n International Journal of Analytical Chemistry

ταλαντα

talanta

PERGAMON PRESS
OXFORD · LONDON · NEW YORK · PARIS

✓1963 VOLUME 10 JUNE

WHAT'S NEW FROM B.D.H?

ETHYL-AMMONIUM ETHYL-DITHIOCARBAMATE 50% w/w solution in water

A substitute for H_2S in inorganic analysis

The solution yields sulphides with cations, but is free from the odour or toxicity of H_2S. It is stable, with only a faint and not unpleasant odour, it may be used in readily calculable amounts, and it is recommended as a substitute for H_2S in group analysis. While the final colours of the precipitated sulphides are similar to those from H_2S, intermediate shades which develop during precipitation can also help in identifying radicals.

(1) Sen, B. N., *Anal. Chim. Acta*, 1961, **24**, 386-7.

N-METHYL-2-PYRROLIDONE

A versatile solvent

A non-corrosive, non-toxic liquid of good chemical stability, with powerful solvent and dispersing action. Its use as a solvent for polysaccharides enables many reactions involving the -OH group to be readily carried out, e.g. acetylation, esterification, conversion to sodium compounds, and halogenation (leading to the syntheses of ethers, nitriles, thio-alcohols, etc.)[1].

N-Methyl-2-pyrrolidone has been recommended as a solvent in ultra-violet absorption spectrophotometry[2], and is reported to dissolve over thirty times its own volume of acetylene from natural gas streams.

(1) British Patent No. 806,935.

(2) Schurz, J. and Stubchen, H., *Z. Elektrochem.*, 1957, **61**, 754-63.

NEW CAESIUM SALTS

For many years B.D.H. has manufactured and supplied large quantities of caesium salts with standards of purity to meet the demands of research and industry. In addition to caesium bromide, carbonate, chloride, chromate, dichromate, eosinate, iodide, nitrate, and sulphate, the following are now available in large or small quantities:

Caesium bromate $CsBrO_3$. Caesium chlorate $CsCl_3O$. Caesium iodate $CsIO_3$.

Enquiries for other caesium compounds will be welcomed.

TRIMETHYL-PHENYL-AMMONIUM TRIBROMIDE

A selective brominating agent

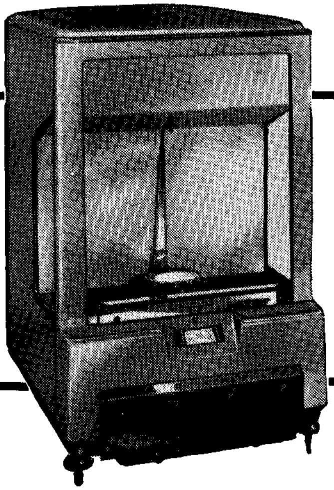
A new brominating agent, used most effectively in solution in tetrahydrofuran; studies in selective bromination have shown the solvent to be a decisive factor[1]. The use of a tetrahydrofuran solution permits α-mono-bromination of ketones and cyclic ketals without affecting ethylenic linkages or active aromatic nuclei, and can be employed in many procedures where direct bromination with bromine gives unwanted by-products. Thus the selective introduction of bromine into a side-chain in, for example, 6-methoxy-2-acetyl-naphthalene, can be effected[2].

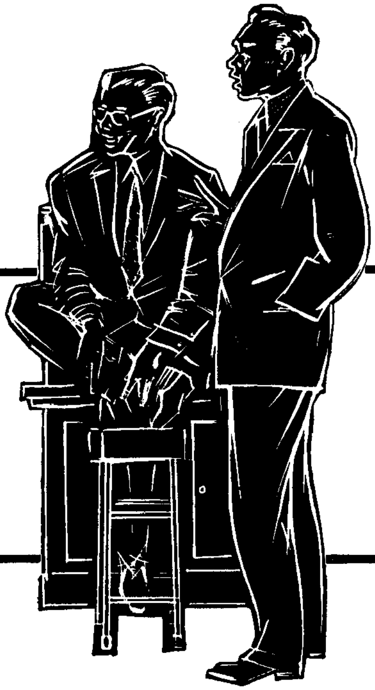
(1) Marquet, A., *et al.*, *Bull. Soc. chim. France*, 1961, 1822-31.

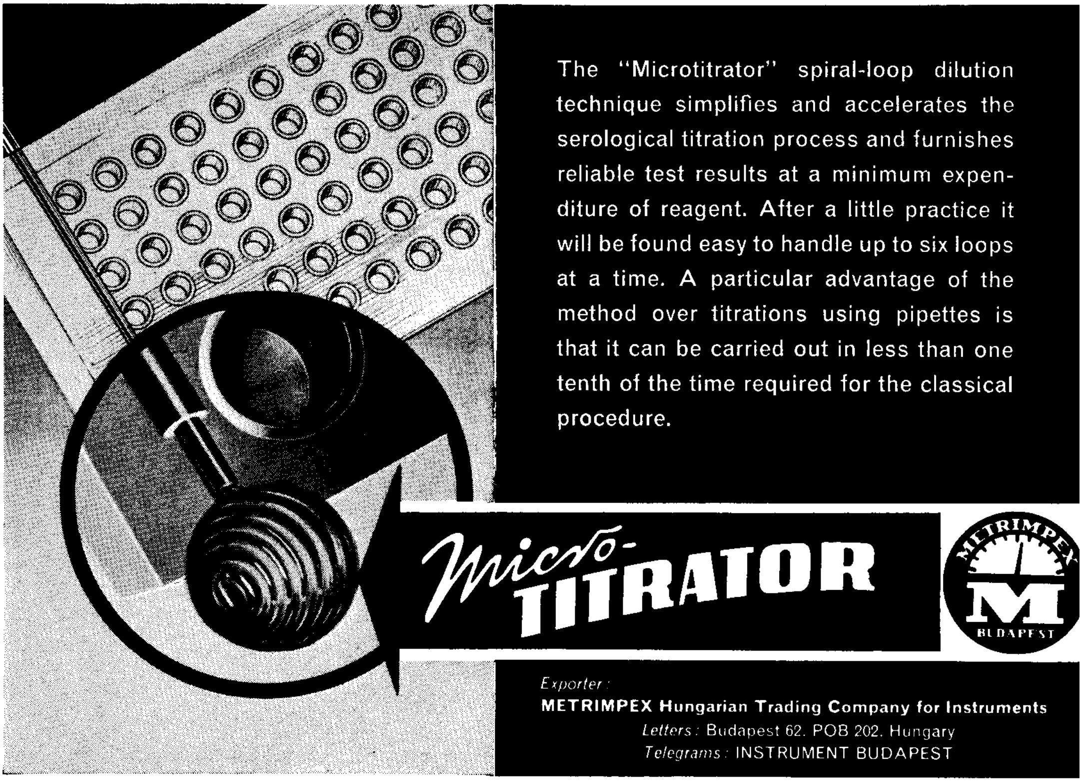
(2) Marquet, A. and Jacques, J., *Bull. Soc. chim. France*, 1962, 90-96.

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

6/2345






Micro-TITRATOR
METRIMPEX
M
BUDAPEST

SUMMARIES FOR CARD INDEXES

Nephelometric examination of barium sulphate precipitation: A. G. Walton and T. Hlabse, *Talanta*, 1963, **10**, 601.

Summary—The formation and growth of barium sulphate precipitates has been followed by a nephelometric technique. Using the Mie theory it has proved possible to estimate both the size and number of particles produced, the results comparing favourably with observations based upon electron microscopy. In the concentration range investigated the precipitate particles are wedge shaped, the major axis being of length about 0·3–0·5 μ. There is no consistent change in the number of particles per unit volume produced at various reactant concentrations. Nucleation is therefore probably heterogeneous.

Determination of thorium in granite by gamma spectrometry and by radiotracer: S. A. Reynolds, *Talanta*, 1963, **10**, 611.

Summary—Thorium in granite samples has been determined by gamma-spectrometric measurement of the 2·6-MeV gamma radiation from thallium-208, a daughter. Concentrations ranged from a few to several hundred ppm, and both untreated and leached samples were analysed. Thorium-234 tracer was successfully applied in finding the sources of error in a difficult chemical analysis and, upon suitable treatment, obtaining the correct analytical values. This study affords an example of the use of a tracer in analysis, and is somewhat unusual in that both negative and positive deviations were discovered. Agreement between results by the two independent methods has been quite good.

Oscillopolarographic detection and determination of dihydric phenols. Jan Doležal, Vasil Koprda and Jaroslav Zýka, *Talanta*, 1963, **10**, 621.

Summary—A 1*M*-potassium nitrate solution has been proposed as supporting electrolyte for the qualitative detection of dihydric phenols by an oscillopolarographic method. Sufficiently distant incisions on curves of the function $dV/dt = f(V)$ permit their determination by the method of comparative titration with an average error of ±3–4%. Monohydric phenol does not interfere in their qualitative detection. Phloroglucinol and pyrogallol interfere in the detection as well as determination. The method of calibration curves permits determination of individual dihydric phenols with an error of ±5%.

Phase titrations-II: New applications and a consideration of the phase titration end-point: D. W. Rogers and A. Özsoğomonyan 1963, *Talanta*, **10**, 633.

Summary—Results are given for the phase titration of binary solutions of aniline with methanol, ethanol, isopropanol, dioxan and acetone, of nitrobenzene with methanol, ethanol, isopropanol, dioxan and acetone, of n-butyl bromide with methanol, ethanol, isopropanol, dioxan and acetone, of methyl aniline with methanol, isopropanol and acetone, of ethyl acetate with acetone and of turpentine with acetone. The titrant in each case was water. Good and bad phase titration end-points are explained in terms of the corresponding three-component phase diagram.

Comparison of fifty-two spectrophotometric methods for the determination of nitrite: E. Sawicki, T. W. Stanley, J. Pfaff and A. D'Amico, *Talanta*, 1963, **10**, 641.

Summary—This paper can be considered as a concise source of spectrophotometric methods for the determination of nitrite. Fifty-two methods, of which about 36 are new, are compared with respect to molar absorptivity, selectivity, sensitivity, simplicity, colour stability, and conformity to Beer's law. A new type of spectrophotometric procedure—autocatalytic in principle—is introduced; a molar absorptivity of 620,000 is obtained. Over 20 new methods have been shown to give higher molar absorptivities with nitrite than any of the Griess-type of reagents. Consequently, they are worthy of further investigation in respect of their application to the analysis of nitrites and nitrite precursors.

Ammonium hexanitratocerate(IV) as an oxidising agent—II: Potentiometric titration of oxalic and mandelic acids at room temperature: G. Gopala Rao, K. S. Murty and P. V. Krishna Rao, *Talanta*, 1963, **10**, 657.

Summary—Conditions have been established for the accurate titration of oxalic and mandelic acids with ammonium hexanitratocerate(IV) at room temperature in a hydrochloric or nitric acid medium with a potentiometric end-point. It has been shown that $0{\cdot}1N$ or $0{\cdot}01N$ solutions of the oxidising agent can be standardised very conveniently, using sodium oxalate as a primary standard. The very rapid reaction now observed between cerate and oxalic acid in a hydrochloric acid medium (where the redox potential of cerate is about 1·28 V) is of fundamental significance, because it shows, unambiguously, that the ease of reaction between ammonium hexanitratocerate(IV) and oxalic acid in a nitric or perchloric acid medium is not caused by the higher oxidation potentials of the cerate obtaining in these acid media, as assumed by previous coworkers.

A thermogravimetric pyrolysis study of the interaction products of dihydrogen-di(1,2,3-benzotriazolatium) hexacyanoferrate(II) with certain organic amines: R. F. WILSON and G. HENRY JR., *Talanta*, 1963, **10**, 667.

Summary—Thermogravimetric pyrolyses of the interaction products of certain organic amines, tetramethylammonium chloride and piperidine with dihydrogen-di(1,2,3-benzotriazolatium) hexacyanoferrate(II) are reported.

Anion exchange of uranium, thorium, iron and aluminium in mineral acid-ether solutions: Separation of uranium from thorium, aluminium and iron: S. URUBAY, J. KORKISH and G. E. JANAUER, *Talanta*, 1963, **10**, 673.

Summary—The adsorption behaviour is described of uranium, thorium, iron^{III} and aluminium on the strongly basic anion exchanger Dowex 1 in mixtures of ethers with hydrochloric or nitric acid. The distribution coefficients of these elements have been determined in diethyl and di-isopropyl ether as well as in dioxan. Based on these results separation methods for uranium, thorium, iron and aluminium have been developed.

Application of Feigl's reactions in biochemistry and agricultural chemistry: A. BONDI, *Talanta*, 1963, **10**, 679.

Summary—A review is presented of applications of Feigl's reactions in biochemistry and agricultural chemistry.

A new principle of activation analysis separations—II: Substoichiometric determination of traces of zinc and copper in germanium dioxide: A. ZEMAN, J. RŮŽIČKA and J. STARÝ, Talanta, 1963, **10**, 685.

Summary—A substoichiometric determination of zinc and copper in germanium dioxide is based on dissolution of the irradiated sample in sodium hydroxide followed by addition of known amounts of carriers for the metals to be determined, then adjustment to suitable conditions for extraction. An irradiated standard sample is treated simultaneously in exactly the same way. The solutions thus prepared are extracted with substoichiometric amounts of dithizone in carbon tetrachloride and the amounts of zinc and copper in the germanium dioxide calculated from the activities of the extracts obtained. The present procedure is far more simple and rapid than previously published methods. It eliminates not only distillation but also many separation steps commonly used, thus shortening the time of analysis to 20 min.

Applications of infrared spectroscopy—XI: The determination of 1,2-diols by modified Zeisel reactions: D. M. W. Anderson and S. S. H. Zaidi, *Talanta*, 1963, **10**, 691.

Summary—Vapour-phase infrared spectroscopy offers a simple, sensitive and specific method for simultaneous determinations of the olefines and alkyl iodides liberated in Zeisel determinations on 1,2-diols.

Zerstörungsfreie spektrochemische Analyse archäologischer Bronzefunde: K. Doerffel und R. Wagner, *Talanta*, 1963, **10**, 693.

Summary—A spectrochemical method of analysis for the non-destructive investigation of archaeological bronzes is described. Samples of any size or shape can be analysed quantitatively if any planar area 2 mm in diameter is available. Little work is required to prepare the samples. By using several locations a better average analysis can be obtained. The spots caused by the operation of the arc can readily be removed after the analysis.

Determination of small amounts of zirconium—I: Gravimetric procedures using mandelic acid and its derivatives: Mohammed Rafiq, Charles L. Rulfs and Philip J. Elving, *Talanta*, 1963, **10**, 696.

Summary—The limiting factors have been investigated for precipitation of zirconium at the milligram level by mandelic acid, *p*-bromomandelic acid and *m*-nitromandelic acid; the latter has only been briefly studied previously. Optimum conditions have been determined for quantitatively precipitating zirconium at 0·1- and 1-mg levels.

Precipitation from Homogeneous Solution with *N*-Benzoylphenylhydroxylamine acetate: P. R. Ellefsen, L. Gordon, R. Belcher and W. G. Jackson, *Talanta*, 1963, **10**, 701.

Summary—A preliminary study has been made of the use of *N*-benzoylphenylhydroxylamine-acetate as a source of *N*-benzoylphenylhydroxylamine in precipitation from homogeneous solution. Initial experiments with a model system in which the separation of copper from cobalt and cadmium was studied have demonstrated the superior applicability of *N*-benzoylphenylhydroxylamine acetate over *N*-benzoylphenylhydroxylamine as a precipitant.

New *o-o′*-dihydroxyazo dyes from 8-hydroxyquinoline: A. Badrinas, *Talanta*, 1963, **10**, 704.

Summary—The preparation and characteristics of a series of *o-o′*-dihydroxyazo dyes of 8-hydroxyquinoline have been studied. The colour and fluorescent reactions of these dyes with several cations are given, especially specific reactions for aluminium and magnesium.

Selective spot test for europium in the presence of other rare earths: Ervin Jungreis and Ezra Levy, *Talanta*, 1963, **10**, 708.

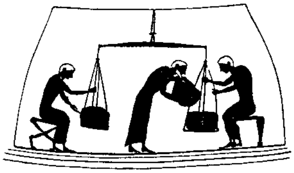
Summary—A new spot test for the detection of europium is described, based on the redox reaction between Eu^{II} and phosphomolybdic acid. The test is specific for europium in the presence of all other rare earth elements.

An improved preparation of ammonium hexanitratocerate(IV), and routine analytical testing procedure to prove primary reference standard purity: G. Frederick Smith, *Talanta*, 1963, **10**, 709.

Summary—Ammonium nitratocerate, $(NH_4)_2Ce(NO_3)_6$, has been employed over a period of years as a primary standard in oxidimetry. An improved method for its preparation is described. Practical routine control laboratory directions are given for proving the purity of the finished product.

TALANTA

An International Journal of Analytical Chemistry



PERGAMON PRESS LTD.

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

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

Published monthly - 1 Volume *per annum*

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

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

Payments must be made in advance

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

PRINTED IN NORTHERN IRELAND AT THE UNIVERSITIES PRESS BELFAST

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. Kortüm	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 Shu-Chuan Liang	Academia Sinica, Peking, China
Professor E. Schulek	L. Eötvös University, Budapest, Hungary
Professor G. Frederick Smith	University of Illinois, Urbana, Illinois, U.S.A.
Dr. M. Steinberg	The Hebrew University of Jerusalem, Israel
Professor E. H. Swift	California Institute of Technology, Pasadena, California, U.S.A.
Dr. E. Wänninen	Åbo Academy, Finland
Dr. T. S. West	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 unbiassed reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor-in-Chief, the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

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

Twenty-five free reprints of each paper will be provided (with ten further free copies for each additional author) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

2. Script Requirements

General

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

Preliminary communications should be limited to less than 1000 words in length and should not contain diagrams. If they do not 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 produced in both tables and figures.

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

References

References should be indicated in the text by consecutive superior numbers; and the full reference should be given in a list at the end of the paper in the following form:

[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*. Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

Footnotes, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, ¶, commencing anew on each page; they should not be included in the numbered reference system.

Proofs

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

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.

WINKLER CENTENARY SYMPOSIUM

Budapest, Hungary 24–27 April 1963

Professor E. SCHULEK (Budapest), Chairman, speaks at the Banquet held at the internationally famous Gundel Restaurant. On the right of Professor SCHULEK is seated Professor W. POETHKE (Jena). Beyond Professor SCHULEK is Frau POETHKE and on her left is Frau WINKLER, widow of Professor L. W. WINKLER.

Professor C. L. WILSON (U.K., Editor-in-Chief) presents to Professor SCHULEK, representing the Hungarian Academy of Sciences, a copy of the *Hungarian Honour Issue of Talanta* (May, 1963). The Honour Issue marks the centenary of the birth of Professor WINKLER and honours the Hungarian School of Analytical Chemistry. All contributions to the issue were made by members of that School.

Professor SCHULEK, a member of the Advisory Board of *Talanta*, displays the *Honour Issue* to the guests at the Banquet.

Talanta, 1963 Vol 10, pp. 601 to 610. Pergamon Press Ltd. Printed in Northern Ireland

NEPHELOMETRIC EXAMINATION OF BARIUM SULPHATE PRECIPITATION

A. G. WALTON and T. HLABSE
Department of Chemistry, Case Institute of Technology
Cleveland 6, Ohio, U.S.A.

(*Received* 28 *August* 1962. *Accepted* 9 *January* 1963)

Summary—The formation and growth of barium sulphate precipitates has been followed by a nephelometric technique. Using the Mie theory it has proved possible to estimate both the size and number of particles produced, the results comparing favourably with observations based upon electron microscopy. In the concentration range investigated the precipitate particles are wedge shaped, the major axis being of length about 0·3–0·5 μ. There is no consistent change in the number of particles per unit volume produced at various reactant concentrations. Nucleation is therefore probably heterogeneous.

INTRODUCTION

OF considerable importance in studies of the growth and stability of solid suspensions are the size, shape and number of suspended particles. Deductions may also be made about the formation of primary particles if the functional dependence between the particle numbers and the concentration of the generating materials is known.[1] In practice the size and shape of particles may often be adequately investigated by electron microscopy.[2] The estimation of particle numbers, particularly when the particles are of submicroscopic size, has, however, proved more difficult. Although electron microscopy is again a method of making such estimates, the method is rather time-consuming and becomes completely ineffective if the particles are not regularly shaped. As a consequence of these difficulties, and also equally in its own right, much attention has been paid to the light scattering properties of suspensions in recent years. In principle, at least, the bulk properties of *in situ* particles are directly measured by the scattered light, whereas data from particle counts or electron microscopy are extrapolated from sample counts.

Because light scattering theory has so far only been developed for certain regular shapes of which spherical particles are the best characterised, it is natural that attempts to verify the theory by experiment have been mainly confined to work with polymers which assume spherical symmetry in solution.[3] The additional criterion of monodispersity required by the theoretical exposition is also attainable to a large degree with commercially available polymer solutions. Some attempts to interpret polydisperse systems in terms of the Mie theory have made use of size distribution functions which are either trial functions or have been established by electron microscopy.[4] The opposite process, namely the calculation of distribution functions from light scattering data, has not proved feasible and, indeed, there is some evidence that spectrophotometric transmission measurements, with which the present work is concerned, are not sensitive to polydispersity until the average particle size (radius) becomes of the order of the wavelength of incident light or larger.[5] Difficulties encountered in analysing the light scattering data from polymer solutions (*e.g.*, estimation of refractive index of solid and solvent in the presence of stabilising surfactants) are generally found to be of minor importance and the experimental evidence is in good agreement with Mie theory. Most inorganic colloids (sulphur sols are an exception[6]) present many more problems associated with anisotropy and the irregularity of particle shapes and sizes than do the organic dispersions. Usually, however, the refractive index ratio of the solid in suspension may be associated with that of the bulk phase. This is only true if the particles are discrete, *i.e.*, not agglomerates. It is apparent, therefore, from an elementary consideration that nephelometry may provide an approximate estimate of particle numbers, the errors involved depending upon the ideality of the suspension. Because even approximate number estimations for small particles (volume $< 10^{-1}\ \mu^3$) are extremely difficult to obtain by other methods, it seemed worthwhile to pursue the nephelometric analysis further. The errors involved are discussed more fully later.

The formation of barium sulphate precipitates by direct mixing is of importance in analytical chemistry and has been investigated quantitatively on numerous occasions, mainly by conductivity methods[7] but also by an approximate nephelometric technique.[8] The kinetics of formation of the solid phase are intimately connected with the total surface area of the precipitate and hence with the number and shape of the precipitate particles. It was partially in an effort to determine the accuracy of the assumptions made in the published kinetic analyses which led to the present work.

Various workers have estimated (either directly or indirectly) the number of particles produced when barium sulphate precipitates are formed by direct mixing procedures[2,7,9] and concluded that the number is virtually invariant with the concentration of reactants, if the initial supersaturation of barium sulphate is less than one hundred times the solubility. The explanation for this phenomenon is that the supersaturation is relieved by crystal growth upon small impurity particles present in solution and, consequently, the final number of particles is dependent only upon the original number of these small heterogeneous centres.

In the present work the size and number of particles produced in barium sulphate precipitations have been investigated by analysis of spectrophotometric measurements.

EXPERIMENTAL

The measurements were performed using a Beckman DU spectrophotometer at a principal wavelength of 5460 Å in vacuo. All glassware was steam cleaned prior to use. There was no consistent evidence of barium sulphate adhering to the cell walls, but in a few runs the reaction cell showed between 0·1 and 0·3% less transmission than before the run. The chemicals used (barium chloride and sodium sulphate) were of Analytical Reagent grade; solutions were further purified by filtration through 100-mμ Millipore filters to remove the larger nucleating impurities. Equal volumes of the two solutions were mixed in the spectrophotometer cell by injection from a syringe; the mixing time was 1–2 sec. Transmission measurements were then performed every 30 sec until the optical density was constant. After remaining constant for about 20–30 min, the density usually decreased very slowly; the cause was presumably sedimentation of the suspended particles. The wavelength exponent of the turbidity was measured during the period of maximum density and samples used for the electron microscopy studies were also withdrawn during this period and sprayed on collodion covered grids.

THEORETICAL CONSIDERATIONS AND PROCEDURE

For a monodisperse sol the ratio of measured to incident intensity of monochromatic light is given by

$$\frac{I}{I_0} = e^{-\tau l} \quad (1)$$

where τ is the turbidity and l is the cell path length.

For a system containing spherical particles the turbidity may be expressed in terms of the Mie scattering coefficient K

$$\tau = N_0 \pi r^2 K \quad (2)$$

where N_0 is the number of particles/ml and r is the radius of the particle.

