry V. Leahy, Nuclear Metals, Inc., West Concord, Massachusetts, U.S.A.

† For residues containing significant amounts of B₄C after distillation, an additional step is suggested. Filter out the insoluble residue after dissolution. Ignite this residue in a platinum crucible and fuse it with a small amount of anhydrous sodium carbonate and potassium carbonate. This small flux can be dissolved along with the residue from the distillate in 6M sulphuric acid.

residue in 15 ml of 6*M* sulphuric acid. Transfer to a 25-ml volumetric flask and make to volume with water. This stock solution is 3.6*M* in sulphuric acid and convenient for 100–350 ppm of boron in alloys. For alloys of higher boron content, stock solutions in larger volumetric flasks can be prepared to be 3.6*M* in sulphuric acid.

In the colour development of boron with carminic acid, the water content must be 7–9%.² Therefore, a 5-ml aliquot of the sample stock in a 50-ml volumetric flask is convenient. The aliquot should contain 10–70 μg of boron. If a smaller aliquot is used, adjust to 5 ml with 3.6*M* sulphuric acid.

Add approximately 20 ml of chilled 18*M* sulphuric acid and swirl, then add 20 ml of carminic acid reagent by pipette. Make to volume with 18*M* sulphuric acid and read in a 1-cm cell on Beckman DU Spectrophotometer at a wavelength of 605 $m\mu$ with a reagent blank in the reference cell.

A standard curve is prepared for each batch of carminic acid solution by pipetting 0.0, 2.0, 3.0 and 5.0 ml aliquots of the 20 $\mu\text{g}/\text{ml}$ boron standard into 50-ml volumetric flasks. Develop the colour and read absorbance as in the sample procedure.

TABLE II. 0.138–0.141% BORON
IN STANDARD ZIRCONIUM-BORON
ALLOYS

Sample No.	B. %
1	0.143
2	0.138
3	0.138
4	0.142
Av. =	0.140

Nuclear Metals, Inc.
Concord, Massachusetts,
U.S.A.

EUGENE N. POLLOCK
LAWRENCE P. ZOPATTI

Summary—The sample is dissolved in methanol and bromine. Boron is distilled out and collected in sodium hydroxide and methanol, then determined spectrophotometrically as the carminic acid complex.

Zusammenfassung—Die Probe wird in Methanol und Brom gelöst, das Bor überdestilliert, in Natronlauge und Methanol auf gefangen und mittels Carminsäure spektrophotometrische bestimmt.

Résumé—L'échantillon est dissout dans un mélange de méthanol et de brome. Le bore est distillé et recueilli dans une solution de soude dans le méthanol. Il est dosé par spectrophotométrie par l'intermédiaire du complexe avec l'acide carminique.

REFERENCES

- ¹ M. Freegarde and J. Cartwright, *Analyst*, 1962, **87**, 214.
² D. G. Higgs, *ibid.*, 1960, **85**, 897.

Ion-exchange study of thiocyanatochloro complexes of rare earth elements

(Received 27 August 1962. Accepted 18 September 1962)

INTRODUCTION

Most ion-exchange separations of rare earth elements have been based on the use of cation exchangers with eluants containing organic complexing agents such as citric, glycolic, lactic, α -hydroxyisobutyric, malic, tartaric, nitrilotriacetic and ethylenediaminetetra-acetic acids. Although these organic reagents are highly effective for separating rare earth mixtures, addition of these reagents to the analytical system causes serious interference in the subsequent determination of the rare earths.

While some separations involving anion exchangers and organic eluants¹ have been reported, attention has recently been turned towards the possible utilisation of anion exchangers with inorganic eluants. Surls and Choppin² have shown that lanthanides and actinides may be separated with strongly basic anion exchangers in thiocyanate solutions. Adsorption of several rare earths from sulphite solutions and of yttrium from ammonium sulphate and sodium carbonate solutions have been reported by Vickery³ and by Saito and Sekine,⁴ respectively. Marcus and Nelson⁵ have reported a successful separation of the lighter rare earth elements using Dowex-1 anion-exchange resin with an eluant containing lithium nitrate. The absorption of lanthanide and actinide ions by Dowex-50 ion-exchange resin has been studied in concentrated solutions of perchloric, hydrochloric, hydrobromic and hydroiodic acids by Choppin and Dinis.⁶ On the basis of these observations it appeared of interest to investigate further the possibilities of utilising cation exchangers for rare earth separations with inorganic reagents.

The present paper reports the ion-exchange behaviour of several rare earths from Diaion SK-1 cation-exchange resin with ammonium thiocyanate-hydrochloric acid solutions.

EXPERIMENTAL

Apparatus and reagents

Ion-exchange resin: Diaion SK-1 (Mitsubishi Kasei Chem. & Ind. Co. Ltd., Japan), styrene-base strong acid type, equivalent to Dowex -50 × 8, 100–200 mesh. Before use the resin must be purified. The resin, free from fine particles, was placed in a large column and washed with a solution 2M in ammonium thiocyanate and 0.5M in hydrochloric acid, and finally with water. Then the resin was converted to the hydrogen form with 3M hydrochloric acid and washed chloride free with water. In the equilibrium studies the hydrogen-form resin was first dried for 2 hr at 80° and kept in a desiccator over a saturated solution of potassium bromide. In the column studies conventional resin columns of internal diameter 0.901 cm, packed at the bottom with glass wool, were used. To prepare the column a slurry of 40 g of resin was poured into the column with water. The bed has a height of 85 cm.

Stock solutions of lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, erbium and lutecium were prepared by dissolving *ca.* 100 mg of the respective metal oxides in a small amount of 3M hydrochloric acid, evaporating to dryness and dissolving in 50 ml of 0.5M hydrochloric acid. A stock solution of cerium was prepared by dissolving *ca.* 100 mg of cerium nitrate in a small amount of concentrated hydrochloric acid, which was evaporated to dryness, then dissolved in 50 ml of 0.5M hydrochloric acid with the aid of a little hydrogen peroxide (to reduce cerium to the trivalent state), and finally boiled to remove the latter. The strength of this solution was determined by titration with 0.01M EDTA, previously standardised against analytical reagent primary standard zinc metal, using Xylenol Orange⁷ as indicator. The purity of these oxides and nitrate listed by Yokosawa Chemical Co. Ltd., Japan, was 99.99% for lanthanum oxide and 99.9% for the others.

Other solutions were prepared from CP-grade ammonium thiocyanate and hydrochloric acid and distilled water.

All measurements were made at room temperature ($15 \pm 2^\circ$). The temperature effect in this range was shown to be within the error of the determination.

Equilibrium studies

The following method was used in the equilibrium studies to determine the equilibrium distribution coefficient, *K_d*, under conditions close to those of column operation. Portions (1.0 g) of Diaion SK-1 resin were weighed accurately and transferred into 100-ml conical flasks, 2 ml of a standard solution of cation in 0.5M hydrochloric acid were added, followed by 40 ml of 0.5M hydrochloric acid containing the correct amounts of ammonium thiocyanate. The flasks were stoppered and shaken in a mechanical shaking device at $15 \pm 1^\circ$ until no further change in the ion concentration occurred, at which time (approximately 100 min) the system was considered to be at equilibrium. The resin was separated from the aqueous phase by filtration, and an aliquot of the filtrate (30 ml) was analysed for the cation by titration with 0.001M EDTA standard solution. The value of the distribution coefficient, *K_d*, was then calculated by the following formula:

$$K_d = \frac{\text{ml}(\text{total}) - \text{ml}(\text{solution})}{\text{ml}(\text{solution})} \times \frac{\text{ml}(\text{solution})}{\text{g}(\text{resin})} \quad (1)$$

where ml is the volume of EDTA consumed in the titration. Because the equation is valid only when the total amount of the cation is less than about 3% of the total column capacity⁸, both the equilibrium and the elution studies were carried out in the presence of the cation less than 3% of the total column capacity.