The value of K oscillates with increase in radius, but for large particles becomes approximately constant ($r \to \infty$, $K \to 2$).

It is this approximation which Nielsen used when assuming that the turbidity is proportional to the surface area of the precipitate in kinetic studies.[8]

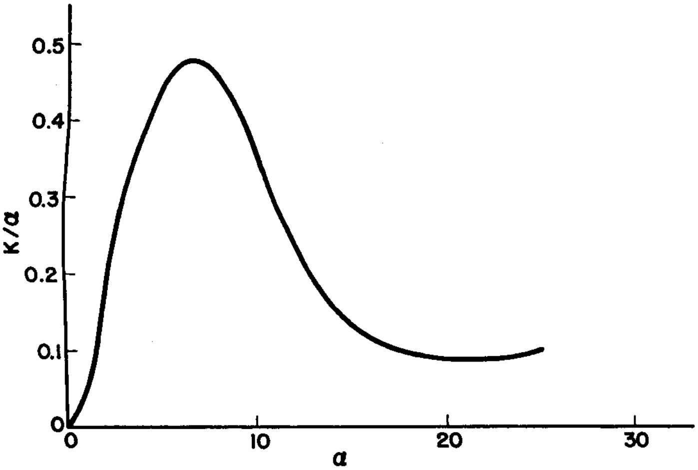


FIG. 1.—The relation between the Mie scattering coefficient K and the size parameter α for a refractive index ratio of 1·23 and λ = 5460 Å (vacuo).

In terms of the mass of solute/ml of solution (c) the turbidity may be expressed as

$$\tau/c = (3\pi/2\rho\lambda')(K/\alpha) \quad (3)$$

where $\alpha = 2\pi r/\lambda'$, ρ is the density of the suspended material and λ' is the wavelength of light in the medium.

The refractive index ratio "m" is found from published data[10,11] to be 1·23. We have obtained scattering coefficients for a refractive index ratio of 1·23 by using tables[12] and the extrapolation method of Heller[13] for α values up to 5.

Above $\alpha = 5$ a direct (approximate) extrapolation was performed from m values of 1·20 and 1·25. Fig. 1 shows K/α versus α for these computed values.

It is evident that for most values of K/α there is no unique value of α. This problem is readily overcome by examination of the wavelength exponent of the turbidity. Quite often the relation between the turbidity and the wavelength enables a maximum to be identified with one or more of the Mie maxima,[14] but in the present case it is sufficient to identify the sign of $\log_{10} \tau$ versus $\log_{10} \lambda$ plots.

The shape of the turbidity/wavelength curves is modified by the change of refractive index of both the medium and the solid phase, *i.e.*, by dispersion. The dispersion coefficient ω was calculated from available data[10,11] and use of the Cauchy formula. $\omega = \left(\frac{m^2 - 1}{m^2 + 2}\right)^2$ varied between $2{\cdot}143 \times 10^{-2}$ at $\lambda = 4000$ Å and $2{\cdot}090 \times 10^{-2}$ at 7500 Å, *i.e.*, a change of 2·5%, which for present purposes is negligible.

The procedure used was therefore to calculate K/α from experimental results and equation (3), then to identify α unambiguously by examination of the gradient of $\log_{10} \tau$ versus $\log_{10} \lambda$ (which is negative for particles of radius $<5\ \mu$).

Errors associated with the spectrophotometer

Modifications of the standard Beckman DU spectrophotometer have often been found necessary to render the light beam parallel and to avoid secondary scattering.[3] Such modifications have been deemed adequate when the specific extinction becomes independent of the concentration of suspended material. One method of eliminating errors without modifying the instrument is to extrapolate the specific extinction to zero concentration. The applicability of this method to certain organic dispersions was formerly disputed[15] but has now been resolved.[5]* In the present work the mass of suspended material was very small (about 10^{-5} g/ml) and no consistent differences in the specific turbidity (τ/c) were obtained either by dilution of the suspension or by the use of cells varying in length from 1 to 10 cm. The error involved between the extrapolated (zero concentration) value and that obtained directly is therefore negligible.

Errors relating to shape

Theoretical computations of scattering curves for particle shapes other than spherical are only available for a few special cases. The Debye theory of light scattering[23] provides a useful means of making such computations, one of the most interesting results, for the present purpose, being that for long cylinders.[16] The scattering coefficient is dependent upon the orientation of the cylinders, but comparison of the scattering curves for spheres and cylinders shows a rather surprising degree of similarity[17]. For intermediate and irregular shapes there is no strictly defined theory, but there have been attempts made to obtain semi-quantitative data by using scattering theory for spherical particles. Such methods have been widely applied in the investigation of dust aerosols, fog, *etc.*, in meteorology[18] where both the shape and the refractive index of the suspended particles are not directly known. Useful information regarding particle size has thus been obtained by these techniques in spite of the considerable difficulties.

* The errors involved in spectrophotometric transmission measurements using an unmodified Beckman DU instrument are discussed in a paper by S. H. Maron, P. E. Pierce and I. N. Ulevitch, "Determination of Latex Particle Size by Light Scattering—V: Transmission Measurements", which has been accepted for publication in *J. Colloid Sci.* The authors find that thoroughly reliable data can be obtained from the unmodified instrument providing that cell corrections are applied and the extrapolated value of the specific turbidity (τ/c) at $c = 0$ is used (thus eliminating extraneous effects). With these precautions $(\tau/c)_0$ becomes independent of the cell length.

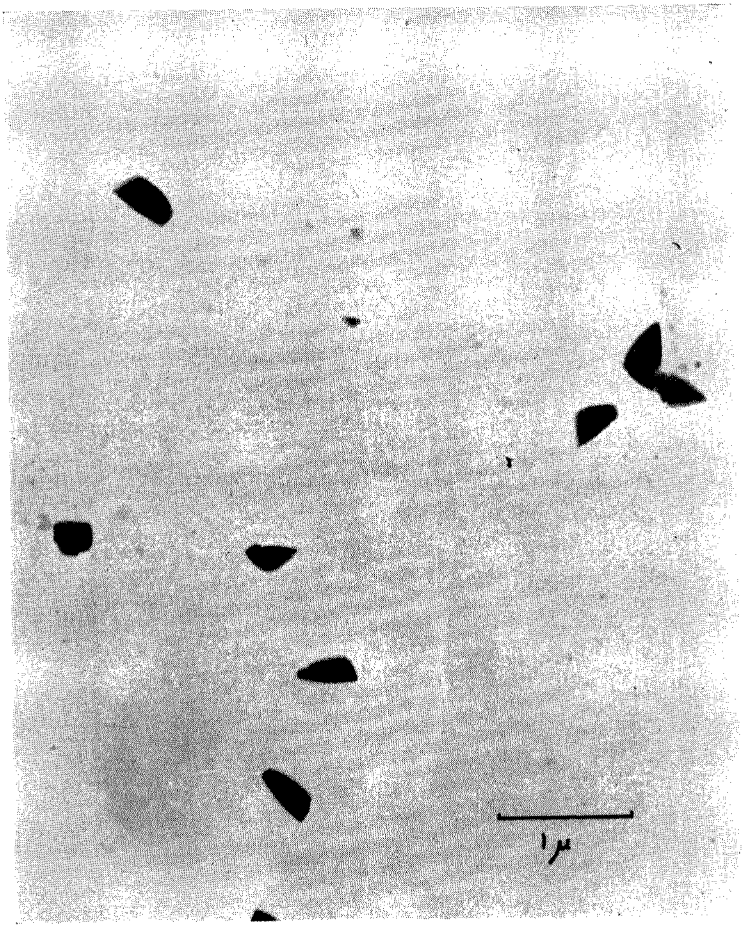


FIG. 3—A typical sample of barium sulphate particles produced in the precipitation runs.

Analysis of the scattering by non-spherical particles in solution has been mainly limited to very small scatterers, for which the Rayleigh theory (which is not sensitive to particle shape) may be used.[19] It is an unfortunate fact, however, that the vast majority of colloids and suspensions can only be conveniently obtained with particles too large for use of the Rayleigh notation and often too small for direct microscopic observation (0·05–1·0 μ).

Again, in spite of the assumptions involved, colloids falling into the indicated size range have been investigated qualitatively[20] and quantitatively[21] by nephelometry, some interpretation involving modifications of the Mie scattering equations.[22] Barium sulphate suspensions (particle radius about 4.6 μ) have also been investigated quantitatively[14] and the particle size calculated from light scattering theory was found to be in agreement with independent methods. The calculated value for the refractive index of the suspended material was, however, lower than that generally accepted for the bulk material[10] (in air), 1.52:1.64. This discrepancy probably arises from a number of factors, including anisotropy and particle shape. Irregularities in particle shape tend to displace the position of the Mie maxima and because the calculation of the refractive index was based upon the identification of these maxima, it seems that the particle shape may have been a major causative factor in this discrepancy.

There is still undoubtedly much to be desired in the development of light scattering theory for colloids and suspensions. The non-ideality of colloidal scatterers does regulate the accuracy of deductions, but an estimate of the extent of the errors involved can often be obtained by independent means, *e.g.*, electron microscopy. Such a check for silver bromide sols showed the particle sizes to be within 10% of that calculated.[22] Thus the combination of light scattering experiment and theory does apparently yield a method suitable for sampling measurements when the particle shape is not spherical. The added convenience of the spectrophotometric transmission technique has provided a basis for the present investigation.

Polydispersity

Published observations of the state of dispersity produced for barium sulphate precipitates using direct mixing techniques vary considerably. Both monodisperse (higher order Tyndall spectra)[24] and polydisperse suspensions[2] have been reported, the result apparently depending upon the method of mixing. In the present case micrographs show the barium sulphate suspensions to be fairly monodisperse.

RESULTS

Accepting that equation (3) may be applied to the present system, K/α has been obtained from the experimental results. For the large majority of runs there are two possible values of α which correspond to each of these values of K/α. As previously mentioned, a definite identification of the correct value was obtained by investigating the sign of the gradient of $\log_{10} \tau$ versus $\log_{10} \lambda$, which would be negative for the smaller particles and positive for the larger particles. Typical plots are shown in Fig. 2, and Table I shows the calculated radius of particles for various precipitation concentrations.

An exact analysis of the particle sizes from the electron micrographs is difficult because of the irregular shape of the particles (see Fig. 3). An approximate assessment

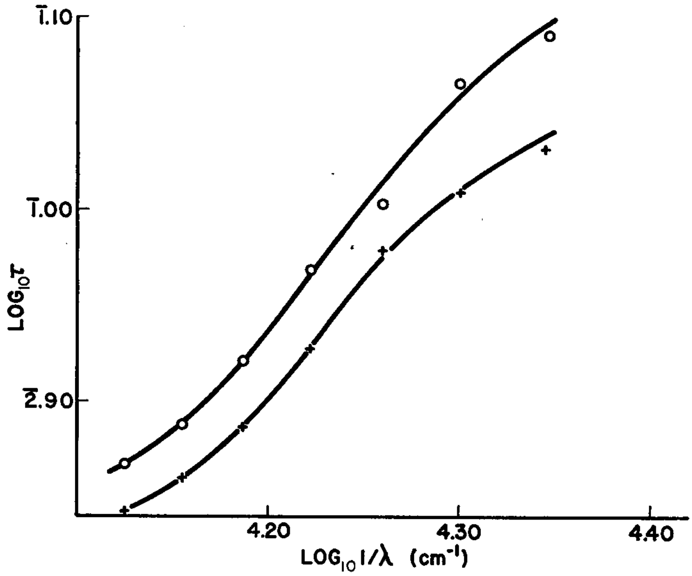


FIG. 2.—The change of turbidity with wavelength for two typical runs shows that the particle size is less than that at the (first) Mie maximum: Run 10 (upper), Run 13 (lower).

TABLE I

Run No.	[Ba^{2+}], *moles*/l	[SO$_4$$^{2-}$], *moles*/l	Particle radius, r, *cm*	N (ml^{-1})
1	$5{\cdot}11 \times 10^{-5}$	$1{\cdot}48 \times 10^{-3}$	$1{\cdot}4 \times 10^{-5}$	$2{\cdot}5 \times 10^{8}$
2	$5{\cdot}11 \times 10^{-5}$	$1{\cdot}48 \times 10^{-3}$	$1{\cdot}4 \times 10^{-5}$	$2{\cdot}2 \times 10^{8}$
3	$5{\cdot}11 \times 10^{-5}$	$1{\cdot}48 \times 10^{-3}$	$1{\cdot}4 \times 10^{-5}$	$2{\cdot}3 \times 10^{8}$
4	$5{\cdot}11 \times 10^{-5}$	$1{\cdot}48 \times 10^{-3}$	$1{\cdot}2 \times 10^{-5}$	$3{\cdot}3 \times 10^{8}$
5	$5{\cdot}11 \times 10^{-5}$	$1{\cdot}33 \times 10^{-2}$	$1{\cdot}3 \times 10^{-5}$	$3{\cdot}1 \times 10^{8}$
6	$5{\cdot}11 \times 10^{-5}$	$1{\cdot}33 \times 10^{-2}$	$1{\cdot}6 \times 10^{-5}$	$1{\cdot}8 \times 10^{8}$
7	$5{\cdot}11 \times 10^{-5}$	$1{\cdot}33 \times 10^{-2}$	$1{\cdot}4 \times 10^{-5}$	$2{\cdot}6 \times 10^{8}$
8	$0{\cdot}99 \times 10^{-4}$	$1{\cdot}48 \times 10^{-3}$	$1{\cdot}2 \times 10^{-5}$	$7{\cdot}2 \times 10^{8}$
9	$0{\cdot}99 \times 10^{-4}$	$2{\cdot}96 \times 10^{-4}$	$8{\cdot}0 \times 10^{-6}$	$2{\cdot}2 \times 10^{8}$
10	$0{\cdot}99 \times 10^{-4}$	$2{\cdot}76 \times 10^{-3}$	$1{\cdot}4 \times 10^{-5}$	$4{\cdot}6 \times 10^{8}$
11	$0{\cdot}99 \times 10^{-4}$	$2{\cdot}21 \times 10^{-3}$	$1{\cdot}3 \times 10^{-5}$	$5{\cdot}3 \times 10^{8}$
12	$0{\cdot}99 \times 10^{-4}$	$9{\cdot}24 \times 10^{-4}$	$1{\cdot}3 \times 10^{-5}$	$6{\cdot}3 \times 10^{8}$
13	$0{\cdot}99 \times 10^{-4}$	$3{\cdot}63 \times 10^{-3}$	$1{\cdot}3 \times 10^{-5}$	$5{\cdot}5 \times 10^{8}$
14	$0{\cdot}99 \times 10^{-4}$	$3{\cdot}26 \times 10^{-3}$	$1{\cdot}0 \times 10^{-5}$	$1{\cdot}2 \times 10^{7}$
15	$2{\cdot}66 \times 10^{-4}$	$2{\cdot}50 \times 10^{-4}$	$8{\cdot}3 \times 10^{-6}$	$4{\cdot}6 \times 10^{9}$
16	$1{\cdot}33 \times 10^{-3}$	$1{\cdot}00 \times 10^{-4}$	$1{\cdot}4 \times 10^{-5}$	$4{\cdot}6 \times 10^{8}$
17	$6{\cdot}65 \times 10^{-4}$	$1{\cdot}00 \times 10^{-4}$	$1{\cdot}4 \times 10^{-5}$	$4{\cdot}4 \times 10^{8}$
18	$1{\cdot}99 \times 10^{-3}$	$0{\cdot}99 \times 10^{-4}$	$1{\cdot}3 \times 10^{-5}$	$5{\cdot}2 \times 10^{8}$
19	$2{\cdot}33 \times 10^{-3}$	$0{\cdot}98 \times 10^{-4}$	$1{\cdot}1 \times 10^{-5}$	$9{\cdot}0 \times 10^{8}$
20	$2{\cdot}53 \times 10^{-3}$	$0{\cdot}95 \times 10^{-4}$	$8{\cdot}0 \times 10^{-6}$	$2{\cdot}2 \times 10^{8}$
21	$1{\cdot}06 \times 10^{-3}$	$1{\cdot}00 \times 10^{-4}$	$1{\cdot}1 \times 10^{-5}$	$9{\cdot}1 \times 10^{8}$
22	$3{\cdot}77 \times 10^{-4}$	$1{\cdot}00 \times 10^{-4}$	$8{\cdot}9 \times 10^{-6}$	$1{\cdot}5 \times 10^{9}$
23	$3{\cdot}28 \times 10^{-3}$	$1{\cdot}00 \times 10^{-4}$	$1{\cdot}4 \times 10^{-5}$	$4{\cdot}2 \times 10^{8}$
24	$2{\cdot}78 \times 10^{-3}$	$1{\cdot}00 \times 10^{-4}$	$8{\cdot}3 \times 10^{-6}$	$2{\cdot}1 \times 10^{9}$
25	$3{\cdot}64 \times 10^{-3}$	$1{\cdot}00 \times 10^{-4}$	$1{\cdot}1 \times 10^{-5}$	$8{\cdot}1 \times 10^{8}$
26	$2{\cdot}96 \times 10^{-3}$	$1{\cdot}00 \times 10^{-4}$	$1{\cdot}0 \times 10^{-5}$	$1{\cdot}2 \times 10^{9}$
27	$2{\cdot}05 \times 10^{-3}$	$1{\cdot}00 \times 10^{-4}$	$8{\cdot}3 \times 10^{-6}$	$2{\cdot}1 \times 10^{8}$
28	$1{\cdot}02 \times 10^{-4}$	$1{\cdot}58 \times 10^{-4}$	$1{\cdot}0 \times 10^{-5}$	$8{\cdot}0 \times 10^{8}$
29	$1{\cdot}02 \times 10^{-4}$	$1{\cdot}00 \times 10^{-3}$	$1{\cdot}2 \times 10^{-5}$	$7{\cdot}0 \times 10^{8}$
30	$1{\cdot}08 \times 10^{-4}$	$1{\cdot}14 \times 10^{-3}$	$1{\cdot}2 \times 10^{-5}$	$7{\cdot}5 \times 10^{8}$

of the volume of the individual crystals from various experiments yields values in the range 5–10 × $10^{-3}\,\mu^3$, which is of the same order as values calculated from transmission measurements. We are led to believe from the micrographs that particle counts are accurate to within a factor of two or better. The accuracy of the counts is further aided by the small particle sizes. For larger particles of irregular shape the estimation of size is made much more difficult by the changed character of the scattering curves. The Mie maxima associated with the scattering coefficient are displaced and for strongly polydisperse systems become obliterated. It is well known that for very small particles (see references 12 and 25 for limiting values) Rayleigh scattering is not sensitive to shape or polydispersity and in the present case the particles, which are intermediate in size, are also intermediate in scattering properties. Dilution of the suspended precipitate conforms to equation (3) (Fig. 4). It is perhaps surprising that the suspended crystals maintain their size under these conditions. No effects of dissolution could, however, be detected. Similar observations have been made by Meehan and Beattie[22] for silver bromide sols.

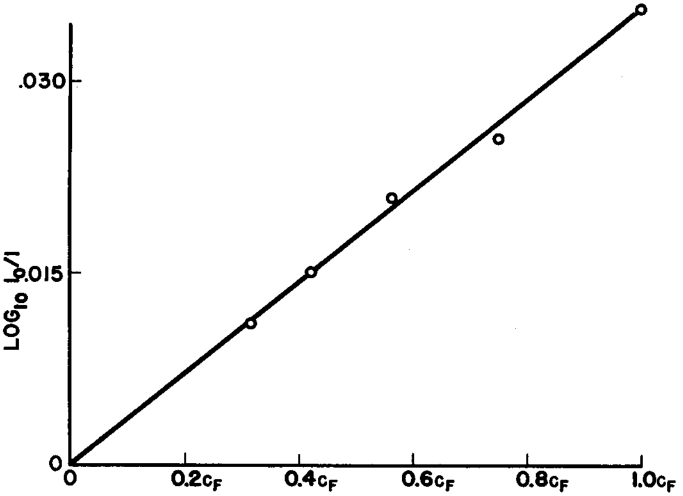


FIG. 4.—Dilution of the suspension demonstrates the relation between τ and c [equation (3)].
[$c_f = 9{\cdot}69 \times 10^{-5}$ moles/l. (Run 21)]

The reproducibility of results is good (see Table I, Runs 1–4, 5–7) provided the mixing technique is not varied. Changes in particle numbers estimated for various runs may probably be accounted for in terms of some inevitable homogeneous mixing, stray sources of nucleating impurities, and inaccuracies associated with the theory.

DISCUSSION

The theories of nucleation of sparingly soluble salts in solution require that the rate of nucleus formation be a function of the ion product of reactants.[26] Consequently, the number of particles which may be identified at the termination of the precipitation process will increase very sharply with increase in the reactant concentration unless agglomeration conceals this effect. Nielsen[1] has observed that the number of barium sulphate particles produced in direct mixing experiments does indeed increase sharply (*i.e.*, by many powers of ten), but only when the initial ionic product of barium and sulphate ions is in excess of 10^{-4} moles^2/l.^{2}. Below this concentration there is no distinct change of particle numbers either with change in reactant concentration or with the duration of the precipitation.

The concentrations of reactants used in the present work are well below the concentrations required for the homogeneous generation of new particles, and it is to be expected that the particle numbers for different runs should be approximately constant unless agglomeration occurs.

In the presence of equal concentrations of barium and sulphate ions, barium ions are preferentially absorbed on the precipitate surface.[27] No flocculation effects could, however, be detected at the low concentrations used, either by nephelometry or by electron microscopy. The consistency of the number estimates at various concentrations is therefore in accord with the theory of heterogeneous nucleation, *i.e.*, barium sulphate precipitates exclusively on very small impurity particles. The source of these impurities is not at present clear, but the number of particles (and hence impurities) per ml of solution determined in this work is well within the range of previously published numbers (between 10^6 and 10^9/ml at low reactant concentrations). Because the results of each worker were self-consistent, the discrepancies appear to be caused by the source of the solvent (water).[28] It is only reasonable that water from various parts of the world should contain various amounts of impurity, but what is rather strange is that substantial numbers of these impurities cannot be removed by filtration or distillation, although they may be disintegrated by ultrasonic sound waves.[29] The nature of the impurities is not known, but some estimate of the size is possible. From the extremely accurate measurements of Turnbull[7] on the early stages of barium sulphate it appears that the heterogeneous nuclei must have an average radius of a few Å only, otherwise deviations from the growth law would ensue.

Contrary to previously published results,[24] we find that steam cleaning the reaction cell has no detectable effect upon the total number of particles produced. This leads us to the conclusion that the cell walls (silica) do not initiate the nucleation process to any measurable degree.

It has also been suggested by Turnbull[7] that nucleation occurs in localised supersaturations formed at the time of mixing. The consistency of the particle numbers obtained in the present work argues against this theory because it is unlikely that the mixing process could be reproduced to the high degree of accuracy required by this localised nucleation process (homogeneous nucleation depends upon a high power of the concentration). It does, however, seem feasible that growth occurs at different rates in localised supersaturation areas. Thus, the method of mixing would produce distinct differences in the polydispersity and hence the rate of precipitation (which is dependent upon the total surface of the precipitate) but not in particle numbers. Comparing the two hypotheses we see that in the first case localised supersaturations would cause more particles with a large surface area and a fast overall precipitation rate to occur. The second possibility causes the opposite result, namely high polydispersity, reduced surface area and reduced growth rate. Turnbull[7] has shown that the precipitation rate of barium sulphate is much faster if equivalent concentrations and equal volumes of barium and sulphate ions are mixed than if a small volume of the more concentrated ion is added to produce the same concentration of barium sulphate. Because the latter method would appear to cause less homogeneous mixing these observations are in accord with the localised growth mechanism. Consequently, it might be inferred that the precipitation rate is indicative of both the effectiveness of the mixing process and the polydispersity of the growing suspension.

CONCLUSION

Nephelometry has been used to estimate the size and number of barium sulphate particles in *statu nascendi.* The particles are irregular in shape but discrete units as revealed by electron microscopy. Within the concentration range studied ($[Ba^{2+}]\ [SO_4^{2-}] < 3{\cdot}6 \times 10^{-7}$ moles^2/l.^{2}), there was no consistent change of particle numbers either with the ion in excess or with the total concentration. These observations are in accord with the theory of heterogeneous nucleation which predicts that the total number of precipitate particles is limited to the number of impurity particles present in solution.

Acknowledgements—We wish to thank Mr. Dale Cheever of this department for aid with the electron microscopy, Dr. K. Takiyama for useful suggestions, and the Case Research Fund for a grant to one of us (T. H.).