Column studies

The tops of the columns were fitted with 500-ml dropping funnels connected by ground-glass joints to the columns. Before use a resin column was pretreated alternately with 200 ml of each of distilled water, 2*M* ammonium thiocyanate-0.5*M* hydrochloric acid mixture, 3*M* hydrochloric acid, and distilled water. During the experiments the flow rate was kept at 0.43 ml/min for columns containing 40 g of dry resin.

RESULTS AND DISCUSSION

Equilibrium studies

In Fig. 1, the effect on K_d of varying concentrations of ammonium thiocyanate in 0.5*M* hydrochloric acid is given for the rare earth elements. It is seen that the dependence of K_d upon ammonium thiocyanate concentration is approximately second power for the 0.5*M* hydrochloric acid system. In

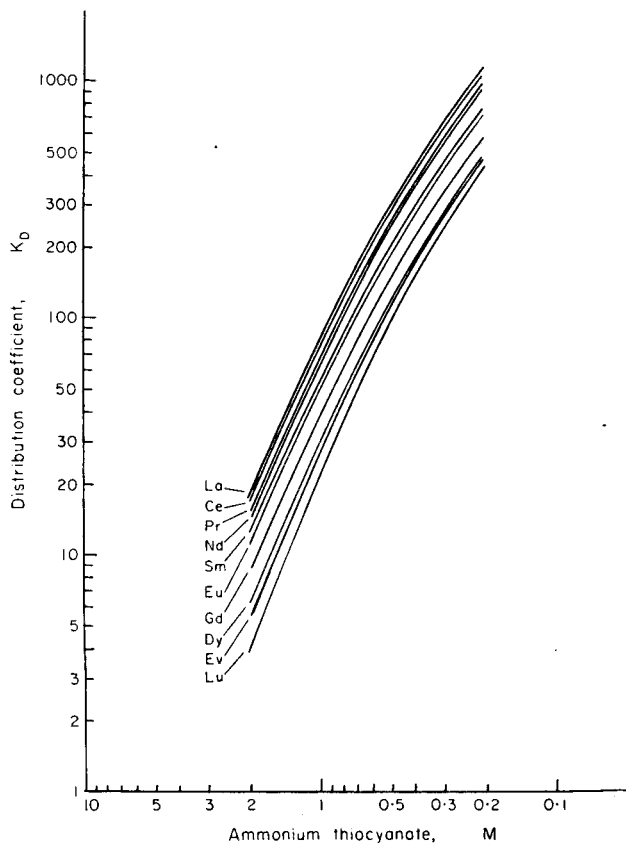


FIG. 1.—Distribution coefficients with Diaion SK-1 at different concentrations of ammonium thiocyanate (concentration of hydrochloric acid: 0.5*M*).

Fig. 2, the effect on K_d of varying concentrations of hydrochloric acid in 1.0*M* ammonium thiocyanate is given for only lanthanum and lutecium. The dependence of K_d value of these rare earths upon hydrochloric acid concentration is approximately first power for the 1.0*M* ammonium thiocyanate system. It is postulated that the composition of rare earth elements in the ammonium thiocyanate-hydrochloric acid medium is likely to be $M(\text{SCN})_2\text{Cl}$ or a similar compound, where M is the rare earth metal. Because the curves for lanthanum and lutecium in Fig. 2 run parallel with each other, all of the following experiments were carried out in 0.5*M* hydrochloric acid media.

From the plots of $\log K_d$ vs. $\log \text{NH}_4\text{SCN}$, it is possible to calculate the values of the separation factor. The values of K_d calculated from smooth curves drawn through the experimental points in

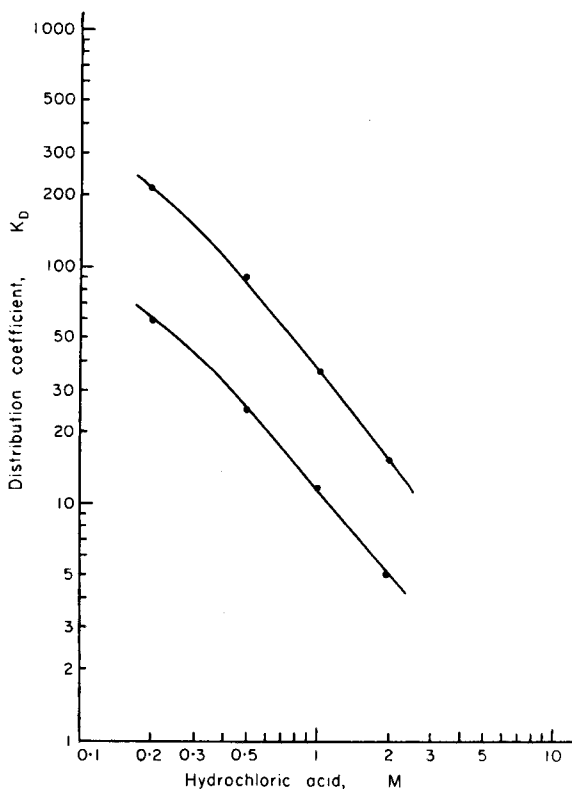


Fig. 2.—Distribution coefficients with Diaion SK-1 at different concentrations of hydrochloric acid (concentration of ammonium thiocyanate: 1.0M).

Upper curve: Lanthanum
Lower curve: Lutetium

Fig. 1 indicate that maximum separation should be achieved at an ammonium thiocyanate concentration of 1.0M.

Some of the data of Fig. 3 are presented in a different fashion from that in Fig. 1 in order to account for the atomic number, Z , effect. In Fig. 3, the variation of $\log K_d$, at a constant concentration (0.5M) of hydrochloric acid, with Z is shown for several different ammonium thiocyanate concentrations. These plots are represented by two curves meeting in the neighbourhood of $Z = 66$. It is to be noted that as the concentration of ammonium thiocyanate increases, the slope of the left-hand portion of the curve decreases more rapidly than does that of the right-hand portion.

From Fig. 3, the separation factor lies between 1.1 and 1.2 for adjacent rare earths from lanthanum to dysprosium. This ratio is somewhat lower than the ratio obtained in the cation-exchange separation of light rare earths ($S \cong 1.6$) with α -hydroxyisobutyric acid¹⁰ and EDTA,¹¹ and in the anion-exchange separation ($S \cong 1.4$) with nitrate.⁵ Of the rare earths heavier than dysprosium, only erbium and lutecium were studied. From Fig. 3, the separation factor for the adjacent rare earths from dysprosium to lutecium is about 1.04.

On the basis of these results, one concludes that the separation of the adjacent heavier rare earths will be more difficult than that of the adjacent lighter rare earths, as is usually the case in the rare earth separations.