Zusammenfassung—Die Bildung und das Wachstum von Bariumsulfatniederschlägen wurde nephelometrische studiert. Unter Verwendung der Mie'schen Theorie war es möglich sowohl Grösse als auch Anzahl der gebildeten Teilchen zu schätzen; die Ergebinsse stimmten sehr gut mit denen, aufgrund von elektronenmikroskopischen Beobachtungen erhaltenen, überein. Im untersuchten Konzentrationsbereich sind die niedergeschlagenen Teilchen keilförmig und haben in der Richtung der Hauptachse eine Länge von 0.3–0.5 μ. Ein konsistenter Wechsel in der, durch verschiedene Reagenzkonzentrationen bestimmte, Teilchenzahl per Volumeinheit konnte nicht beobachtet werden. Die Kernbildung ist daher vermutlich heterogen.

Résumé—La formation et le grossissement des précipités de sulfate de baryum ont été étudiés par néphélométrie. En utilisant la théorie de Mie il a été possible d'évaluer la taille et le nombre des particules formées; les résultats obtenus sont en accord avec ceux donnés par la microscopie électronique. Dans le domaine de concentration étudiée les particules de précipité sont cunéiformes, la longueur de l'axe principal étant comprise entre 0,3 et 0,5 μ. Le nombre de particules par unité de volume produits par les concentrations divers de réactifs, ne varie pas de facon significative. La formation des germes est par suite probablement hétérogéne.

REFERENCES

[1] A. E. Nielsen, *Acta Chem. Scand.*, 1961, **15**, 441.
[2] E. Suito and K. Takiyama, *Bull. Chem. Soc. Japan*, 1954, **27**, 121.
[3] J. B. Bateman, E. J. Weneck and D. C. Eshler, *J. Colloid Sci.*, 1959, **14**, 308.
[4] R. J. Gledhill, *J. Phys. Chem.*, 1962, **66**, 458.
[5] S. H. Maron and P. E. Pierce, private communication.
[6] M. D. Barnes and V. K. LaMer, *J. Colloid Sci.*, 1946, **1**, 79; V. K. LaMer, *J. Phys. Colloid Chem.*, 1948, **52**, 65; E. M. Zaiser and V. K. LaMer, *J. Colloid Sci.*, 1948, **3**, 571.
[7] D. Turnbull, *Acta Metallurgica*, 1953, **1**, 684; R. A. Johnson and J. D. O'Rourke, *J. Amer. Chem. Soc.*, 1954, **76**, 2124.
[8] A. E. Nielsen, *Acta Chem. Scand.*, 1958, **12**, 951.
[9] R. A. Johnson and J. D. O'Rourke, *Analyt. Chem.*, 1953, **27**, 1699.
[10] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry.* Longmans, London, 1923, Vol. III, p. 795.
[11] *International Critical Tables.* McGraw-Hill Company, Inc., New York, 1933, Vol. III, p. 13.
[12] R. B. Penndorf, *New Tables of Scattering Functions for Spherical Particles.* A.S.T.I.A., Arlington, Virginia (1956), Part 6.

[13] W. Heller, *J. Chem. Phys.*, 1956, **26,** 920.
[14] P. C. Lewis and G. F. Lothian, *Brit. J. Appl. Phys.*, 1954, **5,** 571.
[15] W. Heller and R. M. Tabibian, *J. Colloid Sci.*, 1957, **12,** 25.
[16] Review by M. Bender, *J. Chem. Educ.*, 1952, **29,** 15.
[17] H. C. van der Hulst, *Light Scattering by Small Particles.* Chapman and Hall Ltd., London, 1957, p. 177 and 312.
[18] *Idem, ibid.*, section 20, p. 414–437.
[19] G. B. Alexander and R. K. Iler, *J. Phys. Chem.*, 1953, **57,** 932.
[20] M. Kerker, G. L. Jones, J. B. Reed, C. N. P. Yong and M. D. Schoenberg, *J. Phys. Chem.*, 1954, **58,** 1147; C. K. Sloan, *ibid.*, 1955, **59,** 334.
[21] T. Teorell, *Kolloid Z.*, 1930, **53,** 322; 1931, **52,** 58, 150; B. Težak, *ibid.*, 1936, **74,** 16; *Z. physikchem. A.*, 1935, **175,** 219.
[22] E. J. Meehan and W. H. Beattie, *J. Phys. Chem.*, 1960, **64,** 1006; 1961, **65,** 1522.
[23] P. Debye, *J. Phys. Colloid Chem.*, 1947, **51,** 18.
[24] A. E. Nielsen, *Acta Chem. Scand.*, 1957, **11,** 1512.
[25] G. D. Parfitt and M. J. Jaycock, *Nature*, 1962, **194,** 77.
[26] Louis Gordon, D. H. Klein and T. H. Walnut, *Talanta*, 1959, **3,** 187.
[27] A. S. Buchanen and E. Heymann, *J. Colloid Sci.*, 1949, **4,** 137.
[28] R. B. Fisher, *Analyt. Chim. Acta*, 1960, **22,** 501.
[29] A. van Hook, *Crystallization—Theory and Practice.* Reinhold Publishing Corporation, New York, 1961, p. 206–208.

Talanta, 1963, Vol. 10, pp. 611 to 619. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF THORIUM IN GRANITE BY GAMMA SPECTROMETRY AND BY RADIOTRACER

S. A. REYNOLDS

Analytical Chemistry Division, Oak Ridge National Laboratory*
Oak Ridge, Tennessee, U.S.A.

(*Received* 12 *September* 1962. *Accepted* 22 *January* 1963)

Summary—Thorium in granite samples has been determined by gamma-spectrometric measurement of the 2·6-MeV gamma radiation from thallium-208, a daughter. Concentrations ranged from a few to several hundred ppm, and both untreated and leached samples were analysed. Thorium-234 tracer was successfully applied in finding the sources of error in a difficult chemical analysis and, upon suitable treatment, obtaining the correct analytical values. This study affords an example of the use of a tracer in analysis, and is somewhat unusual in that both negative and positive deviations were discovered. Agreement between results by the two independent methods has been quite good.

THE study of low-grade sources of thorium for possible future utilisation is in progress at Oak Ridge National Laboratory. Chemical methods have been used for the determination of thorium in granite; however, it was desired to verify the results obtained. An obvious method was to measure the natural radioactivity of the thorium series.

GAMMA SPECTROMETRY

Thorium was measured by counting the 2·6-MeV gamma radiation of its daughter, thallium-208.[1,2,3] In radioactive equilibrium, as in rocks, a 2·6-MeV photon is emitted following about 35% of the disintegrations of thorium-232.[4] No significant interference was anticipated because of the absence of gamma radiation of such high energy in other natural materials, *e.g.*, uranium[5,6] and potassium.[4]

Experimental

The apparatus consisted of (a) a 3 × 3-in. cylindrical "thallium activated" sodium iodide crystal, NaI(Tl), clad in 5-mil aluminium, coupled to a 256-channel analyser, and (b) a 4 × 4-in. NaI(Tl) crystal with a 20-channel analyser. Most samples weighed 65 g and were contained in plastic Petri dishes of 2·75-in. diameter and 0·75-in. height, although larger and smaller samples were also counted. The dishes were placed directly upon the flat upper surface of the NaI(Tl) crystal. Thorium standards No. 83 (102 ± 2 ppm[7]) and No. 80 (1010 ± 30 ppm[7]) were received from the USAEC New Brunswick Laboratory. Weighed portions of these standards were placed in dishes, and the 2·6-MeV activities were compared in equal weights of standard and sample. Overnight counts (15-16 hr) were taken. The spectrum of the 102-ppm standard is shown in Fig. 1. It was decided to sum channels at the 2·6-MeV peak spanning 0·16 MeV.

Results and Discussion

Both NBL standards gave essentially equal calibrations for 65-g samples: (a) on the 3 × 3-in. crystal, 6·9 counts per hour per ppm of thorium (cph/ppm), and (b) 10·7 cph/ppm on the 4 × 4-in. crystal. Better sensitivity was actually obtained on the 3 × 3-in. crystal, because backgrounds in the peak channels were (a) 103 cph, and (b) 290 cph. On the basis of these values, the limit of detection is *ca.* 1 ppm, and the

---

* Operated for the U.S. Atomic Energy Commission by Union Carbide Corporation.

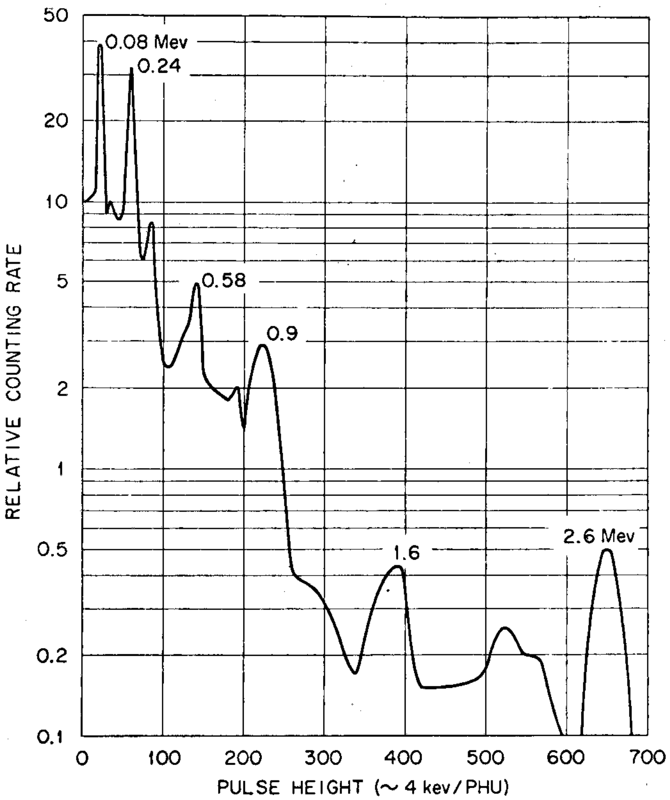


FIG. 1.—Gamma spectrum of thorium ore

limit of measurement *ca.* 2 ppm. The precision (standard deviation) is about 0·6 ppm or 2%, whichever is greater.

Results on samples typical of the first ones studied, most of which were from Colorado, are shown in Table I. The average difference between chemical and "radiometric" analysis was 3·3%.

TABLE I.—THORIUM ANALYSES

Sample	Thorium, *ppm* Gamma	Chemical	Other[a]
G-1[b]	51	51	51–52
1	115	112	95
2	77	76	70
3	80	76	77
4	9	9–10	
5	20	20	
6	30	30	
7	12	10	
8	93	91	
9	12	12	12

[a] U.S. Geol. Survey, Rice Institute, or other.
[b] "Standard rock," U.S. Geol. Survey.

Leached samples

In the work described above, none of the samples had been chemically treated prior to gamma measurement; they were, therefore, in radioactive equilibrium. The process for removal of thorium from granite includes leaching with sulphuric acid, and it was desired to analyse some of the leached solid by gamma spectrometry. Spectra of typical original granite, leached material, and leach solution are shown in Fig. 2. It will be noted that little radium or potassium was removed in leaching. By examining the detailed genetic relationships in the thorium series, it is apparent that one can calculate the 2·6-MeV gamma activity, *i.e.*, the "apparent thorium", at any

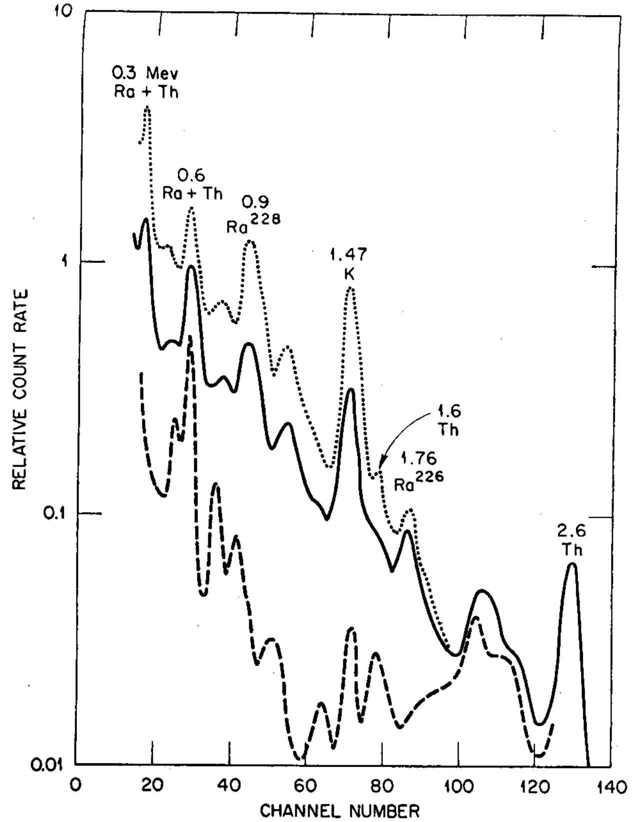


FIG. 2.—Gamma spectra of granite samples (normalised at 2·6 MeV):
——rock, equilibrium,
– – –leach solution, thorium-rich,
· · · ·leached rock, radium-rich.

TABLE II.—ANALYSES OF LEACH SAMPLES

	Thorium, *ppm*	
Sample	Gamma	Chemical
Solid	10, 9	10
Filtrate	43, 47	46
Wash	~5	5

time after a single leach, assuming no removal of radium or lead daughters. Such calculations were made by computer, and curves are shown in Fig. 3, for values of the fraction leached, L, varying from 0·1 to 0·9 (*i.e.*, 10 to 90 %). To use the curves, it is necessary to know the time elapsed since the leaching, and the approximate value of L (from experience, or by successive approximations from the gamma-activity data). A set of samples was submitted, consisting of leached solid, filtered leach solution, and a wash of the solid. Data are given in Table II, showing the results of gamma measurements at two different times after leaching, compared with chemical analysis.

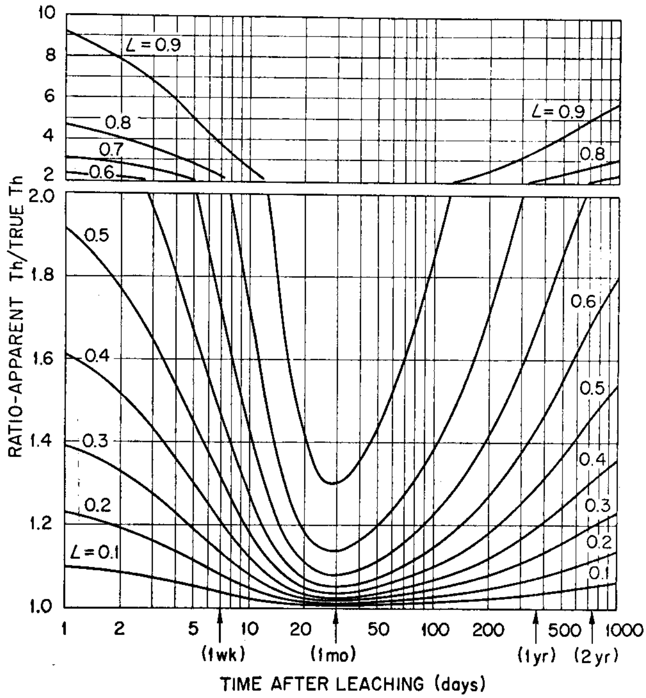


FIG. 3.—Apparent thorium after a single leach (no radium or lead removal).

RADIOTRACER STUDIES

The chemical method (Table III) had yielded good results on many granite samples, and was in routine use. However, when certain samples began arriving, particularly Conway (New Hampshire) granites, chemical results were found to be erratic and low. The author, in collaboration with those using the method, therefore studied it by means of thorium tracer.

The tracer

Thorium-234 (UX$_1$) is a beta-emitting nuclide of 24-day half-life, with gamma radiations of 0·092 MeV (*ca.* 10 %) and 0·063 MeV (*ca.* 7 %). As used, it is in radioactive equilibrium with its daughter, protactinium-234 (UX$_2$), a 1·2-min beta emitter, with gammas of 0·76 (0·5 %) and 1·00 MeV (0·7 %). This radioisotope is, therefore, a practical tracer for thorium, employing a well-type scintillation counter for measurement. Thorium-234 was obtained from the ORNL Isotopes Division. The preparation was of very good quality, containing only about 3 μg of thorium per millicurie of thorium-234, much of which was ionium (thorium-230). It was purified by carrying on lanthanum fluoride and extracting with thenoyltrifluoroacetone (TTA)-xylene.[8] Gamma-spectrometric examination of the fractions in the purification process indicated no foreign radioactivity, and the extraction behaviour showed that the thorium was in a normal chemical state (*e.g.*, no "radiocolloid").

TABLE III. BRIEF OUTLINE OF CHEMICAL METHOD

1. Dissolution (acid treatment and fusion).
2. Addition of iron carrier, precipitation with potassium hydroxide and filtration.
3. Dissolution in nitric acid.
4. Addition of aluminium nitrate and extraction with tri-octylphosphine oxide–cyclohexane. Washing.
5. Stripping with dilute sulphuric acid.
6. Evaporation and dissolution in dilute hydrochloric acid.
7. Addition of "thoron" colour-forming reagent and spectrophotometric measurement at 545 mμ.

TABLE IV. WASTE LOSSES AND YIELDS

Step	Percentage
Granites	
Hydroxide filtrate (2)[a]	<1
Extraction (4)	2 to 29
Stripping (5)	1 to 44
Product (7)	41 to 83
Leaches	
Extraction (4)	≤ 1
Stripping (5)	15 to 17
Product (7)	82 to 86

[a] Step no., Table III

TABLE V. THORIUM DETERMINATIONS

Method	Thorium, *ppm*[a]		
	Sample 10	Sample 11	Sample 12
Chemical, uncorrected	46–74	17–24	15–23
Radiometric correction	94	32	—
Isotope dilution	93	32	—
Gamma spectrometry	76 ± 2	25 ± 1	30 ± 1

[a] Each value represents several determinations.

Evaluation of method

A measured portion of tracer solution was added to each granite sample before dissolution, or to solutions resulting from leaching granite batches. In each of a number of analyses employing tracer, waste losses and yields were determined. It will be noted in Table IV that high and erratic losses were experienced in the extraction and stripping (steps 4 and 5, Table III) in the analysis of granites, and in the stripping in the analysis of leach solutions.

It was expected that if the amount of thorium indicated by spectrophotometric measurement was corrected for tracer yield, the proper values would be obtained. The data of Table V indicate that this expectation was not fulfilled. Isotope dilution,[9] with a "standard addition" of the order of 20 ppm of thorium, similarly gave high values. Thus, the possibility of positive interference, previously masked by losses, was indicated. Zirconium was present in the "problem" granites; therefore, an exploratory experiment was performed in which a small amount of zirconium was added. The values, corrected radiometrically, were high, and stripping (but not extraction) was "inhibited."

TABLE VI.—REPURIFICATION PROCEDURE

1. Evaporation with concentrated nitric acid.
2. Dissolution in 2*M* nitric acid.
3. Extraction with TTA-xylene
4. Adjustment of pH to 1·4–1·5.
5. Extraction of thorium with TTA-xylene.
6. Stripping with dilute nitric acid.
7. Evaporation with concentrated nitric acid and twice with hydrochloric acid.
8. Measurement of tracer yield.
9. Spectrophotometric measurement of thorium.

TABLE VII.—VALUES BY REPURIFICATION

Method	Thorium, *ppm*		
	Sample 10	Sample 11	Sample 12
Chemical, repurified	75	24	27
	76	27	30
	78	27	31
Gamma spectrometry	76 ± 2	25 ± 1	30 ± 1

TABLE VIII.—QUALITATIVE SPECTROSCOPIC DATA

Fraction	Elements present
1st TTA ext. (3)[a]	Cr, Cu, Fe, Zr
Aq. from Th ext. (5)	Cu, Fe, Mn
Stripped TTA (6)	Cr, Cu, Fe

[a] Step no., Table VI.

Removal of interferences

It was decided to repurify the thorium separated by the chemical procedure, rather than undertake a tedious study of the effects of individual elements. The repurification outlined in Table VI was, therefore, performed upon the coloured solution used for spectrophotometric and tracer-yield measurements. Step 3 was designed to remove zirconium and other elements extractable at low pH, while step 5 isolated thorium from elements extractable at higher pH. Results of repurification are given in Table VII. Significant findings by spectroscopic analyses of repurification fractions are shown in Table VIII.

Test of modified method

The chemical method under study was modified,[10] in that sodium peroxide fusion was used in step 1, and larger volumes were used in extraction and stripping. In Table IX, results of analysis of three samples by old and new methods are shown. Agreement of the values, corrected for tracer yield, is most pleasing. Precision and accuracy

TABLE IX.—COMPARISON OF METHODS

Sample	Method	Total loss, %	Corrected ppm of Th
13	Old	20	32
	New	1·1	32
14	Old	14	27
	New	0·6	28
15	Old	20	23
	New	0·5	24

TABLE X.—EXTRACTION OF THORIUM INTO TTA-XYLENE

$NaNO_3 + HNO_3$ conc., *M*	Calculated thorium conc., *M*	Contact time, *min*	Thorium extracted, %[a]	Material balance, %
0·2	2·4 × 10^{-10}	10	89[b]	96[b]
0·2	2·9 × 10^{-10}	10	50[b]	76[b]
0·2	3·9 × 10^{-10}	10	72[b]	92[b]
0·2	1·1 × 10^{-9}	10	76[b]	93[b]
0·4	7·7 × 10^{-10}	10	65[b]	70[b]
0·4	5·9 × 10^{-6}	15	99·5	100
0·4	5·9 × 10^{-6}	15	99·6	98
0·4	5·9 × 10^{-6}	15	99·5	105(?)
0·54	1·7 × 10^{-8}	10[c]	98·5	—
0·54	1·7 × 10^{-8}	20[c]	99·6	99
0·54	1·7 × 10^{-8}	6	95·8	—
0·54	1·7 × 10^{-8}	10	99·3	100
0·54	1·7 × 10^{-7}	1[c]	99·5	—
0·54	1·7 × 10^{-7}	2[c]	99·9	100
0·54	2·6 × 10^{-7}	2	99·5	—
0·54	2·6 × 10^{-7}	4	99·5	100
0·54	2·6 × 10^{-6}	1	97·1	—
0·54	2·6 × 10^{-6}	2	99·7	101
0·54	2·6 × 10^{-5}	1	99·0	—
0·54	2·6 × 10^{-5}	2	99·8	100
2·0	9·7 × 10^{-10}	10	97·3	97
[1*M* $Al(NO_3)_3$]	1·7 × 10^{-6}	10	99·9	—

[a] Based on aqueous phase, except those in note *b*.

[b] Possible reagent impurity or hydrolytic behaviour; % extracted determined by direct measurement.

[c] 0·25*M* TTA; all others 0·5*M*.

depend primarily on the method used for measurement of the recovered thorium. In spectrophotometric analysis, as in the present study, values of 3–5% should be anticipated.

Study of thorium extraction

In connection with the work described above, an exploratory study was made of the extraction of thorium into thenoyltrifluoroacetone (TTA)-xylene. Because Moore[8] and others recommended extraction for 10–15 min, it was thought that the extraction might be slow, as in the case of zirconium[11] and plutonium^{IV}.[12] Aqueous nitrate solutions at pH 1·4–1·5 containing thorium-234 tracer and added carrier, up to 6 μg/ml, were contacted, by moderate hand shaking, with equal volumes of 0·5*M* (or

0·25M) TTA-xylene solution. Data are shown in Table X. Little effect of transfer rate was shown, *i.e.*, the half-time for transfer was short compared to the contact times used. Actually, the rate of thorium extraction would be expected to be much higher than that of zirconium and plutonium because of the higher pH used. It appears that the thorium concentration and the ionic strength of the aqueous phase affect the degree of extraction. However, the effects shown may be caused by impurities; the chemicals used were of ordinary reagent quality.

CONCLUSIONS

Such information as that above may be useful in determining low concentrations of thorium in natural substances, as in geochemical and raw-materials problems. A simplified version of the chemical method studied, or another suitable procedure[13] for thorium, could be generally used for isotope-dilution or radiometric-yield[9] analysis for thorium, when quantitative recovery is not feasible. The data on thorium extraction with TTA indicate that the concentration of thorium should be at least $10^{-9}M$, and that the ionic strength of the aqueous solution should not be too low.

Acknowledgements—J. M. Peele and his colleagues carried out the separations and spectrophotometer readings necessary in the chemical method studied. J. C. White, W. J. Ross, H. Kubota, and R. F. Apple gave valuable advice. All are members of the ORNL Analytical Chemistry Division. Personnel of the ORNL Chemical Technology Division, especially F. J. Hurst, encouraged the work, and supported it in part. The USAEC Division of Isotopes Development furnished part of the support for the research, in furtherance of its programme for applications of radioisotopes. Computer evaluation of the function plotted in Fig. 3 was done under the supervision of the late Mrs. Nancy Dismuke, ORNL Mathematics Panel.

Zusammenfassung—Thorium wurde in Grantiten bestimmt durch Gammaspektrometrie der 2.6 Mev Gammastrahlung des Tochterelementes Tl-208. Konzentrationen von wenigen zu Hunderten ppm, behandelte und unbehandelte Proben wurden analysiert. Th-234 wurde als "tracer" zum Auffinden von Fehlerquellen in einer komplizierten Analyse verwendet. Die Studie ist ein Beispiel für den erfol greichen Einsatz von Traceranalyse und ist einigermassen ungewöhnlich insofern sowohl positive als auch negative Abweichungen gefunden wurden. Ubereinstimmung zwischen zwei unabhängigen Metohden war zufriedenstellend.

Résumé—L'auteur a dosé le thorium dans des échantillons de granit par mesure par spectrométrie gamma de la radiation gamma de Tl 208 de 2,6 Mev. Des concentrations de quelques parties par million à plusieurs centaines, et des échantillons non traités et traités sont analysés. Le traceur, thorium 234, a été appliqué avec succès pour trouver les sources d'erreur d'une analyse chimique difficile et après un traitement convenable, pour obtenir les valeurs analytiques correctes. Cette étude donne un exemple de l'utilisation de traceur en analyse, et est quelque peu inhabituelle, car des écarts négatifs et positifs sont découverts. Les deux méthodes indépendantes donnent un accord tout à fait bon entre les résultats.

REFERENCES

[1] P. M. Hurley, *Geol. Soc. Amer. Bull.*, 1956, **67**, 395, 405.
[2] P. M. Hurley and H. W. Fairbairn, *Trans. Amer. Geophys. Union*, 1957, **38**, 939.
[3] J. L. Mero, *Geophysics*, 1960, **25**, 1054.
[4] D. Strominger, J. M. Hollander and G. T. Seaborg, *Rev. Mod. Phys.*, 1958, **30**, 585.
[5] R. L. Heath, *Scintillation Spectrometry Gamma Ray Spectrum Catalog*, AEC Report IDO-16408, 1957.

[6] C. E. Crouthamel, *Applied Gamma-Ray Spectrometry.* Pergamon Press Ltd., Oxford, 1960.

[7] C. J. Rodden, NBL, unpublished data, 1960, 1962.

[8] F. L. Moore, *Analyt. Chem.*, 1958, **30**, 1020.

[9] C. Rosenblum, *Nucleonics*, 1956, **14**, No. 5, 58; *Analyt. Chem.*, 1957, **29**, 1740.

[10] H. Kubota, R. F. Apple and J. M. Peele, unpublished data.

[11] F. L. Moore, *Analyt. Chem.*, 1956, **28**, 997.

[12] F. L. Moore and J. E. Hudgens, Jr., *ibid.*, 1957, **29**, 1767.

[13] E. K. Hyde, *The Radiochemistry of Thorium*, U.S. Nat. Res. Coun. Rept. NAS-NS-3004, 1960.

Talanta, 1963, Vol. 10, pp. 621 to 632. Pergamon Press Ltd. Printed in Northern Ireland

OSCILLOPOLAROGRAPHIC DETECTION AND DETERMINATION OF DIHYDRIC PHENOLS

JAN DOLEŽAL, VASIL KOPRDA and JAROSLAV ZÝKA
Department of Analytical Chemistry, Charles University, Prague, Czechoslovakia

(*Received* 5 *November* 1962. *Accepted* 25 *November* 1962)

Summary—A 1*M*-potassium nitrate solution has been proposed as supporting electrolyte for the qualitative detection of dihydric phenols by an oscillopolarographic method. Sufficiently distant incisions on curves of the function dV/dt = f(V) permit their determination by the method of comparative titration with an average error of ±3–4% Monohydric phenol does not interfere in their qualitative detection. Phloroglucinol and pyrogallol interfere in the detection as well as determination. The method of calibration curves permits determination of individual dihydric phenols with an error of ±5%.

WITH progressing industrialisation, the determination of phenols in waste waters becomes an ever more important problem, important especially because of their high toxicity.

The colorimetric, chromatographic and titrimetric methods mainly used for the detection and determination of phenols in waste waters require too much time, and in most cases they do not permit the determination of these substances in mixtures.

To solve this problem, an attempt has been made to apply the oscillographic method, using polarographic investigations in part as the starting point. The behaviour of catechol, hydroquinone and resorcinol has been investigated at the dropping mercury electrode[1–5] as well as at solid electrodes.[6–10] The only substances of this chemical character previously investigated oscillopolarographically have been thiophenols and phenylphenols.[11]

Preliminary investigation of the oscillopolarographic behaviour of phenols by Tichý[12] has shown that di- and trihydric phenols form characteristic incisions on curves of the function dV/dt = f(V) in various media, which might be applicable not only to the detection, but in some cases also to the determination of these substances.

In this paper a description is presented of the oscillopolarographic behaviour and possibilities of the rapid and simple detection and determination of di- and eventually also trihydric phenols when present individually as well as in mixtures.

EXPERIMENTAL

Reagents

Supporting electrolyte solutions were prepared from reagent-grade chemicals manufactured by Lachema. 0·01*M* solutions of hydroquinone, catechol and resorcinol were prepared by dissolving 0·1101 g of the resublimed substance (Lachema or Merck, reagent grade) in 100 ml of twice-distilled water; 0·01*M* pyrogallol and phloroglucinol solutions were prepared from 0·1261 g of the substance (Lachema, reagent grade) in 100 ml of twice distilled water. A 0·01*M* phenol solution was obtained by dissolving 0·0541 g of the resublimed substance (Spolek pro chemickou a hutní) in an equal volume of water. These solutions were prepared fresh every 48 hr.

Apparatus

Qualitative and quantitative determinations were carried out using a Křižík Type P 576 Polaroscope, which has built-in equipment for quantitative analysis. The dependence dV/dt = f(V) was investigated. A mercury dropping electrode was used as the indication electrode and a saturated calomel electrode (Kalousek's vessel) or graphite was used as the reference electrode. In comparative titrations[13] a mercury drop was used as reference electrode. Photographic recording was made with an Exakta Varex camera with spacing rings, from a distance of 30 cm, using Agfa Fluororapid 27 DIN film. Solutions were agitated by bubbling with air. Nitrogen was unsuitable for use, because the incisions of dihydric phenols disappeared after a short time.

Qualitative oscillopolarographic behaviour of phenols

For qualitative detection, the oscillopolarographic behaviour of phenols was investigated in various supporting electrolytes. Especially the oscillopolarographic behaviour of hydroquinone, catechol and resorcinol was investigated, the other phenols only being investigated in such media as were found suitable for the dihydric phenols.

TABLE I.—DETECTION OF PHENOLS

Supporting electrolyte	Compound	Most sensitive incisions*		Further incisions			
		Q	pD	Q	Q	Q	pD
1*M* KCl	Hydroquinone	A_1 0·08	5·4	A_1 0·10			
	Catechol	C_1 0·14	5·7	C_2 0·43	A_1 0·14		
	Resorcinol	C_1 0·58	5·1	C_3 0·14			
1*M* KF	Hydroquinone	A_1 0·11	6·1	C_1 0·11	C_2 0·30		
	Catechol	C_1 0·18	6·1	A_1 0·17	A_4 0·08		
	Resorcinol	C_1 0·60	6·2	C_2 0·30			
1*M* CH_3COONa	Hydroquinone	A_1 0·11	5·9	C_1 0·11	A_4 0·08		
	Catechol	C_1 0·17	6·1	A_1 0·14			
	Resorcinol	C_1 0·60	6·7	C_2 0·30			
1*M* Na_2SO_4	Hydroquinone	A_1 0·09	5·9	C_2 0·32			
	Catechol	C_1 0·17	5·7	A_1 0·16			
	Resorcinol	C_1 0·60	5·2	C_2 0·30			
Saturated solution $KClO_3$	Hydroquinone	A_1 0·16	5·7	C_1 0·16			
	Catechol	C_3 0·25	6·1	A_3 0·24			
	Resorcinol	C_1 0·62	5·5	C_2 0·30			
1*M* KNO_3	Hydroquinone	A_4 0·11	6·0	C_4 0·11	A_1 0·14	C_5 0·20	
	Catechol	C_1 0·19	6·1	C_2 0·48	A_1 0·18		
	Resorcinol	C_2 0·28	6·4	C_1 0·60	C_3 0·31		C_1 6·1
1*M* K_3PO_4	Hydroquinone	C_2 0·27	5·5	C_1 0·10	A_1 0·10		
	Catechol	C_3 0·24	5·5	C_1 0·12	C_2 0·42	A_1 0·12	
	Resorcinol	C_2 0·23	6·2	C_1 0·56	A_2 0·24		C_1 5·7
2*M* NaOH	Hydroquinone	C_3 0·50	5·8	C_1 0·13	C_2 0·27	C_5 0·60	
	Catechol	C_2 0·50	5·6	C_3 0·23	C_1 0·12	A_2 0·45	C_3 5·4
	Resorcinol	C_1 0·50	5·7	C_2 0·16	A_2 0·16		C_2 5·5

* C = cathodic incision,
A = anodic incision.

It was found that in media of bromides, iodides, cyanides and thiocyanates of the alkali metals and in media of strong acids, phenols do not show depolarising activity. In 1*M* potassium chloride, chlorate, fluoride, nitrate and phosphate solutions and 1*M* sodium acetate, sulphate and hydroxide solutions they form characteristic and sensitive incisions. Table I reviews the results obtained; the sensitivity of the qualitative detection is given in pD values, and the position of the incisions by the Q quotient.[18] pD values have been calculated mainly for the anodic hydroquinone incision, for the cathodic catechol incision and the more negative cathodic resorcinol incision. Experiments were carried out in the concentration range 0 to 0·11 mg of dihydric phenol/ml.

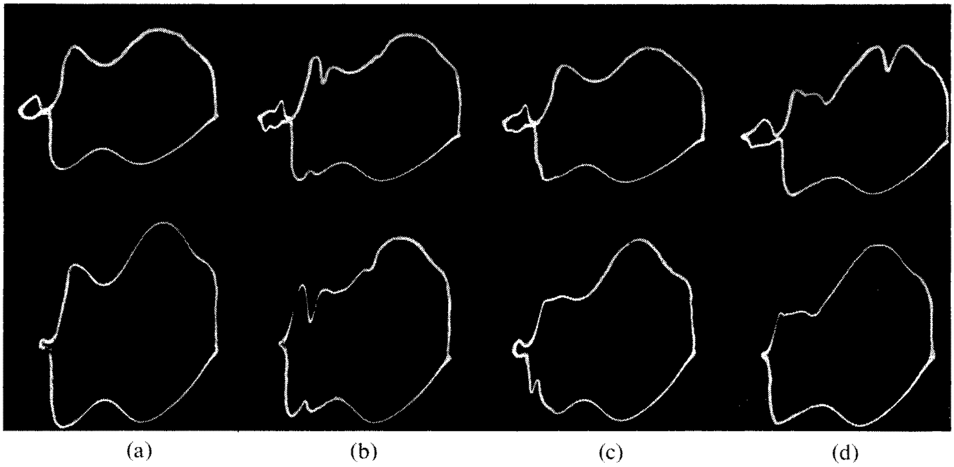


FIG. 1—Oscillopolarographic behaviour of dihydric phenols in a medium of $1M$ potassium nitrate (series I: AC = 1·1 mA, DC = 1·0 mA; series II: AC = 0·4 mA, DC = 2·0 mA)
(a) $1M$ potassium nitrate,
(b) catechol, 1·37 mg/ml,
(c) hydroquinone, 1·37 mg/ml,
(d) resorcinol, 1·37 mg/ml.

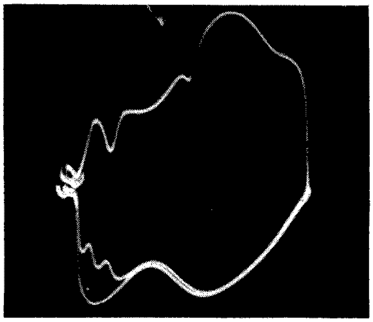


FIG. 2—Detection of catechol, hydroquinone and resorcinol in mixtures (electrolyte: $1M$ KNO_3; hydroquinone 1·37 mg/ml; catechol: 1·37 mg/ml; resorcinol: 1·37 mg/ml; AC = 1·1 mA, DC = 1·0 mA).

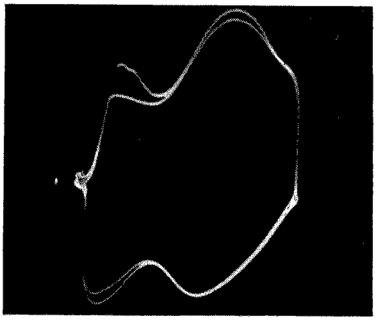


FIG. 3—Oscillopolarographic behaviour of phenol (electrolyte: $1M$ KNO_3; phenol: 10 mg/ml; AC = 0·4 mA, DC = 2·0 mA).

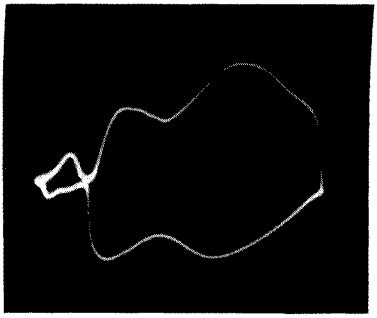


FIG. 4—Oscillopolarographic detection of pyrogallol (electrolyte: $1M$ KNO_3; pyrogallol: 1 mg/ml; AC = 1·1 mA, DC = 1·0 mA).

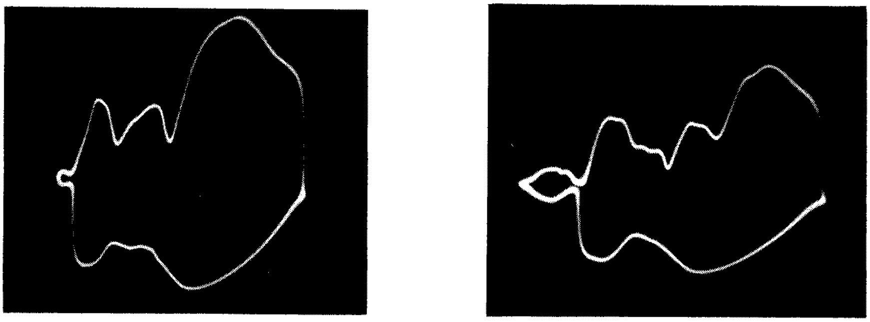


FIG. 5—Oscillopolarographic behaviour of phloroglucinol (electrolyte: $1M$ KNO_3; phloroglucinol: 1 mg/ml):
(a) AC = 1·1 mA, DC = 1·0 mA,
(b) AC = 0·4 mA, DC = 2·0 mA.

From the results obtained it follows that for the qualitative detection of dihydric phenols the most suitable electrolyte is potassium nitrate; in this medium the incisions of the phenols are sufficiently sensitive and their potentials are sufficiently different. Furthermore, the $dV/dt = f(V)$ curve of this electrolyte does not undergo any large changes in a broad range of values of the alternating and direct component of the current.

As follows from Table I, hydroquinone gives mainly an anodic incision in most media. The corresponding reversible incision on the cathodic side is observed only at higher hydroquinone concentrations ($>10^{-5}$ g/ml).

It has been found by observing the dependence on pH (Britton-Robinson's buffer) that the hydroquinone incision appears only at pH values $>3{\cdot}9$. With increasing pH (4–8), the sensitivity of the cathodic incision increases and that of the anodic incision decreases. At pH >10 the incisions do not appear.

The highest sensitivity of the detection may be obtained in media of potassium fluoride and nitrate.

Differing from hydroquinone, catechol forms mainly a cathodic incision, with a smaller anodic one. Both incisions, however, disappear already in weak acid media (pH <6). In media of potassium chloride or nitrate and in alkaline solutions another negative incision appears (C_2), which is most distinct in alkaline media (pD 5·6). The most sensitive detection, however, is in media of potassium fluoride or nitrate and sodium acetate. Using chlorate as electrolyte, a further cathodic and anodic incision appears on the curves (C_3, A_3); using hydroxide only the cathodic incision appears (C_3; pD 5·4).

Resorcinol mainly forms two very distinct incisions, of which the more negatively positioned one is the more distinct and more sensitive. Only when using nitrate and phosphate as electrolyte is the more positive incision ($Q = 0{\cdot}28$, $0{\cdot}23$) more sensitive. Detection of resorcinol is most sensitive in media of $1M$ sodium acetate or potassium nitrate.

Differing from hydroquinone and catechol, resorcinol does not form under the same current conditions stable incisions (see Fig. 1). The incisions appear at the beginning of growth of the mercury drop, but with its increasing surface they disappear. Incisions may be investigated during growth of the drop only with a larger current density of the a.c. component (AC) (0·8–3·4 mA) and a lower value of the d.c. component (DC). The oscillopolarographic behaviour of resorcinol has been investigated under the following conditions: AC = 1·1 mA, DC = 1·0 mA.

It may be said that, in general, the sensitivity of detection does not noticeably change with acidity variations in the region of pH 7 for any of the dihydric phenols. For this it may be concluded that the different behaviour of the substances investigated in various media of the same pH value is connected with the character of the supporting electrolyte. Fig. 2 shows the detection of dihydric phenol mixtures in a nitrate medium. Variation of concentration relations of phenols in the mixtures does not influence the position of the incisions.

The most suitable concentration for the detection of dihydric phenols is of the order of magnitude of 1 mg/ml, calculated as total concentration of all components. More concentrated solutions do not give sharp incisions, and overall deformation of the curve occurs, the incisions attaining lobal form. At concentrations of the order of magnitude of 10 mg/ml, detection becomes impossible.

In order to verify the possibility of applying oscillopolarographic analysis to the detection of dihydric phenols in mixtures with other phenols, the behaviour of phenol, pyrogallol and phloroglucinol was further investigated in a medium of potassium nitrate as supporting electrolyte. Phenol does not form an incision in this medium, even at concentrations of 35 mg/ml, but already in slight amounts it causes a decrease of the more positive parts of the anodic as well as the cathodic branch of the curve of the supporting electrolyte (Fig. 3). Phenol in no way interferes in detection of the dihydric phenols.

To investigate the behaviour of trihydric phenols in the medium mentioned, experiments have been carried out showing that pyrogallol, as well as phloroglucinol, forms incisions, when present in the solution analysed in very low concentrations.

Pyrogallol forms a very sensitive incision ($Q = 0{\cdot}07$, pD 6·0) which increases on bubbling air through the solution. At concentrations higher than about 1 mg/ml the incision already practically touches the potential axis, and shortens the width of the oscillopolarographic curve (Fig. 4). At concentrations of the order of magnitude of 1 mg/ml further incisions may be observed on the cathodic part of the curve: $Q = 0{\cdot}17, 0{\cdot}27$ and $0{\cdot}32$; on the anodic part of the curve the corresponding anodic incisions may be observed.

Phloroglucinol forms a very sensitive cathodic incision in a nitrate medium ($Q = 0{\cdot}41$, pD 5·7). At concentrations of the order of magnitude of 1–10 mg/ml further incisions appear, at $Q = 0{\cdot}25$ on the cathodic part and $Q = 0{\cdot}27$ and $0{\cdot}37$ on the anodic part of the curve. The number and size of incisions greatly depends on the current conditions used.

Pyrogallol forms a larger number of incisions at lower values of the alternating current component; with phloroglucinol, the reverse is true. Under current conditions mentioned in the detection of resorcinol (AC = 0·4 mA, DC = 2·0 mA), pyrogallol forms the hints of incisions which, however, greatly influence the catechol incision investigated. Because the more positive part of the curve disappears, the detection of hydroquinone is also impossible. Besides this, traces of incisions Q = 0·27 and 0·32 lie in the potential region where resorcinol forms its most sensitive incision. Phloroglucinol interferes in the determination of resorcinol under current conditions AC = 0·4 mA, DC = 2·0 mA (Fig. 5). Under the conditions AC = 1·1 mA, DC = 1·6 mA, the phloroglucinol incision at Q = 0·23 interferes with the detection of catechol.

Determination of dihydric phenols

From the qualitative experiments carried out, a possibility of quantitative determination of the dihydric phenols followed, using those media which had proved most suitable for qualitative detection,

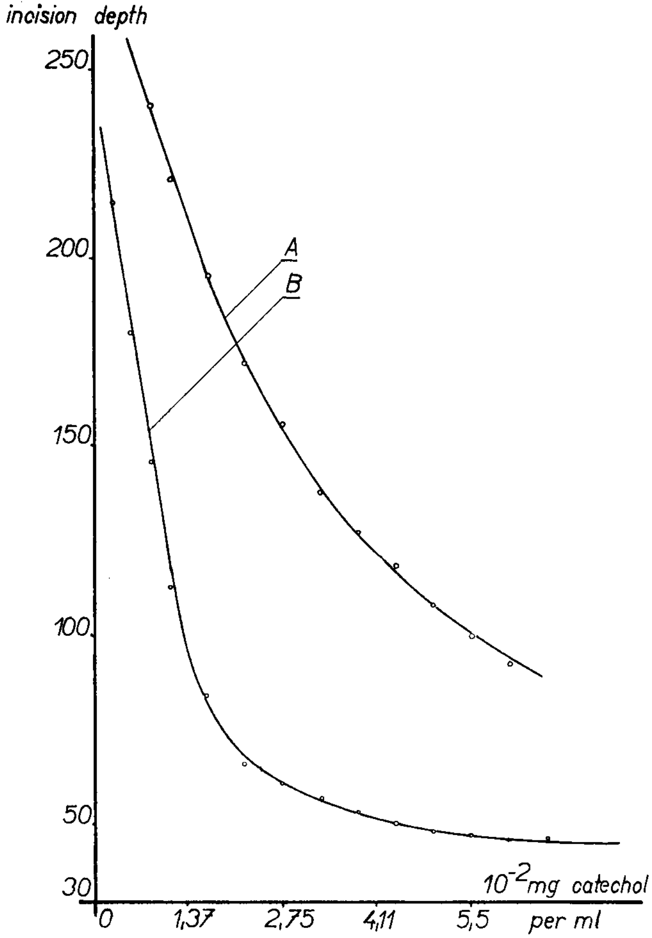


FIG. 6.—Dependence of the depth of incisions on catechol concentration in a medium of 1*M* potassium fluoride:
A—anodic incision, Q = 0·18;
B—cathodic incision, Q = 0·19.

i.e., potassium nitrate and potassium fluoride. For quantitative application the incision of highest sensitivity was always investigated, and especially a method was searched for which would permit determination of phenols in mixtures. For the individual determinations of dihydric phenols the method of the calibration curve proved to be the most suitable.

As follows from Fig. 6 it is possible to apply to the determination of catechol in a medium of

1*M* potassium fluoride the sensitive cathodic incision at Q = 0·18 for the low concentration range, and the reversible anodic incision for higher concentrations. In the case of hydroquinone (Fig. 7) the anodic incision at Q = 0·11 can be used for determinations only up to concentrations of 5 × 10^{-2} mg/ml. At higher concentrations an incision appearing at Q = 0·08 interferes in the determination,

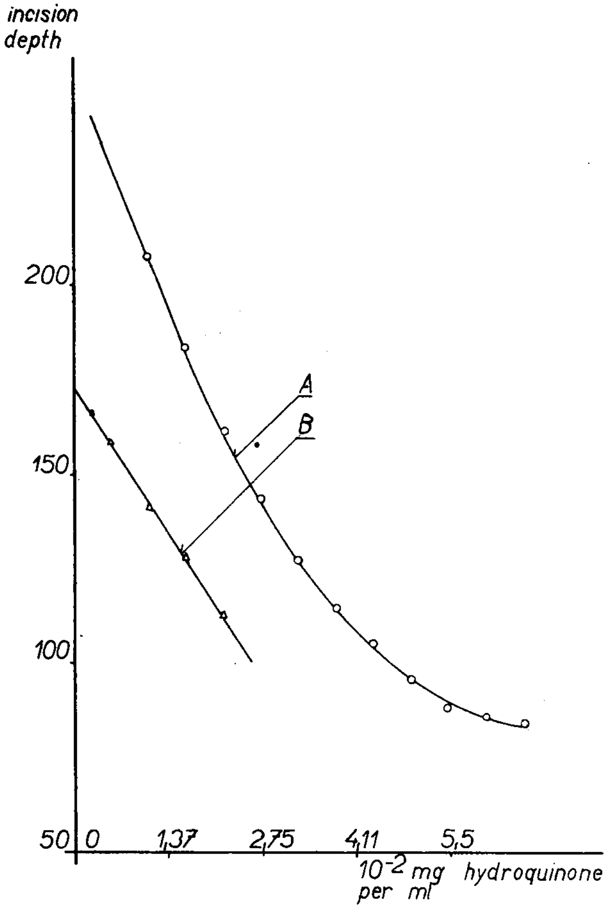


FIG. 7.—Dependence of the depth of incisions on hydroquinone concentration in a medium of 1*M* potassium fluoride:
A—anodic incision, Q = 0·10;
B—cathodic incision, Q = 0·20.