Column separation studies

The following experiments demonstrate some of the separations which may be achieved with ammonium thiocyanate-hydrochloric acid solutions. Mixtures of neodymium-samarium and europium-gadolinium were added to two columns having the same column size and resin weights. Elution was carried out at room temperature (15°) with 1.0M ammonium thiocyanate-0.5M hydrochloric

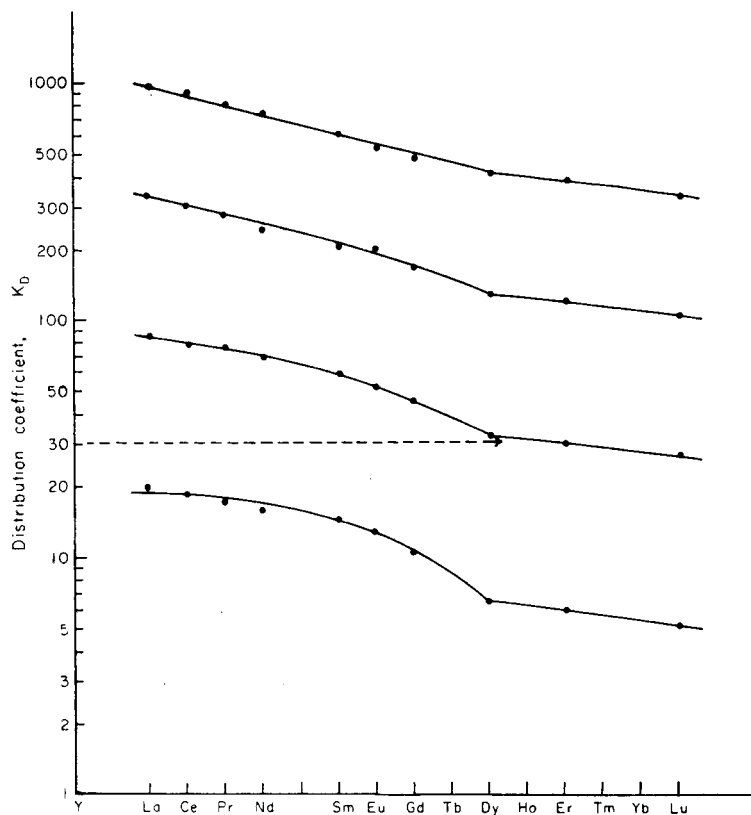


FIG. 3.—Adsorption of rare earths onto Diaion SK-1 from ammonium thiocyanate solutions of selected molarity as a function of atomic number (concentration of hydrochloric acid: 0.5M).

From top to bottom: 0.25M, 0.5M, 1.0M, 2.0M NH_4SCN

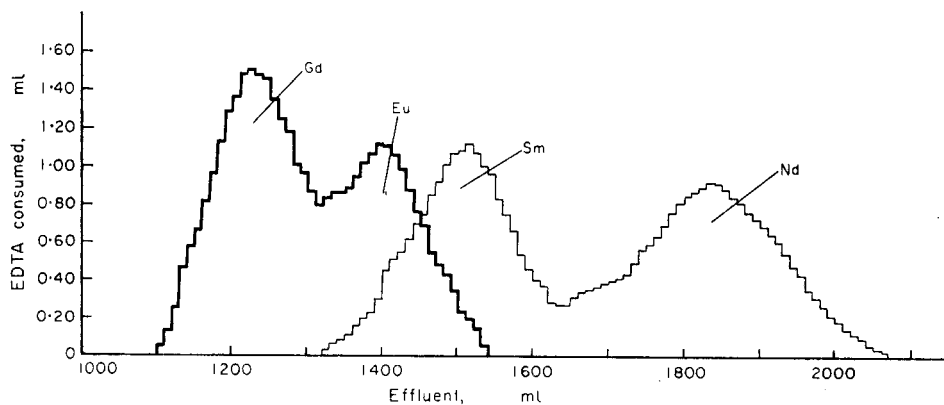


FIG. 4.—Separation of Eu-Gd and Sm-Nd mixtures in 1.0M NH_4SCN -0.5M HCl solution (15° ; $0.64 \text{ cm}^2 \times 85 \text{ cm}$ column).

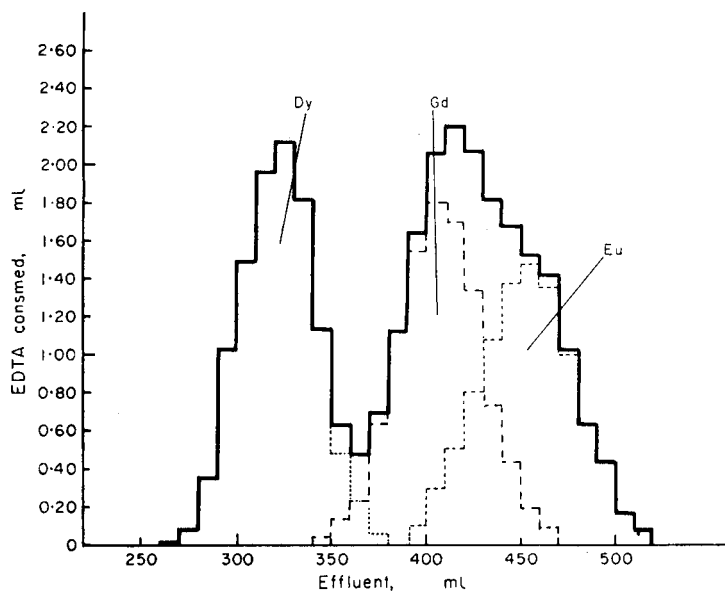


FIG. 5.—Separation of Eu, Gd and Dy in 2.0M NH_4SCN -0.5M HCl solution (15° ; $0.64 \text{ cm}^2 \times 85 \text{ cm}$ column).

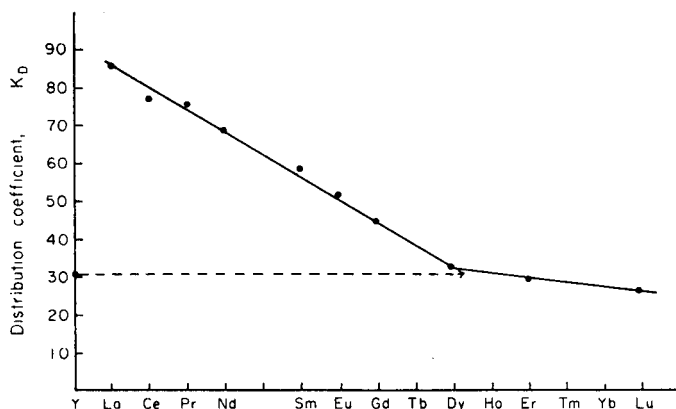


FIG. 6.—Distribution coefficients of rare earth elements in 0.1M NH_4SCN -0.5M HCl solution.

acid solution as eluant. Elution curves for these mixtures are given in Fig. 4. The analysis⁹ of the europium-gadolinium elution curve indicates that the theoretical plate numbers for europium and gadolinium are 576.6 and 440.2, respectively, and the complete separation of these adjacent rare earth elements may be achieved by a column, 0.901 cm in diameter and 376 cm in length. In a system in which the atomic number is different by two, however, there is only 3% cross contamination in the neodymium-samarium mixture elution curve. Fig. 5 presents the result of an experiment in which europium, gadolinium and dysprosium were present and 2.0M ammonium thiocyanate-0.5M hydrochloric acid solution was used as eluant. This indicates that the separation is somewhat less effective as compared with the case of the 1.0M ammonium thiocyanate-0.5M hydrochloric acid system, but it is not time-consuming.

In the present experiment, the distribution coefficient of rare earth elements from ammonium thiocyanate-hydrochloric acid solutions decreased with increasing atomic number and some difference is found between the lower and the higher subgroups. As shown in Fig. 6, the differences in K_d value

between adjacent rare earth elements from lanthanum to dysprosium and from dysprosium to lutecium are 5.77 and 1.40, respectively. The different behaviour of these two subgroups is probably caused by the ionic radius, stability of complexing species, and other characters.

Department of Chemistry
Faculty of Science
Tokyo Kyoiku University
Otsuka, Tokyo, Japan

HIROSHI HAMAGUCHI
ROKURO KURODA
NAOKI ONUMA

Summary—The ion-exchange behaviour of several rare earths—La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er and Lu—on Diaion SK-1 cation-exchange resin with ammonium thiocyanate-hydrochloric acid solutions has been studied. The distribution coefficient (Kd) of the rare earth elements decreases with increasing atomic number. The differences in Kd value were found to permit separation of the lighter rare earths. The composition of the complex in the ammonium thiocyanate-hydrochloric acid medium is likely to be $M(\text{SCN})_2\text{Cl}$ or a similar compound, where M is the appropriate rare earth metal.