To determine resorcinol both cathodic, highly sensitive incisions may be used up to concentrations of 2 × 10^{-2} mg/ml (Fig. 8).

Catechol has been determined by measuring the depth of the incision at Q = 0·19 in a medium of 1*M* potassium nitrate (Fig. 9), hydroquinone has been determined by measuring the depth of the anodic incision at Q = 0·14 (Fig. 10). In the case of resorcinol we have found that the use of the more negative incision is more suitable for determinations (Fig. 11). The course of the calibration curve for the more sensitive resorcinol incision (Q = 0·31) is a premonition of the formation of a new incision at concentrations of about 1·3 × 10^{-2} mg/ml appearing close to the incision investigated. The graphic dependences mentioned have been measured under the following conditions of current:

in 1*M* KF: AC = 0·2 mA, DC = 0·8 mA

in 1*M* KNO_3: AC = 0·2 mA, DC = 1·5 mA.

The possibility of determining dihydric phenols has been further studied in mixtures by the method

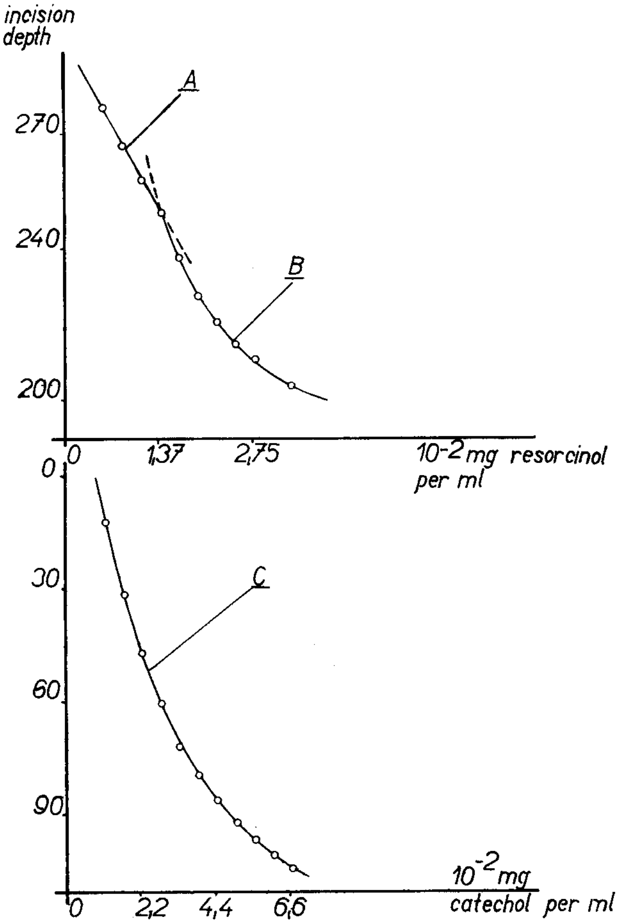


FIG. 8.—Dependence of the depth of incisions on resorcinol and catechol concentration in a medium of 1*M* potassium fluoride: A—cathodic incision, Q = 0·31; B—cathodic incision, Q = 0·28; C—cathodic incision, Q = 0·19.

TABLE II.—CONCENTRATION LIMITS OF THE DETERMINATION OF PHENOLS

Supporting electrolyte	Compound	Incision*	Concentration, $\times 10^{-2}$ *mg/ml*
1*M* KNO_3	Catechol	C Q = 0·19	2·75
		A Q = 0·18	6·05
	Hydroquinone	A Q = 0·11	5·25
		C Q = 0·20	2·2
	Resorcinol	C Q = 0·30	3·1
1*M* KF	Catechol	C Q = 0·18	3·75
		A Q = 0·08	9·2
	Hydroquinone	A Q = 0·11	4·95
	Resorcinol	C Q = 0·30	3·5
		C Q = 0·60	3·25
1*M* CH_3COONa	Catechol	C Q = 0·18	3·25
		A Q = 0·14	3·2
	Hydroquinone	A Q = 0·11	3·25
		C Q = 0·11	7·6
	Resorcinol	C Q = 0·60	2·2

* C = cathodic incision,
A = anodic incision.

of the calibration curve in nitrate and fluoride media. The corresponding dependences have been studied by varying the concentration of one component in the presence of a different amount of the second component. From the dependences previously mentioned it followed that the depth of the incision is strongly influenced by the second component of the mixture, and that the method of the calibration curve cannot be applied to the evaluation of these analyses. For the same reasons the method of standard additions could not be used (in the determination of catechol in concentrations of 1×10^{-2} mg/ml in the presence of hydroquinone of maximum concentration $1{\cdot}3 \times 10^{-2}$ mg/ml the mean error was about ±15%). The same applies to the method of dilution analysis.[13] The method of the calibration curve is therefore suitable only for the determination of individual dihydric phenols. The error of the determination does not surpass ±5%, as long as the concentration in the sample analysed is not higher than as given in Table II.

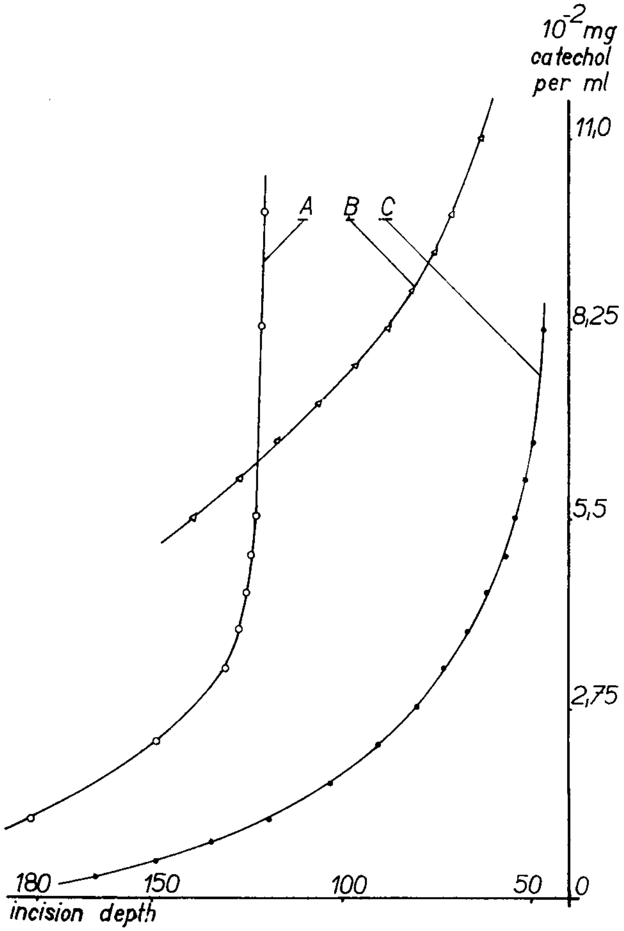


FIG. 9.—Dependence of the depth of incisions on catechol concentration in a medium of 1*M* potassium nitrate:
A—anodic incision, Q = 0·17;
B—anodic incision, Q = 0·08;
C—cathodic incision, Q = 0·18.

For the determination of phenol mixtures the method of oscillopolarographic comparative titrations has been chosen, two curves of functions dV/dt = f(V) being observed on the oscillographic screen. The curves could be mutually shifted along the horizontal axis. The same supporting electrolyte was used in the comparison solution and the solution studied. The procedure for the determination of mixtures of dihydric phenols was such that first that phenol whose concentration in the mixture

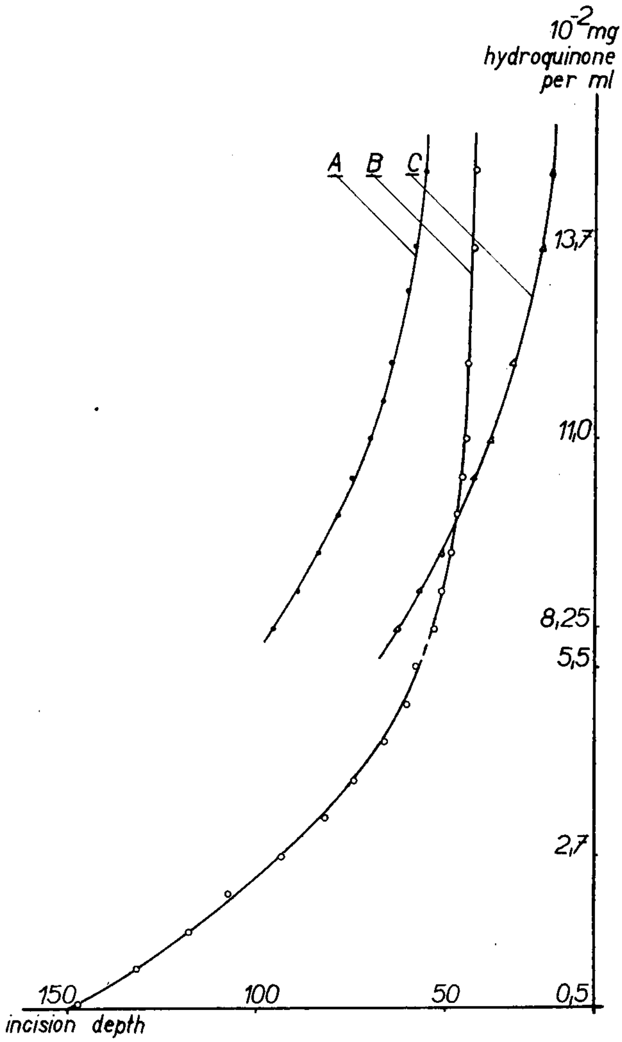


FIG. 10.—Dependence of the depth of incisions on hydroquinone concentration in a medium of 1*M* potassium nitrate:
A—cathodic incision, Q = 0·12;
B—anodic incision, Q = 0·11;
C—anodic incision, Q = 0·08.

was largest, was titrated nearly to equivalence. Then the titration was stopped and a standard solution of the second component of the mixture was added until the incisions studied began to overlap, or if the curves had been shifted near to each other, until the incisions seemed to be of nearly the same size. Then the first incision was titrated to the end in the same way. After registering these lower volumes of titrant used, the solutions were slightly overtitrated in the same order, *i.e.*, when the curves had been shifted close to each other, the depth of the incisions seems to be practically equal. Amounts of standard solutions needed to reach equivalence were then determined from these two limiting values. 1*M* potassium nitrate was used as supporting electrolyte.

First, two-component mixtures were studied: catechol–hydroquinone, catechol–resorcinol, hydroquinone–resorcinol, in total concentrations of $5 \cdot 5 \times 10^{-2}$ mg/ml and also a mixture of catechol–hydroquinone of $1 \cdot 1 \times 10^{-2}$ mg/ml total concentration, the ratios of the individual components in the mixtures being varied.

Titration of catechol in linear mixtures with hydroquinone up to concentrations of 2·75 × 10^{-2} mg/ml was carried out by studying variations of the area of the cathodic incision Q = 0·19; at higher concentrations the reversible anodic incision was used. The most suitable conditions of current are: AC = 0·3 mA, DC = 2·0 mA. Hydroquinone was quantitatively determined by comparing the anodic incision at Q = 0·11 (conditions of current: AC = 0·2 mA, DC = 2·0 mA). At catechol:hydroquinone ratios of 4:1 the anodic hydroquinone incision changes into a delay. In this case, as well as for concentrations lower than 3 × $10^{-5}M$, titrations must be carried out at AC = 0·1 mA and DC = 1·0 mA. Table III shows a review of the errors of determination of catechol–hydroquinone mixtures for total concentrations of 5·5 × 10^{-2} and 1·1 × 10^{-2} mg/ml.

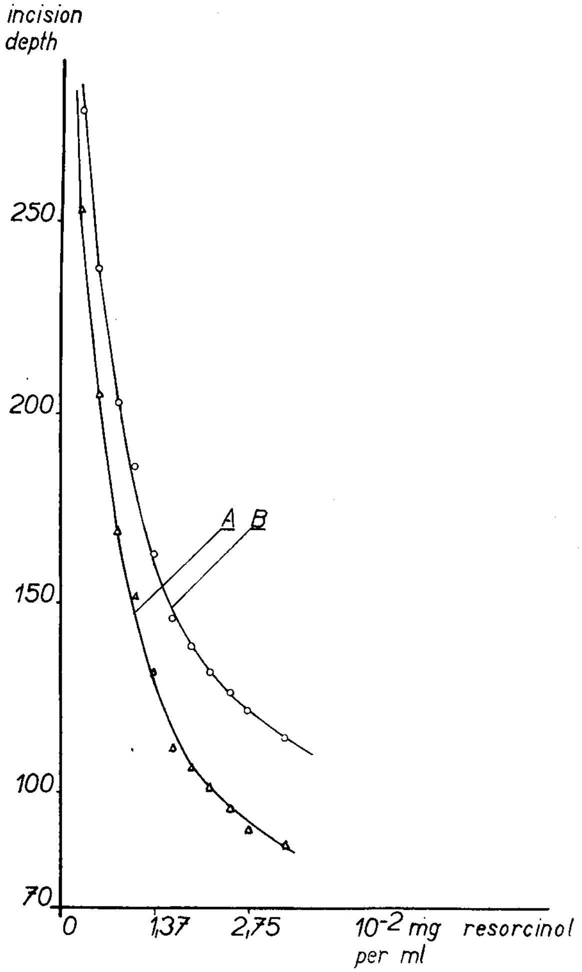


FIG. 11.—Dependence of the depth of incisions on resorcinol concentration in a medium of 1M potassium nitrate:
A—cathodic incision, Q = 0·60;
B—cathodic incision, Q = 0·30.

The maximum concentration ratio of catechol–hydroquinone is 15:1 for a total concentration of both components in the mixture of 1·1 × 10^{-2} mg/ml; maximum hydroquinone concentration is 7 × 10^{-4} mg/ml. At a total concentration of 5·5 × 10^{-2} mg/ml, catechol may be determined with the error mentioned, ±10%, by following the area of the cathode incision at Q = 0·19 up to a ratio of 1:10, and by following the cathodic incision Q = 0·48 up to a ratio of 1:15. The more positive catechol incision is, according to the selected conditions of current, partially disturbed by the reversible hydroquinone incision at catechol concentrations of the order of magnitude 10^{-3} mg/ml.

TABLE III.—DETERMINATION OF MIXTURES OF DIHYDRIC PHENOLS

Total concentration of dihydric phenols = 5·5 × 10^{-2} mg/ml			Total concentration of dihydric phenols = 1·1 × 10^{-2} mg/ml		
Ratio of catechol:hydroquinone	Error, ±% catechol	Error, ±% hydroquinone	Ratio of catechol:hydroquinone	Error, ±% catechol	Error, ±% hydroquinone
1:10	10	2	1:10	2·5	0·8
1:6	6·2	0·5	1:6	4·8	1·1
1:4	0	3·5	1:4	3·5	0
1:2	3·2	6·1	1:2	1·3	4·8
1:1	2·7	1·8	1:1	0·9	0
2:1	2·3	4·5	2:1	1·4	2·7
4:1	1·7	0	4:1	3·4	0
6:1	3·7	3·7	6:1	2·1	6·3
			10:1	2	10

The determination of catechol in mixtures with resorcinol has been carried out up to concentrations of 2·5 × 10^{-2} mg of pyrocatechol/ml by comparing the cathodic incision at Q = 0·19 at the following conditions of current: AC = 0·3 mA, DC = 1·0 mA; concentrations higher than 2·5 × 10^{-2} mg/ml have been determined by comparing the reversible anodic incision.

Good results have been obtained in the determination of catechol in mixtures with resorcinol, because it is possible to select such conditions of current at which resorcinol does not form an incision even at concentrations of 6 × 10^{-2} mg/ml.

Resorcinol has been determined by comparing the size of its more positive incision at Q = 0·27 and 0·30 (AC = 0·8 to 1·7 mA, DC = 1·0 mA). Table IV summarises the errors of the determination of catechol–resorcinol and hydroquinone–resorcinol mixtures for total concentrations of both components of 5·5 × 10^{-2} mg/ml.

TABLE IV.—DETERMINATION OF MIXTURES OF CATECHOL–RESORCINOL AND OF HYDROQUINONE–RESORCINOL (TOTAL CONCENTRATION OF DIHYDRIC PHENOLS: 5·5 × 10^{-2} mg/ml).

Ratio of catechol:resorcinol	Error, ±% catechol	Error, ±% resorcinol	Ratio of hydroquinone:resorcinol	Error, ±% hydroquinone	Error, ±% resorcinol
10:1	2·0	10·0	10:1	2·0	5·0
6:1	4·4	4·0	6:1	1·7	2·5
4:1	2·3	4·0	4:1	1·7	2·3
2:1	2·6	2·7	2:1	1·4	1·4
1:1	1·9	1·9	1:1	0·9	0
1:2	2·7	0·7	1:2	2·8	2·1
1:4	2·3	0·6	1:4	2·2	2·3
1:6	0	0·3	1:6	5·8	0·4
1:10	5·0	3·0	1:10	5·0	3·0
1:20	9·4	1·0	1:20	6·6	0·7

The maximum ratio of dihydric phenols in binary mixtures at which an individual component may be determined with an error of ±10% at a total concentration of 5·5 × 10^{-2} mg/ml is 1:20 and 20:1 for catechol–resorcinol and hydroquinone–resorcinol mixtures, respectively. At these limiting concentrations (2·75 × 10^{-3} mg/ml) hydroquinone has been determined under the following conditions: AC = 0·3 mA, DC = 1·2 mA, by comparing the area of the anodic incision at Q = 0·11. Catechol has been determined at the limiting concentration (2·75 × 10^{-3} mg/ml) by comparing the size of the more negative cathodic incision at Q = 1·48 (AC = 0·8 to 1·1 mA, DC = 1·0 mA).

Conditions of current for the determination of hydroquinone and resorcinol in mixtures (Table IV) are the same as for the determination of catechol and resorcinol.

In the range of ratios mentioned (Tables III and IV) two-component mixtures of dihydric phenols may be determined with an average error of ±3%. Catechol in the order of magnitude of concentrations of 10^{-4} mg/ml, hydroquinone and resorcinol in concentrations of 2·75 × 10^{-3} mg/ml at

Fig. 12—Reaching equivalence in the determination of a mixture of dihydric phenols (electrolyte: $1M$ KNO_3; total phenol concentration: 6×10^{-2} mg/ml; catechol:hydroquinone:resorcinol = 3:7:1; AC = 0·2 mA, DC = 2·0 mA).

concentrations of the second component of the binary mixture 5·5 × 10^{-2} mg/ml may be determined with errors of ±10%.

The determination of all three isomers when present together has been studied at a ratio of 1:3:7 in a total concentration of 6 × 10^{-2} mg/ml under the conditions of current given for their determination in binary mixtures. The error of the determination has been calculated for each component of the ternary mixture. Some of the results are given in Table V and Fig. 12. The average error of the determination for the individual components at a total concentration of dihydric phenols equal to 6 × 10^{-2} mg/ml is less than ±4%.

TABLE V.—DETERMINATION OF MIXTURES OF HYDROQUINONE, CATECHOL AND RESORCINOL

Ratio of catechol: hydroquinone: resorcinol	Amount present, *mg*			Amount present in comparative solution, *mg*			Error, ± %		
	catechol	hydroquinone	resorcinol	catechol	hydroquinone	resorcinol	catechol	hydroquinone	resorcinol
1:3:7	0·11	0·33	0·77	0·115	0·34	0·785	4·5	3·0	2·0
1:7:3	0·11	0·77	0·33	0·12	0·76	0·35	9·0	1·3	6·0
3:1:7	0·33	0·11	0·77	0·31	0·12	0·77	6·0	9·0	0
3:7:1	0·33	0·77	0·11	0·335	0·78	0·115	1·5	1·3	4·5
7:1:3	0·77	0·11	0·33	0·775	0·11	0·345	0·6	0	4·5
7:3:1	0·77	0·33	0·11	0·77	0·34	0·12	0	3·0	9·0

A small concentration of phenol in the solution analysed (5·5 × 10^{-3} mg/ml) already interferes in the determination of dihydric phenols. The area of the anodic hydroquinone incision is especially influenced, and at higher phenol concentrations also the depth of the cathodic catechol incision and the positive resorcinol incision. Phenol itself does not influence the oscillopolarographic curve in any characteristic manner sufficient to compensate its interference in the comparison solution. The presence of trihydric phenols in the solution makes the determination of dihydric phenols totally impossible.

We have attempted to explain the oscillopolarographic behaviour of the substances investigated by carrying out further experiments. The results obtained up to now, however, do not permit any unambiguous conclusions. It seems that (a) the most positive catechol and hydroquinone incisions correspond probably to the electrolytic reaction dihydroquinone–quinone, (b) incisions of dihydric phenols at Q = 0·27 and 0·30 in alkaline medium are of capacity origin, (c) the resorcinol incision at Q = 0·60 and the same catechol incision (at pH 12) correspond to a secondary electrochemical artefact, and (d) the most negative resorcinol incision is of kinetic character and is formed by chemical reaction from the artefact after the electrode reaction. In this direction we are continuing our studies of the behaviour of phenols.

Acknowledgement—The authors express their thanks to Dr. R. Kalvoda (Polarographic Institute, Czechoslovak Academy of Sciences, Prague) for useful discussions concerning this manuscript.

Zusammenfassung—Die Lösung von 1M-KNO_3 wurde empfohlen als Grundelektrolyt für den qualitativen oszillopolarographischen Nachweis von Dihydroxyphenolen. Genügend differenzierte Einschnitte auf den Kurven der Funktion dV/dt = f(v) ermöglichen ihre Bestimmung mit Hilfe der Methode der Vergleichungstitrationen mit einem Durchschnittfehler von ±3–4%. Monohydroxyphenolen stören den Nachweis nicht. Phluoroglucinol und Pyrogallol stört den Nachweis sowie die Bestimmung. Die Methode der Kalibrationskurven ermöglicht die Bestimmung der Dihydroxyphenolen mit einem Durchschnittfehler von ±5%.

Résumé—Une solution de nitrate de potassium 1 *M* a été utilisée comme électrolyte dans l'analyse des diphénols à l'aide d'une méthode oscillopolarographique. Les vagues correspondantes sont suffisamment éloignées sur la courbe dV/dt = f(V) pour permettre la détermination par une méthode de dosage comparé, avec une précision moyenne de ±3 à 4%. La présence du monophénol ne gene pas dans l'analyse. Le phloroglucinol et le pyrogallol, par contre, sont genants, pour la recherche et le dosage. La méthode des courbes d'étalonnage permet la détermination de chaque diphénol avec une erreur de ±5%.

REFERENCES

[1] J. Doskočil, *Coll. Czech. Chem. Comm.*, 1950, **15,** 599.

[2] V. D. Bezugly and V. M. Dimitrijeva, *Zavodskaya Lab.*, 1957, **23,** 914.

[3] R. Berkey, E. W. Blaha, M. E. Runner and S. Wawzonek, *J. Electrochem. Soc.*, 1956, **103,** 456.

[4] V. Bergerová and S. Škramovský, *Pracovní lékařství*, 1952, **4,** 64.

[5] P. Zuman, *Coll. Czech. Chem. Comm.*, 1956, **15,** 1107.

[6] S. S. Lord and L. B. Rogers, *Analyt. Chem.*, 1954, **26,** 284.

[7] A. L. Conrad, P. J. Elving and V. F. Caylor, *ibid.*, 1953, **25,** 1078.

[8] N. N. Altamanenko and E. M. Skobec, *Zavodskaya Lab.*, 1949, **15,** 1921.

[9] L. Beníšek and L. Sommer, *Chem. listy*, 1954, **50,** 1215.

[10] A. L. Crittenden and J. Shain, *Analyt. Chem.*, 1954, **26,** 1281.

[11] J. Drahoňovský and V. Racek, *Chem. průmysl*, 1961, **11,** 22.

[12] M. Tichý, Thesis No. P 7, Charles University, Praha, 1961.