Zusammenfassung—Das Verhalten von La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er und Lu am Ionenaustauschersystem Dianion SK-1 und Ammoniumthiocyanat-Salzsäure wird studiert. Die Verteilungskoeffizienten steigen mit der Atomnummer an. Die Unterschiede in den Koeffizienten erlauben abtrennung der leichteren Erden. Die Zusammensetzung der Komplexe in Rhodanid-HCl Medium ist vermutlich $M(\text{SCN})_2\text{Cl}$, wobei M das Ion eines seltenen Erdmetalles bedeutet.

Résumé—Les auteurs ont étudié le comportement de plusieurs terres-rares: La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er et Lu, avec la résine échangeur de cations Diaion SK-I en milieu acide chlorhydrique-thiocyanate d'ammonium. Le coefficient de partage (Kd) des terres-rares en milieu $\text{NH}_4\text{SCN-HCl}$ décroît avec le numéro atomique. Les différences entre les valeurs des Kd permettent la séparation des terres-rares les plus légères. La formule du complexe en milieu $\text{NH}_4\text{SCN-HCl}$ semble être $M(\text{SCN})_2\text{Cl}$ dans laquelle M représente la terre-rare.

REFERENCES

- ¹ E. H. Huffman and R. L. Oswalt, *J. Amer. Chem. Soc.*, 1950, **72**, 3323.
- ² J. P. Surls, Jr., and G. R. Choppin, *J. Inorg. Nuclear Chem.*, 1957, **4**, 62.
- ³ R. C. Vickery, *J. Chem. Soc.*, 1955, 2360.
- ⁴ N. Saito and T. Sekine, *Nature*, 1957, **180**, 753.
- ⁵ Y. Marcus and F. Nelson, *J. Phys. Chem.*, 1959, **63**, 77.
- ⁶ G. R. Choppin and R. H. Dinius, *Inorganic Chemistry*, 1962, **1**, 140.
- ⁷ J. Körbl and R. Přibil, *Chemist Analyst*, 1956, **45**, 102; J. Körbl, R. Přibil and A. Emr, *Chem. Listy*, 1956, **50**, 1440; *Coll. Czech. Chem. Comm.*, 1957, **22**, 961.
- ⁸ F. W. Cornish, *Analyst*, 1958, **83**, 634.
- ⁹ J. Beukenkamp, W. Rieman, III and S. Liendenbaum, *Analyt. Chem.*, 1954, **26**, 505.
- ¹⁰ G. R. Choppin and R. J. Silva, *J. Inorg. Nuclear Chem.*, 1956, **3**, 153; H. L. Smith and D. C. Huffman, *ibid.*, 1956, **3**, 243.
- ¹¹ S. W. Mayer and E. D. Freiling, *J. Amer. Chem. Soc.*, 1953, **75**, 5647.

LETTER TO THE EDITOR

Arsenic in glass

Sir:

We have read the account by Dr. Stross¹ in which he describes the effect of fluoride on glassware during the determination of arsenic, and it may be of interest to relate our own experience in this connection.

Some years ago we encountered similar circumstances during the development of a method for the determination of arsenic in hydrolysed uranium hexafluoride. Our information at the time was that Pyrex glass contained about 0.4% of arsenic as As_2O_3 . For the separation and determination of arsenic we employed a modification of the Heron and Rogers method² in which the arsenic is electrolytically liberated as arsine and determined as molybdenum blue. Under our experimental conditions we found that 200 μg of arsenic were extracted from the glass during the determination, but the addition of aluminium as sulphate in an amount equal to a seven-fold excess of aluminium over that required for the formation of $(AlF_6)^{3-}$ successfully reduced the extracted arsenic to negligible amounts in comparison to the 1 ppm of arsenic determined in a 5-g sample of uranium hexafluoride. The method has been in use for a long period without difficulties and the experimental details have been reported elsewhere.³

We are grateful to Dr. Stross for drawing attention to the present level of arsenic in Pyrex glass.

*Chemical and Metallurgical Services Dept.,
U.K.A.E.A. Production Group,
Springfields Works,
Salwick, nr. Preston, Lancs., England
6 September 1962*

J. A. RYAN
J. R. SANDERSON

REFERENCES

¹ W. Stross, *Talanta*, 1962, **9**, 740.

² A. E. Heron and D. Rogers, *Analyst*, 1946, **7**, 414.

³ J. A. Ryan, J. R. Sanderson and T. Mason, *U.K.A.E.A. Report S.C.S.-R-328 Declassified Reprint*, 1959.

EDITORIAL NOTE

THE Editorial Board of TALANTA has recently considered ways in which the publication of Preliminary Communications and of Letters to the Editor can be speeded up. In consequence, it has been decided that in future Preliminary Communications should be limited to less than 1000 words in length, and should not contain diagrams. They should preferably contain no Tables. They will then be refereed urgently, and will be accorded priority in publication. If they do not fulfil the conditions indicated, they will be treated as Short Communications (full refereeing and no priority.)

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.

ADVISORY BOARD OF TALANTA

The Editorial Board and Publishers of TALANTA take pleasure in welcoming the following new members to the Advisory Board of the journal:

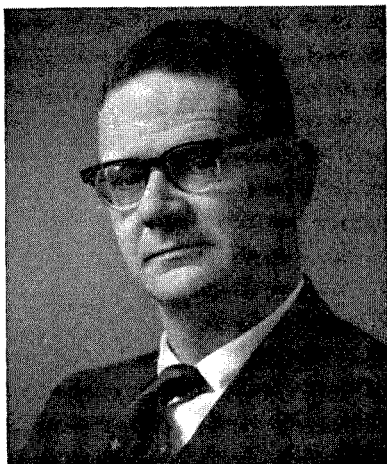
E. BISHOP	D. F. C. MORRIS
E. A. M. F. DAHMEN	G. A. RECHNITZ
J. K. FOREMAN	W. RIEMAN III
H. FREISER	M. STEINBERG
R. B. HAHN	E. WÄNNINEN
K. J. KARRMAN	D. H. WILKINS
G. KORTÜM	A. F. WILLIAMS

P. ZUMAN

Also, they would like to record their sincere thanks for the help given by the retiring members of the Advisory Board:

H. BODE	J. J. LINGANE
C. CIMERMAN	S. J. LYLE
P. DELAHAY	W. WAYNE MEINKE
C. DRĂGULESCU	F. NYDAHL

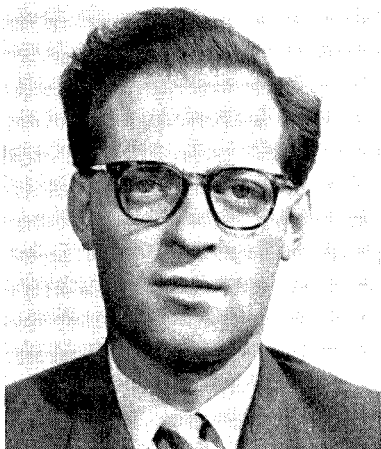
F. J. WOODMAN



E. BISHOP (England) studied at the University of Glasgow for his B.Sc. (1942). Following a period as a research chemist at the Explosives Directorate, Armaments Research Department (1944-1946), Mr. Bishop returned to Glasgow as Assistant Lecturer at the Royal College of Science and Technology until 1946, when he moved to King's College, University of Durham. There he was Lecturer in Analytical Chemistry until 1953. Since that time he has been Lecturer in Inorganic and Analytical Chemistry at the University of Exeter. He is interested in the fundamental investigation of titrimetric reactions, particularly electron-transfer processes, theoretical (mathematical) interpretation of equilibria in titrimetric reactions, electrode processes, electrometric studies of titrimetric reactions, DEP, *etc.* He is a past member of the Council of the Society for Analytical Chemistry.