[13] J. Heyrovský and R. Kalvoda, *Oscillographische Polarographie mit Wechselstrom.* Akademie-Verlag, Berlin, 1960.

Talanta, 1963, Vol. 10, pp. 633 to 639. Pergamon Press Ltd. Printed in Northern Ireland

PHASE TITRATIONS—II*

NEW APPLICATIONS AND A CONSIDERATION OF THE PHASE TITRATION END-POINT

D. W. Rogers and A. Özsoǧomonyan
Department of Chemistry, Robert Kolej, Bebek, Istanbul, Turkey

(*Received* 24 *November* 1962. *Accepted* 22 *December* 1962)

Summary—Results are given for the phase titration of binary solutions of aniline with methanol, ethanol, isopropanol, dioxan and acetone, of nitrobenzene with methanol, ethanol, isopropanol, dioxan and acetone, of n-butyl bromide with methanol, ethanol, isopropanol, dioxan and acetone, of methyl aniline with methanol, isopropanol and acetone, of ethyl acetate with acetone and of turpentine with acetone. The titrant in each case was water. Good and bad phase titration end-points are explained in terms of the corresponding three-component phase diagram.

Phase titrations, because they depend on the physical characteristics of a system and not on its chemical characteristics, should be capable of extremely wide application. One purpose of this paper and those that follow is to extend the scope of application of phase titrations to a much larger number of analytical problems than has been previously reported. To that end, 20 new binary mixtures have been analysed by phase titration. The theoretical basis of this method was given in the first paper of this series.[1]

Previous work[2–7] has covered, in large measure, the titration of mixtures of liquids which are extremely immiscible in water (usually aromatics) in binary combination with alcohols, using water as the titrant. In this work, binary mixtures showing various solubility relationships with water were studied. These differences in solubility resulted in differences in behaviour at the end-point.

The most common end-point behaviour is that followed by the systems studied by Siggia and Hanna,[2] Caley and Habboush,[7] and most of the systems investigated in this series. As the amount of water necessary to bring about turbidity becomes larger, the end-point becomes less and less distinct. In unfavourable cases there may be as much as a 0·5-ml uncertainty in locating the end-point. This kind of behaviour usually does not interfere with the analytical determination because the poor end-point is encountered on the portion of the calibration curve for which the titre is large and the calibration curve is steep. These factors counteract the end-point uncertainty and give final results which are comparable to those obtained under more favourable end-point conditions.

A few cases have been encountered in which this end-point behaviour is reversed, causing an increase in the average error for a series of determinations.

THEORY

Consider the phase diagram in Fig. 1. A and B are immiscible in each other and C is completely miscible in both A and B. If a binary mixture of A and C is titrated with B, the titration can be represented by the long and short lines from side AC

---

* Part I: see reference 1.

crossing the solubility curve in the direction of apex B. The long line represents the titration of a mixture which requires a large titre and for which a small change in the ratio of A to C brings about a large change in the titre. It is on the steep portion of the calibration curve shown in the first paper of this series.[1] The short line represents the titration of a mixture which requires a small titre and for which a small change in the ratio of A to C brings about a small change in the titre.

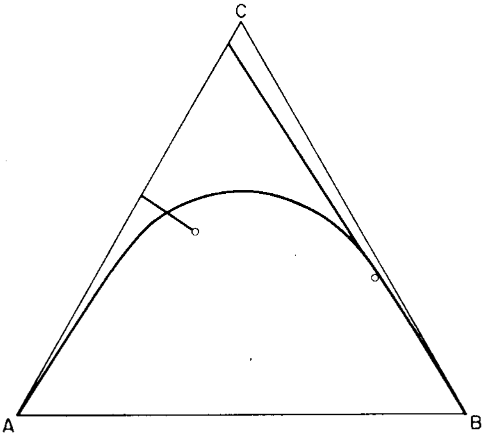


FIG. 1.—A three-component phase diagram showing two titration lines. The longer one intersects the solubility curve at a small angle giving a poor end-point, while the shorter intersects the solubility curve at a large angle giving a good end-point.

Both lines are drawn a little past the solubility curve to show the addition of a slight excess of titrant after the solubility limit has been reached. The long titration line, because it meets the solubility curve almost tangentially, extends only a small amount into the two-phase region under the curve. The short titration line, because it intersects the solubility curve at a large angle, extends well into the two-phase region. All other things being equal, phase separation should be more distinct and the end-point should be clearer in the second case.

A second factor influencing the phase titration end-point can be understood by considering Fig. 2. It is a hypothetical three-component phase diagram with tie lines, representing the composition of co-existing phases, drawn in. If a three-component system is made up with the over-all composition corresponding to a point under the solubility curve, say on a tie line, it will be heterogeneous, splitting into a B-rich phase with a composition corresponding to the intersection of the tie line with the solubility curve on the right and an A-rich phase with composition corresponding to the intersection of the tie line with the solubility curve on the left. The tie lines would be parallel to the base line if C distributed itself equally between A and B at all concentrations but this is unlikely and tie lines usually slope towards one lower apex or the other.

Consider the two short titration lines shown in Fig. 2. The one representing titration by B, if extended, cuts the tie lines at a nearly perpendicular angle. When an excess of titrant is added, the over-all composition of the system is represented by the intersection of the titration line and the dotted tie line. The system splits into two phases with compositions corresponding to the ends of the tie line and the end-point is sharp.

If the titration is carried out using A to titrate a binary mixture of B and C, the titration line is on the B side of the diagram. A slight excess of titrant gives a system having an over-all composition corresponding to the intersection of the titration curve with one of the longer tie lines. It can be shown that the length along the tie line from the over-all composition point to its intersection with the solubility curve is related to the amount of each phase at equilibrium. Hence, in the first case, in which the tie line is intersected near its centre by the titration line, the solution separates into two nearly equal parts. In the second case, the system separates into a large amount of a phase very close in composition to the over-all composition of the system and a very small amount of a phase consisting of nearly pure titrant. The end-point is not clear in the second case and, indeed, there may be no turbidity at all. Clearly, the situation is reversed with respect to the better titrant, A or B, if the slope of the tie lines is opposite to that shown in Fig. 2.

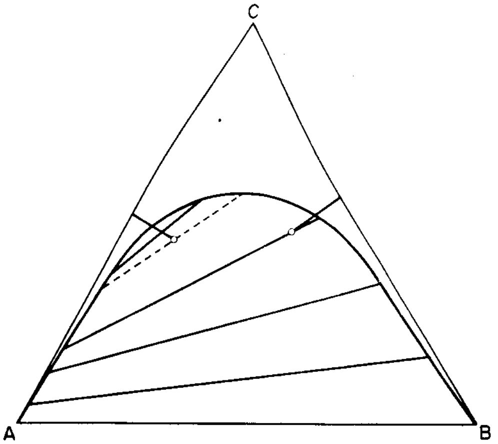


FIG. 2.—A three-component phase diagram showing titration lines for the two titrants A and B. The line representing titration with A intersects the solubility curve well away from the plait point giving a poor end-point, while the line representing titration with B intersects the solubility curve near the plait point giving a good end-point.

In summary, the best end-point is obtained when the titration line cuts both the solubility curve and the tie lines at a nearly perpendicular angle; a good end-point is obtained when the titration line intersects the solubility curve at a small angle but is near the shortest tie line (plait point). A fair end-point may be obtained if the titration line intersects the solubility curve at a large angle but is nearly parallel with the tie lines (depending on emulsion stability, *etc.*) and the end-point will almost certainly be poor if the titration line intersects the solubility curve at a small angle well away from the plait point.

The effects just described are most noticeable outside the range which has been previously[1] referred to as the optimum titration range and in many cases it is possible to titrate systems in the optimum titration range with relatively small loss in accuracy even though the end-point conditions do not satisfy all of the criteria listed. If this is not the case, one may add a known amount of one or the other of the components in the original mixture to shift the system to a more favourable portion of its phase diagram, titrate, and determine the composition of the original from the composition of the new mixture. If necessary, it should be possible to select a new titrant using tie line data in the literature or even to guess the orientation of tie lines for which data has not been published by applying the qualitative rule: polar solutes—let C be arbitrarily called the solute—tend to concentrate themselves in the phase which is rich in the polar solvent.

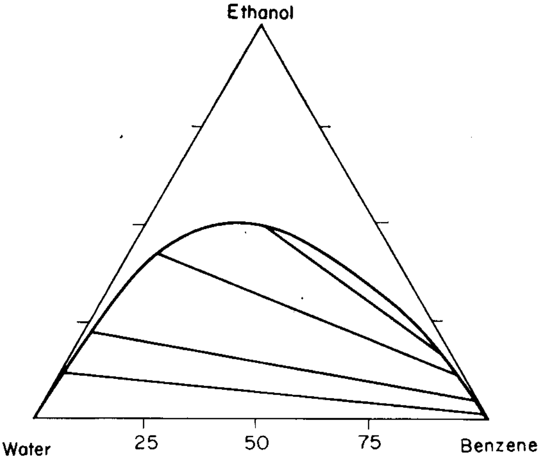


FIG. 3.—The phase diagram for the system water-benzene-ethanol. Partially reproduced from the data of Bancroft and Hubbard.[8]

In order to test these generalisations about the phase titration end-point, phase diagrams were selected from the literature which had sloping tie lines like those in Fig. 2. In the case of the water-benzene-ethanol system, the tie lines slope towards the benzene apex, while in the water-benzene-dioxan system they slope towards the water apex. The first system, Fig. 3, is taken from the data of Bancroft and Hubbard[8] and the second, Fig. 4, from the data of Berndt and Lynch.[9] In both cases, only a few of the tie lines given by the original authors are reproduced. Nine

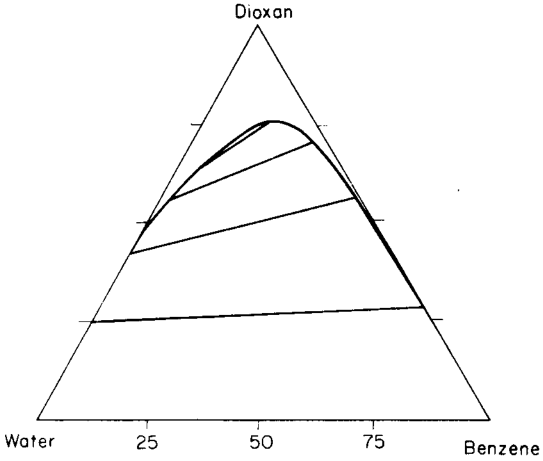


FIG. 4.—The phase diagram for the system water-benzene-dioxan. Partially reproduced from the data of Berndt and Lynch.[9]

binary mixtures of ethanol and benzene were made up covering the volume concentration range 10%–90% benzene at 10% intervals. These were titrated with water; the quality of the end-point is given in Table II, part A. Similarly, binary mixtures of water and ethanol covering a 10%–90% range were titrated with benzene, part B, dioxan-benzene mixtures were titrated with water, C, and water-dioxan mixtures were titrated with benzene, D. These data represent the titration of systems with very different solubility relationships in such a way that the solubility curves and tie lines are intersected by the titration line at all possible angles.

EXPERIMENTAL

Reagents

Reagent-grade aniline, nitrobenzene, ethyl acetate, n-butyl bromide, methanol, isopropanol, dioxan and acetone were used. Technical-grade turpentine, ethanol and methyl aniline were used.

Procedure

As given in the first paper of this series.[1]

RESULTS AND DISCUSSION

Table I shows the results for 20 new binary systems which have been analysed by phase titration. Most represent the titration of reagent-grade chemicals, but crude chemicals like turpentine can also be titrated provided only that the calibration curve is constructed with the same quality of turpentine. If a substance like gasoline or petroleum ether, which is itself a mixture, is one of the components of the original

TABLE I.—RESULTS FOR THE TITRATION OF 20 HOMOGENEOUS BINARY SYSTEMS WITH WATER. THE END-POINT WAS INDICATED BY THE APPEARANCE OF A DISTINCT PERMANENT TURBIDITY. TITRATIONS AND DETERMINATION OF THE CALIBRATION CURVE WERE CARRIED OUT ON THE SAME DAY

Sample	Optimum range, %	Number of titrations	Average error, *absolute* %
Aniline-methanol	40–80	12	0·42
Aniline-ethanol	50–85	15	0·20
Aniline-isopropanol	40–80	12	0·18
Aniline-dioxan	30–50	12	0·08
Aniline-acetone	20–50	12	0·38
Nitrobenzene-methanol	4–25	15	0·09
Nitrobenzene-ethanol	5–30	12	0·07
Nitrobenzene-isopropanol	10–40	11	0·09
Nitrobenzene-dioxan	5–25	12	0·09
Nitrobenzene-acetone	5–25	18	0·20
Methyl aniline-methanol	8–30	14	0·10
Methyl aniline-acetone	8–30	12	0·12
Methyl aniline-isopropanol	15–45	12	0·09
Turpentine-acetone	2–15	16	0·13
Ethyl acetate-acetone	30–55	9	0·45
n-Butyl bromide-methanol	2–20	12	0·11
n-Butyl bromide-ethanol	3–30	18	0·12
n-Butyl bromide-isopropanol	10–40	11	0·06
n-Butyl bromide-dioxan	2–20	12	0·06
n-Butyl bromide-acetone	3–20	11	0·22

mixture, it is not a binary mixture. It can, however, be treated as though it were a binary mixture and titrated in the same way as a true binary mixture. Indeed, there are pseudo ternary phase diagrams reported in the literature for systems which contain many more than three components.[10]

Parts A and B of Table II show the end-point characteristics of phase titrations involving the water-benzene-ethanol system, Fig. 3. Parts C and D show the end-point characteristics of phase titrations involving the water-benzene-dioxan system, Fig. 4.

TABLE II.—END-POINT CHARACTERISTICS OF SOME PHASE TITRATIONS. THE NUMBERS IN PARENTHESES IN THE SECOND AND FOURTH COLUMNS GIVE THE APPROXIMATE NUMBERS OF DROPS OF TITRANT NECESSARY TO BRING ABOUT TURBIDITY. ALL PERCENTAGES ARE BY VOLUME. THE TITRANTS ARE: A, WATER; B, BENZENE; C, WATER; D, BENZENE.

A. Benzene-ethanol system

Benzene, %	End-point
10	poor (10)
20	fair (3)
30	good (1–2)
40	excellent (<1)
50	excellent (<1)
60	excellent (<1)
70	v. good (1)
80	good (2)
90	fair (5)
100	phase separation

B. Ethanol-water system

Water, %	End-point
10	fair (4)
20	good (2)
30	fair (4)
40	poor (6)
50	poor (>10)
60	v. poor (>10)
70	phase separation
80	—
90	—
100	—

C. Benzene-dioxan system

Benzene, %	End-point
10	good (2)
20	good (2)
30	fair (4)
40	poor (>5)
50	phase separation
60	—
70	—
80	—
90	—
100	—

D. Dioxan-water system

Water, %	End-point
10	good (3)
20	excellent (1)
30	excellent (1)
40	good (2)
50	fair (3)
60	poor
70	v. poor
80	phase separation
90	—
100	—

Part A shows complete agreement with the theory of the phase titration just given. The end-point is excellent at and near the plait point, the end-point is adequate throughout the optimum titration range and particularly good where the titre is small. Part A is an example of the best end-point conditions.

Part B gives poorer end-points throughout because the tie lines are nearly parallel to the titration line. When the titration line intersects the solubility curve near the plait point, however, the end-point is fair to good. In this situation, the usual rule —that the end-point is best for the shorter titre—is reversed.

The notation "phase separation" has been used to indicate the lack of a definite turbidity or opalescence at the end-point. At a 70% or greater concentration of water in part B, the addition of benzene to the binary pair results in the formation of tiny transparent globules of the second phase. As more titrant is added, the globules simply grow in size but at no point is there any turbidity. The appearance of the globules is very difficult to observe and cannot be used as an end-point. Although phase separation is controlled in part, at least, by other factors, such as emulsion stability and interfacial tension between the phases, phase separation has only been observed in this work at the lower extremities of the solubility curve.[11]

Parts C and D of Table II are the opposite of A and B because the tie lines slope in the opposite direction. Both show earlier phase separation than their counterparts in the water-benzene-ethanol system because the solubility curve approaches the solute apex more closely.

CONCLUSION

Each case taken up by Table II supports the criteria given in the theoretical section for the best end-point, *i.e.*, the titration curve must cross the solubility curve at (1) an angle as near as possible to the perpendicular, and (2) as near as possible to the plait point. Experimental results indicate that the second of these factors is more important than the first.

Acknowledgement—The authors gratefully acknowledge a grant by the Society of Sigma Xi in support of this research.

Zusammenfassung—Ergebnisse für die Phasentitration binärer Gemische von Anilin mit Methanol, Äthanol, Isopropanol, Dioxan und Aceton, von Nitribenzol und n-Butylbromid mit den gleichen Verbindungen, von Methylanalyn mit Methanol, Isipropanol und Aceton, von Äthylacetat mit Aceton und von Terpentin mit Aceton werden mitgeteilt. Titrationsmittel (in allen Fällen) ist Wasser. Die Güte der Endpunkte wird aufgrund der betreffenden Dreiphasendisgramme erläutert.

Résumé—On donne les résultats obtenus pour le dosage de phase des systemes binaires suivants: aniline et méthanol, éthanol, isopropanol, dioxane, acétone. Nitrobenzène et méthanol, éthanol, isopropanol, dioxane, acétone. Bromure de n-butyle et méthanol, éthanol, isopropanol, dioxane, acétone. Méthyl-aniline et méthanol, isopropanol, acétone, Acétate d'éthyle et acétone. Térébenthine et acétone. Le dosage est effectué dans chaque cas au moyen de l'eau. Les valeurs correctes et aberrantes des points équivalents du dosage de phase sont explicités par rapport aux diagrammes ternaires correspondants.

REFERENCES

[1] D. W. Rogers, *Talanta*, 1962, **9**, 733.
[2] S. Siggia and J. G. Hanna. *Analyt. Chem.*, 1949, **21**, 1087.
[3] C. D. Bogin, *Ind. Eng. Chem.*, 1924, **16**, 380.
[4] S. L. Spiridonova, *Analyt. Chem.* (*U.S.S.R.*), 1949, **4**, 169; *Chem. Abs.*, **44**, 2886.
[5] *Idem*, *J. Appl. Chem.* (*U.S.S.R.*), 1947, **20**, 635; *Chem. Abs.*, **43**, 6946.
[6] *Idem*, *ibid.*, 1948, **19**, 966; *Chem. Abs.*, **43**, 6946.
[7] E. R. Caley and A. Habboush, *Analyt. Chem.*, 1961, **33**, 1613.
[8] W. D. Bancroft and S. S. Hubbard, *J. Amer. Chem. Soc.*, 1942, **64**, 347.
[9] R. I. Berndt and C. C. Lynch, *ibid.*, 1944, **66**, 282.
[10] *Chemical Engineer's Handbook*. McGraw-Hill, New York, 1950, pp. 728–729.
[11] See also E. R. Washburn and A. E. Beguin, *J. Amer. Chem. Soc.*, 1940, **62**, 579.

Talanta, 1963, Vol. 10, pp. 641 to 655. Pergamon Press Ltd. Printed in Northern Ireland

COMPARISON OF FIFTY-TWO SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF NITRITE

E. SAWICKI, T. W. STANLEY, J. PFAFF and A. D'AMICO
Laboratory of Engineering and Physical Sciences, Division of Air Pollution
Robert A. Taft Sanitary Engineering Center, Public Health Service
U.S. Department of Health, Education and Welfare, Cincinnati 26, Ohio, U.S.A.

(*Received* 29 *November* 1962. *Accepted* 3 *January* 1963)

Summary—This paper can be considered as a concise source of spectrophotometric methods for the determination of nitrite. Fifty-two methods, of which about 36 are new, are compared with respect to molar absorptivity, selectivity, sensitivity, simplicity, colour stability, and conformity to Beer's law. A new type of spectrophotometric procedure—autocatalytic in principle—is introduced; a molar absorptivity of 620,000 is obtained. Over 20 new methods have been shown to give higher molar absorptivities with nitrite than any of the Griess type of reagents. Consequently they are worthy of further investigation in respect of their application to the analysis of nitrites and nitrite precursors.

INTRODUCTION

THE experimental material in this manuscript complements a previous paper,[1] which consisted of an extensive review (143 references) of methods for the determination of nitrite and nitrite precursors, with special emphasis on spectrophotometric procedures. Nitrite precursors are defined as compounds from which nitrous acid is obtained by hydrolysis, oxidation or reduction. Some nitrite precursors are nitrogen oxides, inorganic and alkyl nitrates, nitrosoamines, alkyl nitrites, aromatic nitro compounds, nitroalkanes, alkyl and aryl nitroso compounds and ketonic isonitro compounds.

The authors believe that better analytical methods are needed for the analysis of nitrites and their precursors. This paper is considered a step toward the development of such methods. Many of the methods presented in this paper are thought to be worthy of further investigation.

Many of the methods described in the review paper mentioned above are critically compared with a large number of new methods in Table I. In this table the procedures are arranged according to the molar absorptivity. Other factors such as sensitivity, determination limit, percent deviation, colour stability, conformity to Beer's law, and simplicity (as shown by procedural time) are compared.

EXPERIMENTAL

Reagents and apparatus

Reagents were obtained from Aldrich Chemical Co., Milwaukee 10, Wisconsin; Distillation Products, Rochester 3, New York; K and K Laboratories, Jamaica 3, New York; and Laboratory Services, Inc., Cincinnati 9, Ohio. Benzaldehyde 2-benzothiazolone hydrazone, m.p. 223–224°, was prepared by a literature procedure.[4] 3-Nitrobenzalphenylhydrazone, m.p. 127°, was prepared by heating a methanolic solution of 3-nitrobenzaldehyde and phenylhydrazine. All reagents were purified either by crystallisation to a constant melting point or by distillation.

Cary Models 11 and 14 recording spectrophotometers with 1-cm path-length cells were used in the spectrophotometric methods.

TABLE I.—COMPARISON OF METHODS FOR THE DETERMINATION OF NITRITE

Reagents	Procedure or (Ref.)	Type of chromogen	λ max, mμ	ε × 10⁻³	% S[a]	Dilution factor[b]	Sensitivity[c]	Det. limit,[d] μg	Colour stability, *min*	Proc. time, *min*	Beer's law
4,4′-Bis-(dimethylamino)thiobenzophenone	A	Diarylmethane cation	648 648	560[e] 620[h]	7·5 7·5	10 100	56 6·2	0·5	20[f]	32	g
Azulene	B	Diarylamine cation (XVI)	617	150[i]	5·8	4	37·5	0·1	5[j]	20	k
p-Phenylazoaniline + 1-naphthylamine	(2)	Bisazo dye dication (IV)	643	93		3	31	0·74	>4 hr	37	0·7–20
p-Aminoacetophenone + 1-anilinonaphthalene	C	Azo dye anion	617	88	2·55	10	8·8	0·52	25	4	0·5–13
p-Nitroaniline + 1-anilinonaphthalene	C	Azo dye anion (III)	657	82	1·07	10	8·2	0·56	>20	4	0·6–14
4-Nitro-1-naphthylamine + 1-anilinonaphthalene	C	Azo dye anion	695	77	3·65	10	7·7	0·60	60	4	0·6–15
p-Phenylazoaniline	(3)	Triazene anion (V)	595	67	1·03	10	6·7	0·80	18 hr[l]	6	0·8–16[k]
4-Nitro-1-naphthylamine + 1-anilinonaphthalene	D	Azo dye anion	682	62	2·18	4	15·5	0·30	>5	4	—
p-Nitroaniline + 1-napthhol	C	Azo dye anion	630	61·5	1·10	10	6·15	0·75	15	4	0·8–12
3-Nitrobenzalphenylhydrazone	E	?	580 620	63[m] 62	5·8 5·5	100	0·63 0·62	0·6	Fades[n]	4	o
p-Nitroaniline + 1-anthrol	C	Azo dye anion	670	60		10	6·0	0·77	>10	4	0·8–19
p-Phenylazoaniline + benzaldehyde 2-benzothiazolylhydrazone	(4)	Formazan anion	590	58		2	29	0·79	>20 hr	3	0·8–20[o]
4-Nitro-1-naphthylamine + 1-naphthol	C	Azo dye anion	665	57·5	2·3	10	5·75	0·80	>5	4	0·8–20

p-Aminoacetophenone + anthrone	C	Azo dye anion	619	57		10	0·81	0·81	>5	4	0·8–20
4-Nitro-1-naphthylamine + 1-anthrol	C	Azo dye anion	720	56		10	5·6	0·82	>5	4	0·8–20
p-Nitroaniline + azulene	F	Azo dye cation	515	51	2·53	4	12·8	0·36	>1 hr	4	0·4–9
Anthranilic acid + 1-anilinonaphthalene	G	Azo dye cation	571	50	2·11	4	12·5	0·37	>1 hr	16	0·4–9
p-Nitroaniline + diphenylamine	C	Azo dye anion	655	50		10	4·7	0·98	5	4	1–24
p-Nitroaniline + benzaldehyde 2-benzothiazolylhydrazone	(4)	Formazan anion (VI)	595	49		2	24·5	0·94	>24 hr	3	
4-Nitro-1-naphthylamine + anthrone	C	Azo dye anion	685	47		10	4·7	0·98	>5	4	1–24
p-Aminoacetophenone + azulene	F	Azo dye cation	521	47		4	11·8	0·39		4	0·4–10
p-Aminophenylsulphone + azulene	F	Azo dye cation	510	47	1·91	4	11·8	0·39		4	0·4–10
Sulphanilic acid and *N*-(1-naphthyl)-ethylenediamine	(5)	Azo dye cation (II)	550	46		25	1·84	2·5	~16 hr	16	2·5–60
p-Nitroaniline + anthrone	C	Azo dye anion	653	44		10	4·4	1·05	5	4	1–24
p-Phenylaniline + azulene	F	Azo dye cation	549	44		4	11	0·42		4	0·4–10
p-Aminoacetophenone + 1-anthrol	C	Azo dye anion	597	41		10	4·1	1·12	5	4	1·1–24
4-Nitro-1-naphthylamine + diphenylamine	C	Azo dye anion	705	40		10	4·0	1·15	5	4	1·2–30
Sulphanilamide and *N*-(1-naphthyl)-ethylenediamine	(6)	Azo dye cation	550	~40		1·43	28	5·8	>60	34	5·8–35
p-Aminoacetophenone + 1-naphthol	C	Azo dye anion	565	38	3·0	10	3·8	1·21	>5	4	1·2–30
Chloro-*p*-phenylenediamine	(7)	Diazonium cation (I)	345	37·7	1·50	1·2	31·6	6·0	95	11	6–60
4-Nitro-1-naphthylamine + benzaldehyde 2-benzothiazolylhydrazone	C	Formazan anion	650	36·5		10	3·7	1·26	5	4	1·3–30

TABLE I (cont.)