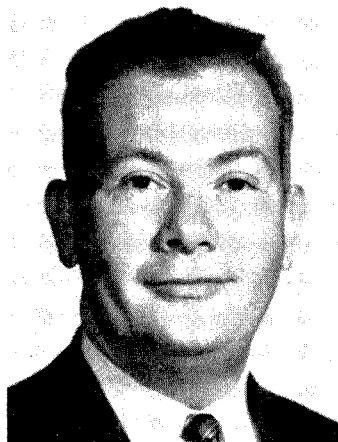


E. A. M. F. DAHMEN (Netherlands), born 1911, studied at the Technological University in Delft. After his graduation in 1939, he remained at the University doing post-graduate work as assistant to Professor H. I. Waterman. This culminated in his Doctor of Technical Science degree in 1946. After working for short periods in other industries, Dr. Dahmen in 1947 joined the Koninklijke/Shell-Laboratorium in Amsterdam. His work in the Organic Chemistry Department led to a live interest in organic analysis. From 1951 he has worked in the Analytical Department, where his main interest has been in the field of functional group analysis and the determination of individual organic compounds. Amongst the techniques especially studied has been titration in non-aqueous media.



After being educated at Ashford Grammar School and Medway Technical College (Kent), JAMES KENNETH FOREMAN (England) obtained his B.Sc. (London) in 1949. Then he joined the Atomic Energy Branch (Woolwich) of the Chemical Inspectorate, Ministry of Supply, moving to Windscale Works, Atomic Energy Authority, in 1952. Currently he is Principal Scientific Officer at Windscale responsible for all research and development in analytical chemistry. His personal interests are chromatographic separation procedures, particularly ion exchange, and chelation of metal ions. Born 1928.

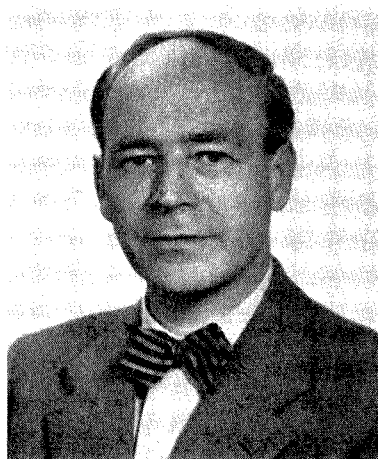
Born in 1920, HENRY FREISER (U.S.A.) received his educational training at City College of New York (B.S., 1941) and Duke University (Ph.D., 1944). Subsequently, he held positions at North Dakota State College, City College of New York, Mellon Institute of Industrial Research, and University of Pittsburgh. From 1958 he has been Professor and Head of Chemistry Department at University of Arizona, Tucson. His research interests are mainly in the fields of chelation and solvent extraction.

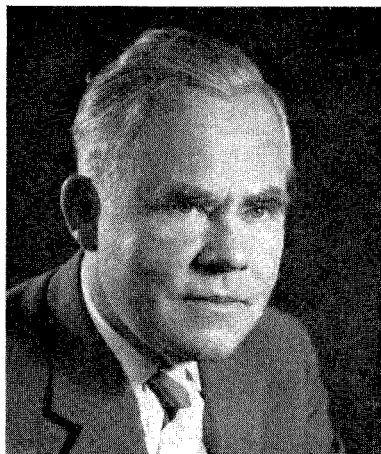


RICHARD B. HAHN (U.S.A.) received his Ph.D. in analytical chemistry under the direction of Professor H. H. Willard at the University of Michigan. He worked as a research chemist in the Analytical Chemistry Division of the Oak Ridge National Laboratory. At present he is Professor of Analytical Chemistry at Wayne State University, Detroit. His research interests include the analytical chemistry of zirconium and hafnium, use of organic reagents in inorganic analysis, and radiochemical methods of analysis.



K. J. KARRMAN (Sweden) was born in 1909. He entered the University of Lund in 1929 and subsequently obtained his Fil. mag. (1932), Fil. lic. (1938) and Fil. Dr. (1941). During the period 1941-1949 he was concerned with research work in organic chemistry, mainly in the phenanthrene and retene field. In 1949 he was appointed Professor (laborator) in Analytical Chemistry at the University of Lund. His current work includes investigation of the determination of oxygen in sulphur-containing organic compounds, high-frequency and turbidimetric titrations, and use of microwaves in analytical chemistry.





Born in 1904, G. KORTÜM (W. Germany) had a grammar school education followed by study at the Technische Hochschule of Karlsruhe (Dr.-Ing., 1928). After periods in the Institutes of Physical Chemistry of the Universities of Berlin, Würzburg and Zürich, he was admitted as Lecturer in Physical Chemistry, University of Tübingen in 1937. Since 1942 he has been Professor and Director of the Institute of Physical Chemistry at Tübingen. His fields of research include thermodynamics, electrochemistry, spectroscopy, and analytical chemistry.



DONALD FRANK CHARLES MORRIS (England) was born in 1928 and educated at Magdalen College School, Oxford, and at St. Catherine's Society and New College, Oxford (Senior Govett Scholar). Subsequently, he became a Scientific Officer at the Atomic Energy Research Establishment, Harwell. Dr. Morris is now Reader in Chemistry at Brunel College, London. His main interests related to analytical chemistry include fundamental studies on metal-ion complexes, development of separation procedures and chemical applications of radio-nuclides. He was a Capper-Pass Award (Institute of Metals and Institution of Mining and Metallurgy) winner in 1956.

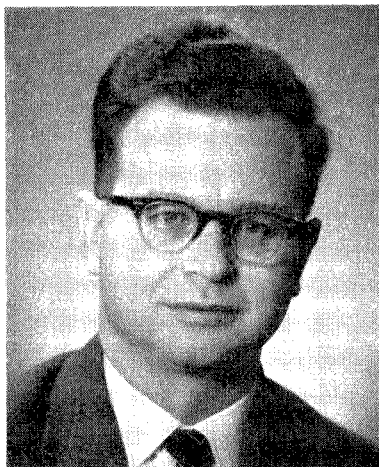


G. A. RECHNITZ (U.S.A.) received his undergraduate and graduate training at the Universities of Michigan and Illinois, respectively, and he is now Assistant Professor of Analytical Chemistry at the University of Pennsylvania. His research interests include the kinetics of analytical reactions, homogeneous catalysis of transition metal complexes, electroanalytical chemistry, and analytical instrumentation.

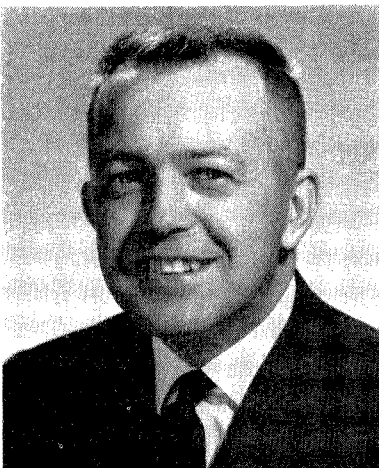
Born in Jersey City in 1899, WILLIAM RIEMAN III (U.S.A.) was educated at Rutgers University, New Brunswick, where he received his B.S. (1922) and Ph.D. (1925). Since that time he has been a member of the Rutgers University staff, becoming Director of the School of Chemistry in 1962. A former Councillor of the Americal Chemical Society, Professor Rieman was Fulbright lecturer at the University of Madrid in 1962. His chief research interest is now chromatography with ion-exchange resins.

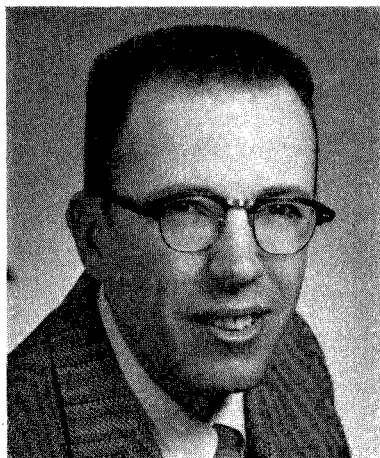


MANACHEM STEINBERG (Israel) obtained his Ph.D. (1959) at the Hebrew University of Jerusalem. In 1959 he was a British Council Scholar at the University of Bristol, England, returning to Jerusalem in 1960. Since then he has been Instructor in Inorganic and Analytical Chemistry at the Hebrew University. Dr. Steinberg became Secretary of the Israel Chemical Society in 1962. His fields of interest in analytical chemistry include the lanthanons, gas analysis, gas chromatography and spectrophotometry.



ERKKI WÄNNINEN (Finland) was born in Åbo in 1925. He entered the Åbo Akademi after receiving his primary education in Åbo, obtaining his M.Sc. in 1952. Following a brief period in industry, he continued his studies at Åbo Akademi as a research assistant with Professor Anders Ringbom, later becoming a Teaching Assistant in Quantitative and Industrial Analysis. His D.Sc. was conferred in 1960. Further study was at the Royal Institute of Technology, Stockholm, under the direction of Dr. Axel Johansson. In 1961 he rejoined the staff of Åbo Akademi with responsibility for the basic courses in inorganic and analytical chemistry. Dr. Wänninen's special interest is in complexometric titrations.





DONALD H. WILKINS (U.S.A.) was born in 1926 in Park Rapids, Minnesota, and received his elementary education there. In 1944 he entered Hamline University, St. Paul, and obtained his B.Sc. (1948). Following service as a research chemist for Lerch Bros., Inc., Hibbing, he entered the University of Illinois, his Ph.D. being conferred in 1954. While at Illinois, he received the Fifth Annual Merck Graduate Fellowship in Analytical Chemistry (1953). Joining the General Electric Company Research Laboratory in 1954, he has supervised the Analytical Chemistry Laboratory and High Purity Materials Laboratory of the Metallurgy and Ceramics Research Department at Schenectady. His principal research activities in analytical chemistry have been utilisation of ion-exchange resins and chelatometric reagents for inorganic analysis. Currently he is Secretary-Treasurer of the Division of Analytical Chemistry of the American Chemical Society.



Whilst working at the South Metropolitan Gas Co., A. F. WILLIAMS (England) studied at Sir John Cass College, London, where he obtained his B.Sc. (London) in 1934. In 1937 he joined the General Chemical Division of Imperial Chemical Industries Ltd. During the years 1941-1944 he worked on problems associated with the raw materials of atomic energy, and in 1948 he moved to the National Chemical Laboratory, Teddington, where he was Head of the Analytical Section of the Radiochemistry Group, and much of his work was directed towards the development of techniques in quantitative inorganic chromatography. In 1952 he became Head of the Analytical Research Section of the Nobel Division of I.C.I. Ltd. He is a past member of the Council of the Society for Analytical Chemistry.



PETR ZUMAN (Czechoslovakia) received his RNDr in 1950 at Charles University, Prague, under Professor J. Heyrovský and R. Brdička. Since 1950 he has been a Research Fellow at the Polarographic Institute of the Czechoslovak Academy of Science, where he obtained his Dr. Sc. (1960). Working mainly in the field of organic polarography, he developed methods for determination of saturated ketones, thiols and other compounds in biological materials and pharmaceutical products reacting with mercury. Recently, he has been interested in mechanisms of electrode and homogeneous reactions and relationships between structure and polarographic behaviour, which form a basis for further analytical applications.

NOTICES

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

AUSTRALIA

Wednesday–Wednesday 13–20 February 1963: First Australian Conference on Electrochemistry. Sydney and Hobart (See *Talanta*, 1962, 9, 545).

FRANCE

29 janvier 1963: Donnees nouvelles sue la chromatographie des glucides: Professeur F. PERCHERON. Faculté de Pharmacie, Paris.

26 février 1963: Les grandes methodes de dosage de la double liaison: Professeur P. MESNARD. Faculte de Pharmacie, aris.

HUNGARY

Wednesday–Saturday 24–27 April 1963: Winkler Centenary Symposium, under the sponsorship of *Hungarian Academy of Sciences.* Budapest.

The Symposium is in memory of Professor L. W. Winkler, the renowned Hungarian Analytical Chemist, who contributed much fundamental research work to the fields of water analysis and gravimetry. The programme will consist partly of a review of his contributions to gravimetry, titrimetry, gas analysis and pharmaceutical chemistry, and partly of original papers on different topics in the pharmaceutical sciences.

UNITED KINGDOM

Monday–Thursday 14–17 January 1963: Annual Exhibition of the Institute of Physics and the Physical Society. Old and New Halls of Royal Horticultural Society, Vincent Square, Westminster, London, S.W.1. 10.00 a.m.–7.00 p.m.

Wednesday 6 February 1963: Meeting on Particle Size Analysis: Society for Analytical Chemistry. Burlington House, London, W.1. 7.00 p.m.

Friday 8 February 1963: Gas Chromatography: Dr. A. T. JAMES: *Society for Analytical Chemistry, North of England Section and Royal Institute of Chemistry, North Lancashire Section.* Harris Technical College, Preston. 7.30 p.m.

Friday 8 February 1963: Gas-Liquid Chromatography: Dr. G. EGLINTON, Dr. J. H. KNOX and Mr. A. F. WILLIAMS: *Society for Analytical Chemistry, Scottish Section and Royal Institute of Chemistry, Glasgow and West of Scotland Section.* Royal College of Science and Technology, Glasgow. 7.15 p.m.

Thursday 14 February 1963: Microbiological Assay of Vitamin B₁₂ and Folic Acid: Society for Analytical Chemistry, Biological Methods Group and Midlands Section, and Association of Clinical Biochemists, Midland Region, University, Birmingham 15. 6.30 p.m.

Friday 15 February 1963: Dithizone and its Reactions: Professor H. M. N. H. IRVING: *Society for Analytical Chemistry, North of England Section and Leeds University Chemical Society.* University, Leeds. 7.15 p.m.

Tuesday 19 February 1963: Luminescence: Professor G. F. GARLICK: *Society for Analytical Chemistry, Western Section and Royal Institute of Chemistry, Bristol and District Section.* Technical College, Gloucester. 7.30 p.m.

Friday 22 February 1963: Annual General Meeting followed by *Address of Retiring Chairman,* Mr. C. WHALLEY: *Society for Analytical Chemistry, Microchemistry Group.* Burlington House, London, W. 1. 6.45 p.m.

Tuesday 26 February 1963: Meeting on Fractionation of High Molecular Weight Compounds: Mr. M. F. VAUGHAN and Dr. F. C. GREENWOOD: *Society for Analytical Chemistry, Physical Methods Group.* Royal College of Surgeons of England, London. 6.00 p.m.

At the **Annual General Meeting** of the *Physical Methods Group* of the *Society for Analytical Chemistry*, Tuesday, 27 November, 1962, the following new Officers of the Group were elected:

Chairman: Dr. W. CULE DAVIES

Vice-Chairman: Mr. L. BREALEY

Hon. Secretary: Dr. T. L. PARKINSON, Product Research Department, Beecham Food and Drink Division Ltd., Harpenden Rise, Harpenden, Herts.

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

B.S. 3557: 1962: Method for the quantitative chemical analysis of mixtures of polyester fibres with cotton or viscose rayon. This provides a method for determining the proportions of fibre in binary mixtures of polyester fibre with cotton or viscose rayon. It is suitable for application to fibres in any textile form, e.g., tow, sliver, roving, yarn, fabric or felt. (Price 3s.)

The following *Amendment Slips* are also announced:

B.S. 1017: The sampling of coal and coke. Part 1: 1960: Sampling of coal.

Amendment No. 2. PD 4649. Part 2: 1960: Sampling of coke. Amendment No. 2. PD 4650. B.S. 1672: Methods of testing rubber latex: Part 2: 1954: Chemical and physical tests. Amendment No. 5. PD 4643. (Amendment No. 4, PD 4602, was cancelled shortly after publication.)