Reagents	Procedure or (Ref.)	Type of chromogen	λ max mμ	$\varepsilon = 10^{-3}$	%S^{a}	Dilution factor^{b}	Sensitivity^{c}	Det. limit,^{c} μg	Colour stability, *min*	Proc. time, *min*	Beer's law
Bis-(4-aminophenyl)sulphide + azulene	F	Azo dye cation	538	35		4	8·8	0·53		4	0·5–12
p-Aminoacetophenone + benzaldehyde 2-benzothiazolylhydrazone	C	Formazan anion	567	33·4		10	3·4	1·37	>5	4	1·4–35
Sulphanilic acid + 1-naphthylamine	(5)	Azo dye cation	520	33					>60	16	
p-Nitroaniline + 1,2-dihydroxybenzene	C	Azo dye anion	660	32		10	3·2	1·44	5	4	1·4–35
p-Nitroaniline + sesamol	H	Azo dye anion	608	31		10	3·1	1·50		9	1·5–37
N,N-Dimethylaniline	(8,9)	*p*-Nitroso-aniline (VII)	423	29^{p}						23	
(4-Aminophenyl)trimethylammonium chloride + *N,N*-Dimethyl-1-naphthylamine	(10)	Azo dye cation	522	26		1·66	15·7	5·3	>7 days	23	5·3–53
1-Naphthylamine	I	Azo dye cation	560	26	3·75	4	6·4	0·70		4	0·7–20
1-Anilinonaphthalene	J		590	19		100	0·19	2·4		3	
9-Ethyl-3-aminocarbazole	K		773	18		4	4·5	1·0		5	
2,6-Xylenol	(11)	*p*-Nitroso-phenol (XIV)	304	18		25	0·72	6·4	120	45	6·4–64^{o}
Sulphanilic acid	(12)	Diazonium cation	270	15·3	0·85	1·04	14·7	15	3–158	5	15–150
Pyrrole	L	Diarylamine cation	502	13		1·05	12·4	18·4		18	
Resorcinol	M	Phenoxazine dication (XI)	555	13		3	4·3	1·1		51	o

Brucine	(13)		410	~11[r]	~2	1·24	9	14		10	14–45
Indole	L	Diarylamine cation (X)	527	9·0		1·05	8·6	26·4		18	
2,6-Xylenol	(14)	*p*-Nitrosophenol (XIV)	324	7·9[s]	~1	10	0·79	5·8		7	
3-Methyl-2-benzothiazolonehydrazone + formaldehyde	N	Formazan cation (XV)	640	6·5				>1	>30	43	70–1000
			670	6·5		10	0·65				
Alkali	(15)	Nitrite ion	211	5·8			5·8				2·4–60
			355	0·023	~3·0	1	0·023		>45	1	590–15000
Thiourea + iron^{III} perchlorate	(16)	Iron^{III} thiocyanate	455	3·5	0·54	2	1·8	66	20	34	66–900
N,*N*-Dimethylaniline + *N*,*N*-dimethyl-3-hydroxyaniline	0	Phenoxazine dication (IX)	635	3·1		10	0·31	15		85	

[a] Percent deviation based on 10 determinations.
[b] Dilution factor = final volume/test solution volume.
[c] Sens. = $\varepsilon \times 10^{-3}$/Dilution factor.
[d] Total μg of NO_2^- in test solution giving an absorbance of 0·1 in a 1-cm cell.
[e] Solution contained 2·8 μg of NO_2^-.
[f] Colour intensity reaches a maximum at 30 min and starts decreasing at 50 min (See Fig. 4).
[g] Linear relation from 0·5 to 9 μg (See Fig. 5).
[h] Solution contained 6·9 μg of NO_2^-.
[i] For 0·36 μg of NO_2^-.
[j] For 0·74 μg of NO_2^- at 0, 5, 30, 60, 120, 188, 375 min, A = 1·52, 1·52, 1·58, 1·61, 1·65, 1·66, 1·39, respectively.
[k] Does not follow Beer's law (See Fig. 6).
[l] In 48 hr the absorbance decreased from an initial 1·28 to 1·24.
[m] For 5·75 μg of NO_2^-. With 7·75 μg of NO_2^-, λ_{max} 620, ε 74000 and λ_{max} 580, ε 77000.
[n] At λ_{max} 580 mμ fades from an initial value of 1·59 to 1·45 and 1·14 in 10 and 20 min.
[o] Does not follow Beer's law.
[p] Theoretical value.
[q] Absorbance read 3–15 min after final step.
[r] With NO_3^- at λ_{max} 410, ε = 20,000.
[s] Assuming a complete conversion of NO_2^- to NO_3^-.

In most of the general procedural directions the absorbance is read immediately. However, for any particular reagent(s) the amount of leeway in time for taking a reading can be obtained from the colour stability reported for that particular method in Table I. The wavelength maxima for all procedures are also given in Table I. For each pair of reagents the first is reagent 1, the second reagent 2.

Procedure A

Use 1 ml of aqueous test solution. Dilute to 10 ml with a 2-methoxyethanol solution containing 0·025% 4,4′-bis(dimethylamino)thiobenzophenone (v/w) and 0.2% concentrated hydrochloric acid (v/v).

Read absorbance 40 min later at λ_{max} 650 mμ. If the colour is too dark to read, dilute the solution 1:10 with the blank solution and then read.

Procedure B

Use 1 ml of aqueous test solution, 3 ml of 0·05% azulene in acetic acid, and 1 ml of 70% aqueous perchloric acid. Allow to stand for 2 min, heat for 15 min at 100°, and cool.

Read within 5 min at wavelength maximum.

Procedure C

Use 1 ml of aqueous test solution, and 1 ml of a solution of 0·05% reagent 1 and 3% concentrated hydrochloric acid in water or 2-methoxyethanol. Mix thoroughly. Add 1 ml of 1% reagent 2 in neutral or weakly acidic dimethylformamide, and 2 ml of 40% benzyltrimethylammonium methoxide in methanol. Dilute to 10 ml with dimethylformamide.

Read immediately at wavelength maximum.

Procedure D

Use 1 ml of aqueous test solution, and 1 ml of a solution of 0·05% reagent 1 (w/v) and 3% concentrated hydrochloric acid (v/v) in water or 2-methoxyethanol. Mix thoroughly. Add 1 ml of 1% reagent 2 in neutral or weakly acidic *N*,*N*-dimethylformamide and 1 ml of 40% benzyltrimethylammonium methoxide in methanol.

Read immediately at wavelength maximum.

Procedure E

To use 4 ml of a fresh solution of 1% 3-nitrobenzalphenylhydrazone in trifluoroacetic acid, add 0·1 ml of aqueous test solution and 1 ml of concentrated sulphuric acid, and mix.

Read immediately at wavelength maximum.

Procedure F

Use 1 ml of aqueous test solution, and 1 ml of 0·5% reagent 1 in acetic acid. Mix thoroughly, add 1ml of 0·1% reagent 2 in acetic acid, and 1 ml of 70% aqueous perchloric acid.

Read immediately at wavelength maximum.

Procedure G

Use 1 ml of aqueous test solution. Add 1 ml of a solution of 1% reagent 1 and 3% concentrated hydrochloric acid in acetic acid and 1 ml of 1% reagent 2 in acetic acid. Allow to stand for 15 min, and add 1 ml of acetic acid.

Read immediately at wavelength maximum.

Procedure H

Use 1 ml of aqueous test solution. Add 1 ml of a solution of 0·05% reagent 1 and 3% concentrated hydrochloric acid (v/v) in 2-methoxyethanol. Mix thoroughly, add 1 ml of 1% reagent 2 in neutral or weakly acidic dimethylformamide, and allow to stand for 5 min. Add 2 ml of 40% benzyltrimethylammonium methoxide in methanol. Dilute to 10 ml with dimethylformamide.

Read immediately at wavelength maximum.

Procedure I

Use 1 ml of aqueous test solution. Add 2 ml of 5% 1-naphthylamine in acetic acid and 1 ml of concentrated sulphuric acid. Mix and cool quickly.

Read immediately at wavelength maximum.

Procedure J

To 5 ml of 2% 1-anilinonaphthalene in trifluoroacetic acid add 0·1 ml of concentrated sulphuric acid and 0·1 ml of aqueous test solution. Dilute to 10 ml with trifluoroacetic acid.

Read immediately at wavelength maximum.

Procedure K

Use 1 ml of aqueous test solution. Add 3 ml of 0·5% 9-ethyl-3-aminocarbazole in sulphuric acid. Cool quickly.

Read immediately at wavelength maximum.

Procedure L

Use 40 ml of aqueous test solution. Add 1 ml of 0·125% indole or pyrrole in methanol and 1 ml of concentrated sulphuric acid. Mix and allow to stand for 15 min.

Read immediately at the wavelength maximum.

Procedure M

To 2 ml of 2% resorcinol in sulphuric acid add 1 ml of aqueous test solution.

Read at 555 mμ, 50–70 min after mixing.

Procedure N

Boil 50 ml of 0·5% aqueous 3-methyl-2-benzothiazolone hydrazone hydrochloride and 0·25 ml of 38% aqueous formaldehyde for 5 min, and then cool. Bring the crystalline precipitate into solution by the careful addition of the minimum amount of concentrated hydrochloric acid. To 5 ml of this reagent solution add 10 ml of aqueous test solution. Allow to stand for 40 min, and dilute to 100 ml with acetone.

Read immediately at the wavelength maximum.

Procedure O

Use 1 ml of aqueous test solution. Add 0·1 ml of an aqueous solution containing 8% *N,N*-dimethylaniline (w/v) and 3% concentrated hydrochloric acid (v/v). Allow to stand for 20 min. Add 1 ml of 2% methanolic *N,N*-dimethyl-3-hydroxyaniline, and heat for 1 hr at 100°. Cool and dilute to 10 ml with methanol.

Read immediately at wavelength maximum.

DISCUSSION

Structure of final chromogens

The structures of the different types of chromogens are shown in Fig. 1. Except for structures IX-XII and XVI, the constitution of these chromogens is based on experimental evidence. Structures IX-XII and XVI are considered the most plausible on the basis of expected chemical reactivity of nitrous acid with the reagents and the similarity of the spectral properties of the final chromogen to dyes of analogous structure.

The reagent, 4,4′-bis-(dimethylamino)thiobenzophenone has been used in the detection of chlorine, bromine and iodine in non-volatile organic compounds. The reaction consists of the formation of free halogen, and its reaction with the reagent to form a green diarylmethane dye.[17] The autocatalytic reaction for the determination of nitrite is postulated in Fig. 2.

General considerations

Because this paper is essentially a survey of various types of methods for the determination of nitrite, a thorough study of the application of any method to some particular mixture has not been attempted. For each basic procedure variables have been adjusted to give a maximum sensitivity with one particular set of reagents. Consequently, most of the methods can be further improved with respect to sensitivity, selectivity, reproducibility, *etc.* Dependent on the type of mixture to be analysed variables could be adjusted so that the procedure would be the most useful.

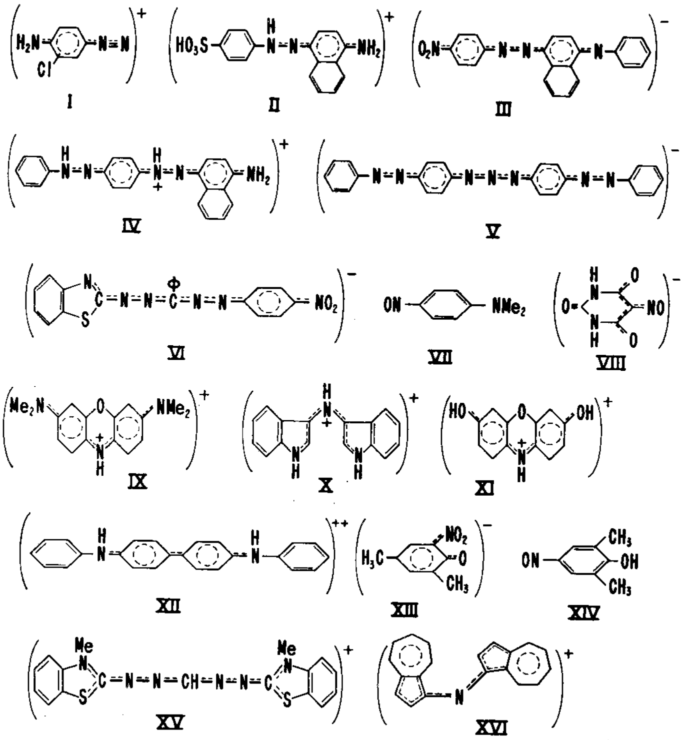


FIG. 1.—Structures of chromogens formed in various procedures.

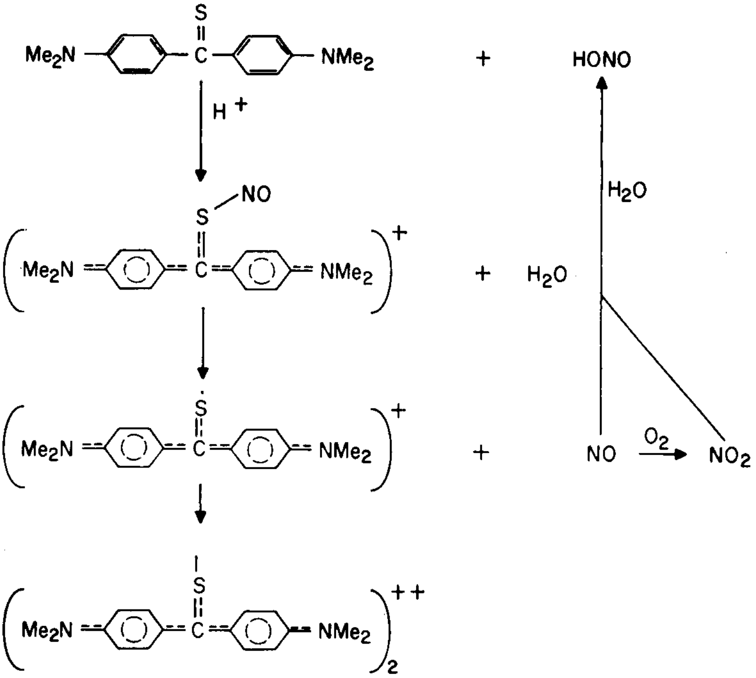


FIG. 2.—Suggested autocatalytic reaction for the determination of nitrite with 4,4′-bis-(dimethylamino)thiobenzophenone.

The various methods are compared in Table I. Only methods making use of the nitrosation or, to a slight extent, the oxidising properties of nitrous acid have been investigated; analytical methods for nitrite precursors, such as nitrates, organic nitro compounds or nitrogen oxides, are not included. Numerous reagents have been investigated. For each type of method only the most sensitive reagents are reported.

Without changing the reagents, the sensitivity of a procedure can be improved in two ways—by increasing the molar absorptivity towards the theoretical or by decreasing the dilution factor (essentially the total volume divided by the test solution volume). In the *p*-aminoacetophenone + 1-naphthol procedure a molar absorptivity of 38000 at the wavelength maximum is obtained. However, the pure dye in the same solvent has a molar absorptivity of 49000 at the same wavelength maximum, so this analytical method could be further improved by an increase in the molar absorptivity.

The following example illustrates an improvement in the dilution factor. Following the absorption of a gas into 10 ml of solution, 1 ml of this solution is analysed in a procedure where the dilution factor is 10. For this whole procedure the dilution factor is 100. On the other hand, if gas is absorbed in 10 ml of a solution of the reagents and the colour is formed directly, the dilution factor is 1. This latter procedure is 100 times as sensitive, if the molar absorptivity is the same in both procedures. However, in the analyses of other types of mixtures a larger dilution factor may be advantageous. Although no attempt has been made to improve the dilution factor in the procedures introduced in this paper, this could be done if the analysis of a particular mixture warranted it.

The determination limit is defined as the number of μg of nitrite in the total volume for which an absorbance of 0·1 in a 1-cm cell is obtained in the analytical procedure. Obviously, this determination limit could be considerably decreased by an increase in the molar absorptivity, a decrease in the dilution factor, or a proportional decrease of all volumes in the procedure. In the last method, assuming no change in molar absorptivity, the lowest determination limit would be readily obtained when the final volume became equivalent to the lowest possible cell volume.

Other important factors are procedural simplicity, colour stability, reproducibility, selectivity, and the linear relation between absorbance and concentration of analysed substance.

Effect of variables

4,4′-*Bis-(dimethylamino)thiobenzophenone procedure:* The distinctive type of absorption spectrum obtained with this procedure is shown in Fig. 3. Optimum intensities were obtained with 0·025–0·05% reagent and with 0·15–0·25% of concentrated hydrochloric acid in the reagent. More than 2% of concentrated hydrochloric acid in the reagent solution gave this solution a green colour. Acetic acid solutions of the thiobenzophenone gave a green solution. This green colour is derived from the cationic salt of the thiobenzophenone. When acetic, phosphoric, methanesulphonic, trifluoroacetic, sulphuric or perchloric acids were substituted for the concentrated hydrochloric acid in the reagent solution, inferior results were obtained. The reagent solution used in the recommended procedure was found to be stable for at least 3 days.

The change in absorbance with time has been measured (Fig. 4). The colour intensity reached a maximum at 30–50 min, and then decreased. A linear relation

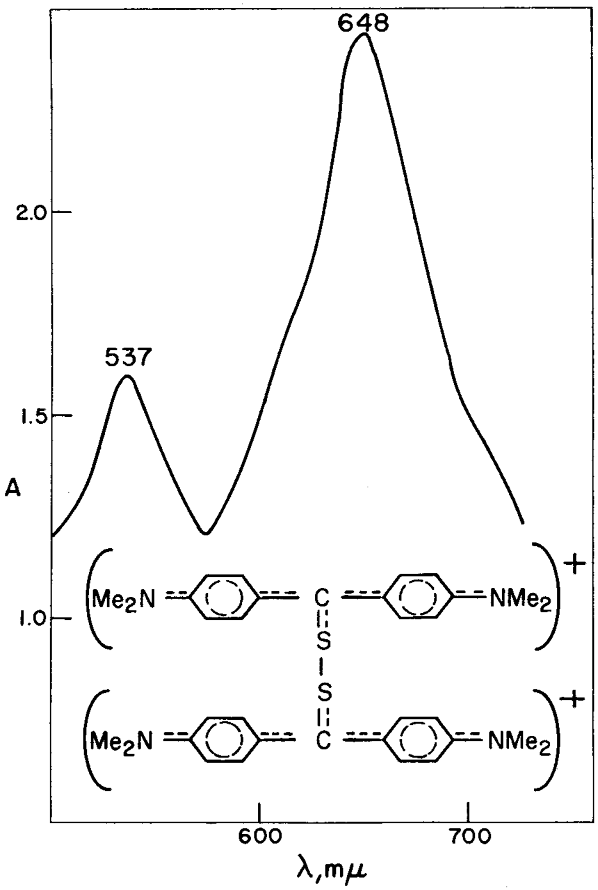


Fig. 3.—Absorption spectrum of chromogen obtained from determination of nitrite (2·30 μg of NO_2^-) with 4,4′-bis-(dimethylamino)thiobenzophenone.

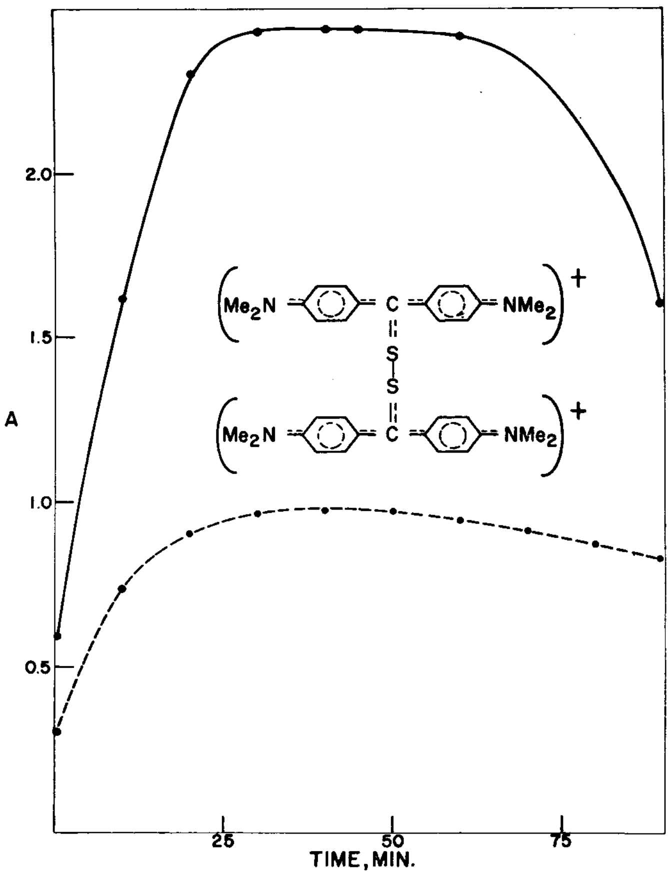


Fig. 4.—Effect of time on absorbance in determination of nitrite with 4,4′-bis-(dimethylamino)thiobenzophenone: ——— 2·30 μg of NO_2^- , — — — 1·15 μg of NO_2.

was found between the absorbance and the concentration of nitrite ion over an extremely wide range of absorbance (Fig. 5).

Negative reactions were obtained with sodium nitrate, ozone, di-t-butylperoxide, t-butylhydroperoxide, cumene hydroperoxide, *p*-menthane hydroperoxide, formaldehyde, acrolein, malonaldehyde, iodoform, iodoacetic acid, potassium iodide, pyridine-*N*-oxide, and *N*-nitrosomethylurea. Positive results were obtained with some inorganic oxidising agents (Table II). For the analysis of any of these miscellaneous oxidising agents the procedure would have to be modified to obtain optimum results. Some of these reactions show promise for application to air-pollution analysis.