B.S. 3338: The sampling and analysis of tin and tin alloys: Part 3: 1961: Determination of antimony in ingot tin (photometric method). Amendment No. 2. PD 4666.

UNITED STATES OF AMERICA

Monday–Thursday 28–31 January 1963: Sixteenth Annual Symposium on Modern Methods of Analytical Chemistry. Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La.

The programme is as follows:

Precipitation from Homogeneous Solution

Polarography and Related Electroanalytical Techniques.

Analysis of Atmospheric Trace Gases.

Developments in Organic Analysis on the Microgram Scale. Organic Elemental Analysis with Special Reference to Analysis of Fluorine.

Automation in Carbon and Hydrogen Determination.

Determination of Sulphur in Organic Compounds.

Phosphorimetry and Fluorimetry.

Lasers and Masers.

Developments in Organic Analytical Methods.

Thermal Methods of Analysis.

Pyrolytic Reactions in Organic Analysis.

Further information may be obtained from Professor P. W. WEST, Department of Chemistry, Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La.

L. GORDON

W. KEMULA

J. P. LODGE

A. M. G. MACDONALD

H. MALISSA

S. MCGLYNN

S. P. S. PORTO

W. SCHÖNIGER

W. WENDLANDT

F. FEIGL

Monday–Friday 4–8 February 1963: American Society for Testing and Materials Committee Week. Queen Elizabeth Hotel, Montreal, Canada.

From 1 October, 1962, the *American Petroleum Institute* assumed responsibility for the distribution of **Hydrocarbon and Sulphur Standard Samples** to all users. Previously, API had issued such standards to the petroleum industry, while the *National Bureau of Standards* had supplied laboratories not associated with the petroleum industry. A total of about 174 specific compounds were transferred from NBS to API Samples Office at Carnegie Institute of Technology, Petroleum Research Laboratory, Pittsburgh 13, Pennsylvania, where request for information about and purchase of the standard samples should now be addressed (attention of BEVERIDGE J. MAIR). The standards are intended primarily for calibrating instruments and apparatus in the research, development and analytical laboratories of the petroleum, rubber, chemical and allied industries.

BOOK REVIEWS

Electrochemical Reactions: The Electrochemical Methods of Analysis: G. CHARLOT, J. BADOZ-LAMBLING and B. TRÉMILLON. Elsevier Publishing Company, Amsterdam, 1962. pp. ix + 376. 80s. Dfl. 40.—.

ONE can fairly say that there is a rapidly expanding interest in all the various aspects of electrochemistry. Those relatively unfamiliar with this wide field may, however, be somewhat discouraged from closer contact by the rather forbidding terminology employed to characterise the various techniques which have become available: this is, perhaps, a particular problem in the case of analytical techniques. The book under review performs a real service in approaching the subject with an emphasis on the fact that all these techniques are basically concerned with the measurement of either potential, or current, or both together.

In some respects the book could be regarded as a general introductory text since some major aspects are not exhaustively treated. That it is not the purpose of the book to be entirely comprehensive is, however, made clear by the authors' preface, where it is pointed out that for the most part those actively interested in specific fields should be prepared to employ other texts in conjunction with this one. On the other hand, in most branches of electrochemistry either useful comments have been made, or a fairly up-to-date set of references (generally up to 1958 although a few 1959 papers are included) is provided. The index is useful and there is a very helpful system of referencing under subject headings.

Although the overall impression made by the book is very favourable, certain criticisms can be made. For example, the definitions of "migration" and "diffusion" on p. 16 are not entirely free from ambiguity; indeed, the introductory treatment of transport of matter in solution might have been better clarified by an earlier cross reference to the further discussion of the Nernst diffusion layer given on p. 127. Again, the definitions of "overvoltage" seem hardly likely to improve the rather poor general understanding of this term. From the point of view of first impressions it is a pity that there is a misprint on page 1 (and others were found) since the appearance of the book and the layout of the text are both attractive. There are 405 figures and, in general, these are clear and useful.

F. A. LEWIS

Hydroboration. H. C. BROWN. W. A. Benjamin, Inc., New York, 1962, pp. xiii + 290, \$10.00.

DR. Brown has written a highly readable and up-to-date account of the hydroboration reaction—the reaction of boranes with olefins. In this age of rapidly exploited research activities it is indeed rare to see a field so completely dominated by one research group. In the short span of five years (the discovery in 1956 of a practicable hydroboration procedure by Brown and Subba Rao) many ingenious ramifications of these reactions have been unfolded, principally by Brown and coworkers. These include reactions of organoboranes with hydrogen peroxide to form alcohols, and with metal salts such as silver and copper to form coupling products; and the use of organoboranes as reducing and trans-metallating agents. However, the principal reactions involved here are the reactions of boranes and organoboranes with olefins and much of the book is concerned with effects of structure on reactivity, directive effects and stereochemistry. Isomerisation of olefins *via* organoborane intermediates and exchange reactions of olefins with organoboranes are discussed. Applications have been made to the formation of optically active products from olefins and active boranes *via* asymmetric induction and to the reaction with dienes and acetylenes. In many instances the hydroboration and subsequent reactions are quantitative and may offer convenient techniques for the analytical chemist, particularly those interested in the analysis of olefins.

Although several review articles on the subject (some by Brown) are available, the value of this book is principally as a convenient summary of the recent developments in hydroboration and the chemistry of organoboranes. Parts of the book are repetitive, but overall they do not materially detract from Dr. Brown's message. Hopefully, *Hydroboration* is a prologue to a fascinating area of chemical research.

JAY K. KOCHI

PAPERS RECEIVED

- A review of applications of controlled-potential coulometry to the determination of plutonium: W. D. SHULTS. (12 October 1962).
- Determination of copper in high-purity niobium, tantalum, molybdenum and tungsten metals with bathocuproine: ELSIE M. PENNER and W. R. INMAN. (16 October 1962).
- Determination of small amounts of zirconium—I: Gravimetric determination using mandelic acid and derivatives: MOHAMMED RAFIQ, CHARLES L. RULFS and PHILIP J. ELVING. (23 October 1962).
- Determination of small amounts of zirconium—II: Analysis of refractory samples: MOHAMMED RAFIQ, CHARLES L. RULFS and PHILIP J. ELVING: (23 October 1962).
- Separation and spectrophotometric determination of rare earths: HIROSHI ONISHI and CHARLES V. BANKS. (24 October 1962).
- Titration of weak acids with tetramethylguanidine: THEODORE R. WILLIAMS and MARGARET LAUTENSCHLEGER. (29 October 1962).
- The application of constant-current potential-limit coulometry to chemical analysis: I. J. MCCOLM, V. M. SINCLAIR and R. S. ROCHE. (1 November 1962).
- Die Bestimmung kleiner Fluormengen—III: New ideas on the reaction mechanism in the determination of small fluorine content: ROMAN VALACH. (1 November 1962).
- Osilopolarographic detection and determination of dihydric phenols: JAN DOLEŽAL, VASIL KOPRDA and JAROSLAV ZÝKA. (5 November 1962).
- Possible use of ethylenediamine-*N*:*N'*-tetra-acetic acid as masking agent of iron in the photometric determination of manganese with formaldoxime: MOTOHARU TANAKA. (6 November 1962).
- The accuracy of gas chromatography: A. F. WILLIAMS and W. J. MURRAY. (9 November 1962).
- Precipitation from homogeneous solution with *N*-benzoylphenylhydroxylamine acetate: PAUL R. ELLEFSEN, LOUIS GORDON and R. BELCHER. (9 November 1962).
- New principle in activation-analysis separations—II: Substoichiometric determination of traces of zinc and copper in germanium: ADOLF ZEMAN, JAROMÍR RŮŽIČKA and JIŘÍ STARÝ. (10 November 1962).
- Spectrophotometric and conductometric studies on the composition and stability of the V^{IV}-8-hydroxy-7-iodoquinoline-5-sulphonic acid complex: S. M. FAZLUR REHMAN and ANEES UDDIN MALIK. (10 November 1962).
- The infrared spectra of chelate compounds—I: A study of some metal chelate compounds of 8-hydroxyquinoline in the region 625–2000 cm⁻¹: R. J. MAGEE and LOUIS GORDON. (13 November 1962).
- Further study of the polarographic behaviour of organic nitrates: J. S. HETMAN. (15 November 1962).
- The infrared spectra of chelate compounds—II: A study of some bivalent metal chelate compounds of 8-hydroxyquinoline in the region 625–250 cm⁻¹: R. J. MAGEE and LOUIS GORDON. (16 November 1962).
- Complex formation between nickel^{III} and thiomalic acid: R. C. KAPOOR, UMA KAPOOR, H. L. NIGMAN and S. C. SRIVASTAVA. (19 November 1962).
- Use of α -nitroso- β -naphthol in inorganic analysis—Part III: S. V. PATIL. (19 November 1962).
- Phase titrations—II: New applications and a consideration of phase titration end-points: D. W. ROGERS and A. UZSOGOMONYAN. (24 November 1962).
- Stability of iron^{III} chelate of cresotic acids: A spectrophotometric study of iron^{III} *p*-cresotic acid chelate: SARVAGYA S. KATIYAR and V. B. S. CHAUHAN. (24 November 1962).
- The preparation of fortified 70–80% perchloric acid employing anhydrous magnesium perchlorate as desiccant: G. FREDERICK SMITH. (26 November 1962).
- New *O*-*O'*-dihydroxy azo dyes from 8-hydroxyquinoline: A. BADRINAS. (27 November 1962).

DICTIONARY OF CHEMISTRY AND CHEMICAL TECHNOLOGY in four languages

General Editor Z. SOBECKA

English Editors Professor H. STEPHEN and Dr. T. STEPHEN

This comprehensive reference work will be invaluable to those who require an authoritative guide to modern terms in chemistry.

A detailed knowledge of the exact terminology in current use has been successfully achieved by reference to the latest documents in the fields of nuclear physics, radiation chemistry, reactor technology and such rapidly developing branches as the chemistry and technology of plastics. The Dictionary, containing 13,000 English terms is alphabetically arranged with corresponding terms in German, Polish and Russian, and includes indexes in those languages.

724 pages

£10 net

THE APPLICATION OF MATHEMATICAL STATISTICS TO CHEMICAL ANALYSIS

V. V. NALIMOV

An important Russian translation giving an up-to-date account of mathematical statistics as applied to problems connected with the chemical and physical methods of analysis.

Chapter Headings include: Problems of Mathematical Statistics; Classification of Analytical Errors; Chance Variables and their Characteristics; Normal Distribution; Poisson's Distribution and Binomial Distribution, Estimation of the results of Analysis.

302 pages

App. 84s

THE APPLICATION OF ORGANIC BASES IN ANALYTICAL CHEMISTRY

E. A. OSTROUMOV, *U.S.S.R. Academy of Sciences*

A collection of systematic studies by the author on the applications of a particular class of organic compounds—organic bases—in the analytical chemistry of inorganic substances. Since the Russians have a large background knowledge to call upon in the methods of analysis involving precipitation by pyridine, this book will be of the utmost interest to all specialists in the field.

Chapter Headings: The precipitation of metals using pyridine; The precipitation of metals by pyridine in the presence of its salts; The precipitation of metals with hydrogen sulphide in the presence of pyridine; The precipitation of metals using alpha-picoline; The precipitation of metals with hydrogen sulphide in the presence of hexamethylenetetramine; Methods for the separation of metals using pyridine alpha-picoline and hexamethylenetetramine.

180 pages

50s net

VOLATILE SILICON COMPOUNDS

E. A. V. EBSWORTH, *Cambridge University*

A critical monograph describing the structural, physical and chemical properties of simple volatile silicon compounds, concentrating on the hydrides and their derivatives. Lucid discussions of previously unpublished research include structural information and nuclear magnetic resonance work on hydrogen and fluorine bound to silicon.

Chapter Headings: The S.I.H. bond; The Halides of Silicon; Compounds containing Silicon bound to elements of Group IV, V and VI; Other Silicon compounds.

250 pages

Illustrated

50s. net

Pergamon Press books are distributed in the Western Hemisphere and the Philippines by the Macmillan Company, 115 Fifth Avenue, New York 11, N.Y., and Collier-Macmillan (Canada) Ltd., 132, Water Street South, Galt, Ontario, Canada.



PERGAMON PRESS

Headington Hill Hall, Oxford

VOLUME 10, No. 1

JANUARY 1963

CONTENTS

TALANTA Medal Award: - - - - -	1
Z. ŠULCEK, J. DOLEŽAL, J. MICHAL and V. SYCHRA: Rapid analytical methods for the determination of metals and inorganic materials—XIII: Determination of tin in metallic antimony - - - - -	3
D. I. RYABCHIKOV and L. V. BORISOVA: New spectrophotometric methods for the determination of rhenium - - - - -	13
L. ERDEY and S. GÁL: Thermoanalytical investigations of high temperature fusion reactions - - - - -	23
M. KOPANICA and R. PRIBIL: Indirect polarographic determination of silver - - - - -	37
JAMES R. STOKELEY and WILLIAM D. JACOBS: A spectrophotometric study of <i>p</i> -nitrosodiphenylamine as a reagent for rhodium - - - - -	43
R. G. MONK and G. C. GOODE: Differential coulometric analysis: A high-precision technique and its application to the determination of dichromate by constant-current generation of iron ^{II} ion - - - - -	51
C. L. CHAKRABARTI, R. J. MAGEE and C. L. WILSON: Analytical applications of the flame emission spectra of lead and titanium - - - - -	57
MAURICE PESEZ et JAROSLAV BARTOS: L'oxalate de <i>p</i> -diméthylaminoaniline dans la colorimétrie des aldéhydes et des céto-stéroïdes - - - - -	69
C. B. BELCHER: Sodium peroxide as a flux in refractory and mineral analysis - - - - -	75
CHONG KUK KIM and W. WAYNE MEINKE: Thermal neutron-activation analysis of titanium using 5-8-minute titanium-51 and rapid radiochemical separations - - - - -	83
JAMES S. FRITZ and BARBARA B. GARRALDA: Cation-exchange separation of bivalent metal ions from rare earths - - - - -	91
COE W. WADELIN: Photometric titration of alkyl aluminium compounds - - - - -	97
M. L. RICHARDSON: Determination of small amounts of calcium in the presence of large amounts of alkali metal salts by amperometric chelatometry - - - - -	103
J. PAUL JONES, ORVILLE E. HILEMAN, Jr. and LOUIS GORDON: Precipitation of metal 8-hydroxyquinolates from homogeneous solution—VI: Zinc - - - - -	111
Short Communications	
TSUTOMU MOMOSE and MASARU NAKAMURA: Organic analysis—XXIX: A new spraying agent for reducing sugars on paper chromatograms - - - - -	115
H. AREND and J. NOVÁK: Use of compounds of the type $M^{II}TiO(C_2O_4)_2 \cdot xH_2O$ in analytical chemistry—I: The determination of potassium in barium titanate - - - - -	116
EUGENE N. POLLOCK and LAWRENCE P. ZOPATTI: Determination of boron in zirconium and Zircaloy - - - - -	118
HIROSHI HAMAGUCHI, ROKURO KURODA and NAOKI ONUMA: Ion-exchange study of thiocyanatochloro complexes of rare earth elements - - - - -	120
Letter to the Editor	
J. A. RYAN and J. R. SANDERSON: Arsenic in glass - - - - -	127
Editorial note - - - - -	128
Advisory Board of TALANTA - - - - -	129
Notices - - - - -	i
Book reviews - - - - -	iii
Papers received - - - - -	iv