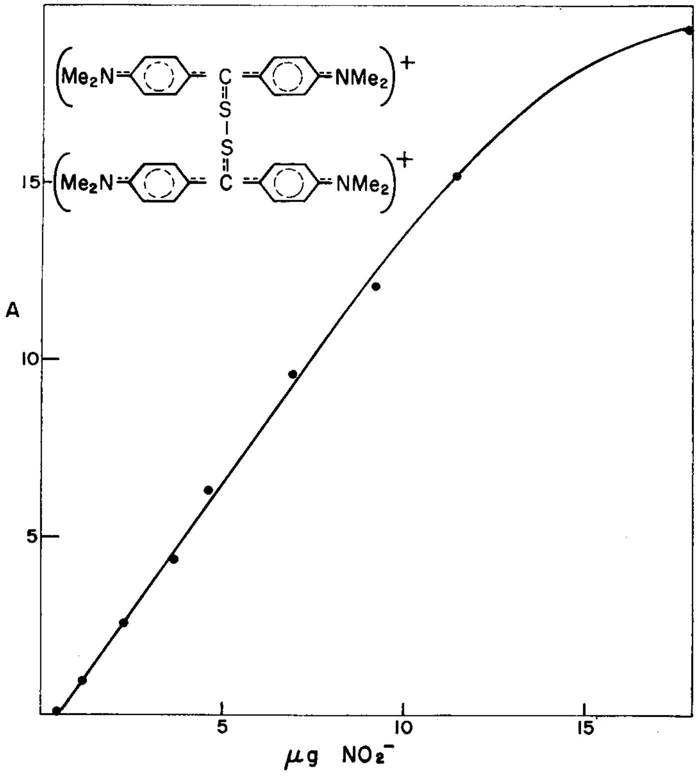


Fig. 5.—Change in absorbance with concentration of nitrite in 4,4′-bis-(dimethylamino)thiobenzophenone (Procedure A).

Table II.—Reaction of oxidising agents in the 4,4′-bis-(dimethylamino)-thiobenzophenone procedure

Oxidising agent	Molarity × 10^4	$\varepsilon \times 10^{-3}$ at λ 648
Potassium periodate	0·1	234
Potassium iodate	0·05	160
Potassium chromate	0·2	65
Copper^{II} chloride	1·0	31
Potassium permanganate	0·05	53
Iron^{III} chloride	2·35	6·6
Iodine	0·1	45[a]

[a] Test solution contained 10% of ethanol

Remainder of procedures: A fairly large group of new methods for the determination of nitrite is introduced. Among these are the azo dye anion, the azulene and the hydrazone methods. The hydrazones, *e.g.*, 3-nitrobenzalphenylhydrazone, are a new type of oxidisable reagent that could prove to be of value eventually in the analysis for oxidising agents. Many other types of hydrazones were found to give brilliant colours with nitrite or nitrate. This type of reagent could be used to analyse for nitrite, nitrate, or both. The hydrazones need to be further studied so as to improve their colour stability and conformity to Beer's law.

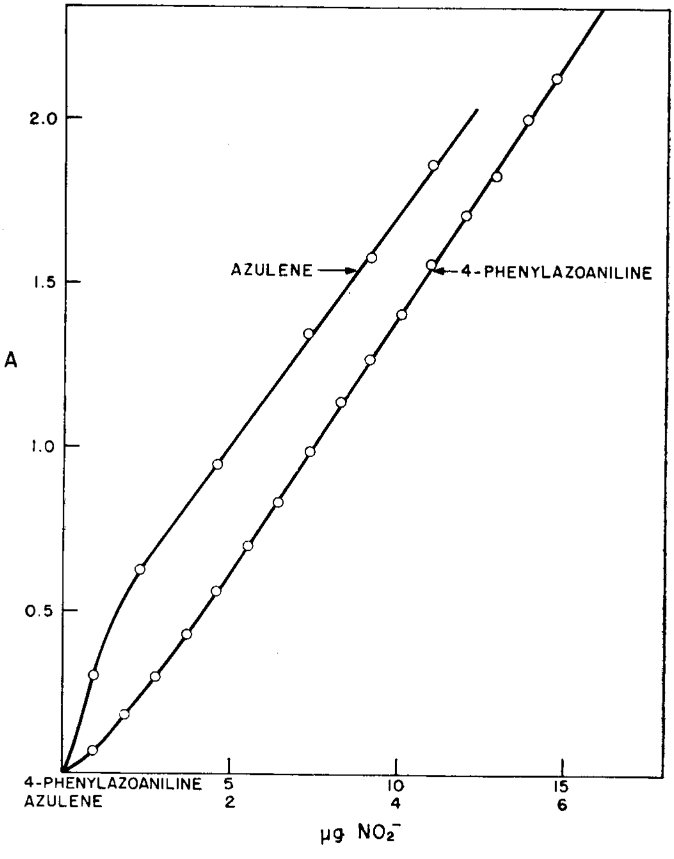


FIG. 6.—Relation between absorbance and concentration of nitrite in the azulene and *p*-phenylazoaniline procedures.

The variables were investigated and chosen so that optimum results were obtained in those procedures that use the following reagents (type of procedure): *p*-nitroaniline + 1-naphthol (C), anthranilic acid + 1-anilinonaphthalene (G), 1-naphthylamine (I), azulene (B), azulene + *p*-nitroaniline (F), and 3-nitrobenzalphenylhydrazone (E). The other reagents listed in Table I were then used in these basic procedures.

The investigated variables were the % reagent, the reagent solvent, the reaction times at room temperature and 100°, the volumes of reagent solution(s) and test solution, and the type and amount of alkali or acid. Numerous reagents were also investigated.

Because variables were not investigated thoroughly for the remainder of the procedures, these procedures might be improved by a more thorough investigation.

Beer's law was followed in most of the procedures except the azulene, 4-phenylazoaniline (see Fig. 6), and 4-phenylazoaniline + benzaldehyde 2-benzothiazolylhydrazone methods. These methods gave a straight-line relationship between absorbance and concentration at appropriate ranges in concentration. It is believed that with some modification the colours in these methods could be made to follow Beer's law.

In all methods involving the formation of diazonium salts some of the interferences could be oxidising and reducing agents, some alkyl nitrites, nitrosamines, and nitroalkanes. In procedures (C) and (F) t-butyl nitrite and *N*-nitrosocarbazole react readily, but other alkyl nitrites and nitrosamines give weak to negative reactions. The azo dye anion, formazan anion, and azulene azo dye cation procedures have the advantage over the Griess type reagents of fast colour formation.

In the methods that depend on the oxidation of the reagent by nitrous acid to a coloured compound, nitric acid and other oxidising reagents would react also, and reducing agents could be expected to interfere.

The simplicity of some of the procedures is adversely affected by the use of heat, as in the *p*-phenylazoaniline procedure;[3] by the use of hydrogen chloride gas, as in the *p*-phenylazoaniline + 1-naphthylamine procedure;[2] or by a necessary standing time, as in the non-azulenic azo dye cation procedures. Most of the procedures need only a short time for colour development; others, like the Griess-type, require about 15 min. A quick colour development would be advantageous in automated analyses.

In the azulene method, nitrate and acrolein gave negative results; malonaldehyde gave a band at 709 mμ with a molar absorptivity of 137,000; and formaldehyde gave a band at 614 mμ with a molar absorptivity less than 10,000. This method could be improved with respect to colour stability and conformity to Beer's law.

In the pyrrole and indole methods, nitrate and formaldehyde gave essentially negative results; malonaldehyde reacted positively, *e.g.*, with pyrrole a band was obtained at 563 mμ with a molar absorptivity of 24,000.

In the resorcinol method formaldehyde and acrolein gave negative results; nitrate gave a band at 555 mμ, ε 543; and malonaldehyde gave bands at 511 and 558 mμ, ε 11,000 and 7000, respectively. These last two compounds could therefore be considered interferences.

It is believed that some of the methods could be used directly or could be improved and modified to fit some particular application in the determination of nitrite or its precursors in a particular mixture.

Comparison of various methods

Many of the comparative results are given in Table I. The method with the lowest determination limit is the azulene procedure. The thiobenzophenone method gave the highest molar absorptivity. Apparently the nitrite ion is regenerated and reacts with the reagent again in a continuous cyclic reaction. Eventually, fantastic sensitivities should be possible in this new type of spectral analytical procedure. It should be possible to develop autocatalytic spectrophotofluorometric methods sensitive to picogram amounts of material. In the future we hope to study the application, in a modified form, of some of these procedures to the determination of nitrites and oxidants, such as ozone, hydroperoxides, *etc.*

CONCLUSION

The choice of any of these methods for the analysis of a mixture would depend on a favourable combination of factors such as sensitivity, selectivity, simplicity, colour stability, precision, conformity to Beer's law, *etc.* Any one of these variables could be the deciding factor in choosing an analytical method. Usually the selectivity is very important. In that case the chosen method is one whose interferences are absent in the mixture to be analysed. The types of interferences in the different methods are discussed in the section on *Comparison of various methods.*

The methods with the shortest procedural time are the azo dye anion, the benzaldehyde 2-benzothiazolylhydrazone and the azulene azo dye methods. For these methods approximately 3–4 min is necessary for a run. In the *p*-phenylazoaniline procedure 6 min is necessary for a run. In most of these methods the colour stability is also good.

Further papers in this series will introduce various types of highly sensitive free radical methods capable of being used with electron paramagnetic resonance spectral techniques, as well as many types of spectrophotofluorometric and autocatalytic methods capable of application in the nanogram and picogram ranges.

Zusammenfassung—Eine ausgedehnte Ubersicht der Methoden zur photometrischen Bestimmung von Nitrit wird gegeben. 52 Methoden, von denen etwa 36 neu sind, werden im Hinblick auf molare Absorption, Selektivität, Empfindlichkeit, Einfachkeit, Farbstabiltät und Befolgung von Beer's Gesetzt verglichen. Eine neue, auf dem Prinzip der Autokatalyse beruhende Methode wird eingeführt. Ein molarer Extinktionskoeffizient von 620 000 wird erhalten. Es wird gezeigt, dass über 20 neue Methoden höhere Extinktionskoeffizienten geben, als mit verschiedenen Typen von Griess'schem Reagens erhalten werden. Sie sind daher einer weiteren Studie wert.

Résumé—Le but de cet article est de recenser d'une manière concise les méthodes spectrophotométriques de détermination des nitrites. Cinquante deux méthodes, dont 36 nouvelles sont comparées, en fonction de l'absorption moléculaire, de la sélectivité, de la sensibilité, de la simplicité, de la stabilité des colorations et de la conformité à la loi de Beer. Description d'un nouveau procédé spectrophotométrique —autocatalytique—, qui permet d'atteindre une absorption moléculaire de 620,000. Parmi ces méthodes nouvelles, une vingtaine fournissent une absorption moléculaire plus élevée que celles obtenues par l'un des réactifs de type Griess. Ainsi, ces méthodes méritent des recherches approfondies pour l'intérêt qu'elles présentent dans l'analyse des nitrites et des composés pouvant évoluer en nitrites.

REFERENCES

[1] E. Sawicki, J. Pfaff and T. W. Stanley, *Revista de la Universidad Industrial de Santander*, 1962, to be published
[2] E. Sawicki and J. L. Noe, *Analyt. Chim. Acta*, 1961, **25**, 166.
[3] E. Sawicki, T. W. Stanley and W. C. Elbert, *Analyt. Chem.*, 1962, **34**, 297.
[4] *Idem, Mikrochim. Acta*, 1961, 891.
[5] B. E. Saltzman, *Analyt. Chem.*, 1954, **26**, 1949.
[6] M. B. Jacobs and S. Hochheiser, *ibid.*, 1958, **30**, 426.

[7] E. F. Kuemmel and M. G. Mellon, *ibid.*, 1956, **28,** 1674.
[8] A. Lecco and R. P. Saper, *Bull. soc. chim. Beograd.*, 1957, **22,** 161.
[9] E. H. Miller, *Analyst*, 1912, **37,** 345.
[10] J. L. Lambert and F. Zitomer, *Analyt. Chem.*, 1960, **32,** 1684.
[11] H. A. C. Montgomery and J. F. Dymock, *Analyst*, 1962, **87,** 374.
[12] J. M. Pappenhagen and M. G. Mellon, *Analyt. Chem.*, 1953, **25,** 341.
[13] F. L. Fisher, E. R. Ibert and H. F. Beckman, *ibid.*, 1958, **30,** 1972.
[14] A. M. Hartley and R. I. Asai, *J. Amer. Water Works Assoc.*, 1960, **52,** 255.
[15] A. P. Altshuller and A. F. Wartburg, *Analyt. Chem.*, 1960, **32,** 174.
[16] K. Hutchinson and D. F. Boltz, *ibid.*, 1958, **30,** 54.
[17] F. Feigl, D. Goldstein and A. R. Rosell, *Z. analyt. Chem.*, 1957, **158,** 423.

Talanta, 1963, Vol. 10, pp. 657 to 665. Pergamon Press Ltd. Printed in Northern Ireland

AMMONIUM HEXANITRATOCERATE(IV) AS AN OXIDISING AGENT—II*

POTENTIOMETRIC TITRATION OF OXALIC AND MANDELIC ACIDS AT ROOM TEMPERATURE

G. GOPALA RAO, K. S. MURTY and P. V. KRISHNA RAO
Department of Chemistry, Andhra University, Waltair, S. India

(*Received* 10 *December* 1962. *Accepted* 1 *January* 1963)

Summary—Conditions have been established for the accurate titration of oxalic and mandelic acids with ammonium hexanitratocerate(IV) at room temperature in a hydrochloric or nitric acid medium with a potentiometric end-point. It has been shown that 0·1*N* or 0·01*N* solutions of the oxidising agent can be standardised very conveniently, using sodium oxalate as a primary standard. The very rapid reaction now observed between cerate and oxalic acid in a hydrochloric acid medium (where the redox potential of cerate is about 1·28 V) is of fundamental significance, because it shows, unambiguously, that the ease of reaction between ammonium hexanitratocerate(IV) and oxalic acid in a nitric or perchloric acid medium is not caused by the higher oxidation potentials of the cerate obtaining in these acid media, as assumed by previous coworkers.

IT is usually believed that the reaction of oxalic acid with cerium^{IV} sulphate in a hydrochloric or sulphuric acid medium is not sufficiently rapid at ordinary temperatures for a direct titration to be possible. Furman[1] showed that the titration of oxalic acid with cerium^{IV} sulphate is not possible in a sulphuric acid medium to a potentiometric end-point even at 50° or 60°. Willard and Young[2] found that the potentiometric titration can be carried out in a hydrochloric acid medium "near the boiling point." They observed further that the same titration is possible at room temperature if iodine monochloride is present as a catalyst. Willard and Young[3] attempted the use of ferroïn in the titration of oxalic acid with cerium^{IV} sulphate; they observed that somewhat satisfactory results are obtained when the titration is carried out in a hydrochloric acid medium at 50° in the presence of iodine monochloride as catalyst.

Although it may be argued that more satisfactory results may be obtained at temperatures higher then 50°, in practice it is not possible to employ a higher temperature because the ferroïn indicator is destroyed at such high temperatures. With reference to this procedure, Smith[4] states that the "sulphatoceric acid solution should not be over 0·5*N* in sulphuric acid. If stronger solutions of sulphuric acid are used in the reagent to be standardised, the addition of this sulphuric acid to the hydrochloric acid solution of the oxalate will cause the reaction to slow in speed to too great an extent. The indicator is not as sharp in its action and the results obtained, less satisfactory." Smith and Getz[5] proposed that the titration of oxalate be carried out in a perchloric acid medium with perchloratocerate in perchloric acid or with nitratocerate in a perchloric acid medium at room temperature, either with a potentiometric end-point or using nitroferroïn as indicator. The feasibility of the titration

---

* Part I: see reference 8.

with nitratocerate or perchloratocerate at room temperature is ascribed by Smith[6] to their higher oxidation potentials. According to him, "solutions of perchlorato- and nitratocerate ions in perchloric and nitric acid solutions, respectively, have been shown to have the oxidation potentials of 1·71 and 1·61 volts at standard state. These potentials might logically be expected to be high enough to cause their reaction with oxalate and arsenite ions to be more rapid at ordinary temperatures than is the case with sulphatocerate solutions in the presence of sulphuric or hydrochloric acid."

Recently, Panduranga Rao and Gopala Rao[7] have shown that the titration of oxalate is feasible at room temperature with cerium^{IV} sulphate provided barium chloride is present in sufficient concentration to remove all of the sulphate ion. They stated that the sulphate ion retards (1) the reduction of ferriin by oxalic acid, and (2) the oxidation of oxalic acid by cerium^{IV}. In the titrations conducted by Panduranga Rao and Gopala Rao, the medium contains hydrochloric acid and the added barium chloride replaces the sulphate ion of cerium^{IV} sulphate by the chloride ion. That the ferriin-oxalic acid reaction is of importance in this titration is further exemplified by the observation of Willard and Young[3] that methylene blue works as a satisfactory indicator in the titration of oxalic acid with cerium^{IV} sulphate in a hydrochloric acid medium in the presence of iodine monochloride as a catalyst even at room temperature.

Subsequently, Gopala Rao, Krishna Rao and Murty[8] proposed a procedure for the titrimetric determination of oxalic acid at room temperature with ammonium hexanitratocerate(IV) in 0·2–0·5*N* hydrochloric acid, using ferroïn as indicator. From the publications of Gopala Rao and coworkers, it appears that it is not the high oxidation potential of the particular cerate ion that matters, but the nature of the accompanying ions and their influence on the speeds of the reactions involved, namely, the reaction between oxalic acid and cerate ion and the reaction between ferriin and oxalic acid. The significant fact that emerges from these publications is that the titration is possible in a hydrochloric acid medium (where according to Smith the redox potential of the cerate ion is only 1·28 V), while it is not possible in a sulphuric acid medium where the redox potential of the cerate ion is definitely higher, being 1·44 V. It thus appears fairly certain that the retardation by the sulphate ion is the important factor to be reckoned with. Recently, Dodson and Black[9] noted that the rate of reaction between oxalic acid and cerium^{IV} sulphate decreases as the concentration of the sulphuric acid is increased, an observation which confirms the earlier findings of Benrath and Ruland.[10]

Because the matter is of fundamental importance, it was decided to investigate the matter further. In order to avoid complications that may be introduced by the presence of the redox indicator ferroïn, titrations of oxalic acid and mandelic acid with ammonium hexanitratocerate(IV) were carried out in a hydrochloric acid medium with a potentiometric end-point. In titrations of 0·05*N* solutions of oxalate in 0·5*N* to 1·0*N* hydrochloric acid with about 0·05*N* solutions of nitratocerate the potential jump at the end-point has been observed to be about 410–440 mV per 0·04 ml of the oxidant, and about 350–390 mV in titrations of 0·01*N* oxalate with about 0·01*N* solutions of nitratocerate. From the potentiometric titration curves, the potential of the cerate-cerous couple in 0·5*N* hydrochloric acid has been observed to be about 1·32 V, which shows that the reacting cerate species is the chloridocerate and not the nitratocerate. Our observations show that the potentiometric titration of even 0·01*N* oxalate solutions can be carried out without any difficulty with ammonium hexanitratocerate(IV) in 1·0–0·5*N* hydrochloric acid media. These results lead us to the conclusion that the reaction of oxalic acid even with a low potential cerate ion, namely, the chloridocerate ion, is very rapid even at room temperature.

EXPERIMENTAL

Reagents

Ammonium hexanitratocerate(IV): Prepared according to the directions of Smith *et al.*[11] Prepare a 0·05*N* solution of the cerate in 1·0*N* nitric acid which has been tested to be free from nitrous acid, and preserve in an amber coloured bottle. Standardise at frequent intervals.

Sodium oxalate: The Guaranteed Reagent of E. Merck, Darmstadt, Germany, was used.

Mandelic acid: A sample (U.S.P., XII) obtained from Mallinkrodt chemical works, U.S.A., was recrystallised and dried. A 0·1*N* solution prepared from this sample was standardised by titration with a standard solution of sodium hydroxide using phenolphthalein as indicator.

Apparatus

Potentiometric titration assembly: Titrations are carried out in a 150–ml Pyrex beaker, with a bright platinum wire as the indicator electrode and a saturated calomel electrode as the reference electrode. The two halves of the cell are connected with a saturated ammonium nitrate bridge. The potentials are measured using a Pye (Junior) potentiometer, graduated in mV, in conjunction with a Cambridge galvanometer connected in parallel with a shunt. During the titrations the mixture is stirred with a B.T.L. stirrer.

RESULTS AND DISCUSSION

An aliquot volume of the standard sodium oxalate solution (0·0507*N*) is taken in a 150-ml Pyrex beaker and enough hydrochloric acid is added to give the desired acid strength when diluted to 50 ml. The mixture is then diluted to 50 ml and titrated with about 0·05*N* ammonium hexanitratocerate(IV) solution, measuring the potentials at suitable intervals. It has been observed that the potentials do not attain steady values immediately after each addition of the oxidant, but show a slight drift, reaching steady values only after 1 min. After the equivalence point is reached, however, the potentials attain steady values in about 10 sec. The observations are recorded in Table I.

TABLE I. POTENTIOMETRIC TITRATION OF SODIUM OXALATE WITH AMMONIUM HEXANITRATOCERATE(IV) IN 1·0*N* HYDROCHLORIC ACID AT ROOM TEMPERATURE (28°)

Cerate added, *ml*	E.m.f (*V*) observed after										
	0 sec	10 sec	20 sec	30 sec	40 sec	50 sec	60 sec	1·5 min	2 min	3 min	5 min
0·00	500	502	506	506	507	507	508	508	509	510	510
1·02	520	525	527	530	532	534	536	537	539	540	540
2·00	545	547	550	553	554	555	556	557	558	559	559
3·00	562	565	567	569	570	571	572	572	573	573	573
4·00	578	580	581	582	583	583	584	586	588	589	589
4·50	592	594	595	594	593	593	593	593	593	593	593
4·70	593	593	593	593	593	593	593	593	594	595	595
4·78	610	606	604	603	603	602	601	601	600	599	599
4·82	750	920	955	970	990	995	1000	1005	1007	1009	1009
4·86	1040	1044	1046	1046	1046	1046	1046	1046	1046	1046	1046
4·90	1055	1057	1058	1058	1058	1057	1057	1057	1056	1055	1053
5·10	1080	1079	1078	1078	1078	1078	1076	1076	1074	1073	1072
7.00	1119	1119	1119	1118	1118	1118	1017	1116	1113	1112	1110
9·64	1134	1131	1130	1130	1129	1129	1128	1128	1126	1125	1123

5·00 ml of sodium oxalate solution ≡ 4·84 ml of cerate solution.

A similar drift in potentials is also observed when the above titration is carried out in 0·5*N* or 1·0*N* nitric acid medium. In view of these observations, potential readings have been taken 1 min after the addition of each portion of cerate solution.

Typical potentiometric titration curves obtained under various experimental conditions are given in Fig. 1. The potential jump at the equivalence point has been observed to be about 410–440 mV for 0·04 ml of the oxidant in the titration of 0·05*N* oxalate with about 0·05*N* cerate solution in 0·5*N* or 1·0*N* hydrochloric acid medium. The method now developed is very convenient for the standardisation of solutions of ammonium hexanitratocerate(IV), using sodium oxalate as a primary standard.

Use of potassium iodide-iodate mixture as catalyst

We have made the interesting observation that the addition of 0·5 ml of a mixed solution of potassium iodide and potassium iodate (both at 0·002*N*) to 50 ml of the titration mixture helps the attainment of steady potentials within 10–15 sec after the addition of each portion of cerate, so that the titration can be made more rapidly. Potassium iodide alone can also be used as a catalyst, but its use involves a slight excess consumption of the oxidant, necessitating appropriate correction. In titrations involving 0·01*N* oxalic acid, 0·1 ml of the catalyst solution is sufficient.

A large number of titrations were carried out in this manner and some typical results are given in Table II. The strengths of cerate solutions determined as described above agree closely with the strengths determined by titrations using standard iron^{II} solutions as described in Part I of this series, the error being ±0·1% for 0·05*N* cerate and ±0·4% for 0·01*N* cerate.

Microtitrations

A solution of 0·01*N* cerate has been freshly prepared by diluting the 0·05*N* cerate solution with the requisite volume of 1·0*N* nitric acid which is free from nitrous acid. The results show that the potentiometric method can be employed for the accurate standardisation of even 0·01*N* solutions of ammonium hexanitratocerate(IV) with standard solutions of sodium oxalate of similar strength. The potential jump at the equivalence point in such titrations has been observed to be about 350–390 mV for 0·04 ml of 0·01*N* cerate solution.

TABLE II. STANDARDISATION OF AMMONIUM HEXANITRATOCERATE(IV) WITH SODIUM OXALATE IN 0·5*N* AND 1·0*N* HYDROCHLORIC ACID

0·05070*N* standard oxalate				0·01015*N* standard oxalate			
Expt. no.	Oxalate taken, *ml*	Cerate required, *ml*	Normality of cerate found	Expt. no.	Oxalate taken, *ml*	Cerate required, *ml*	Normality of cerate found
1.	4·50	4·04	0·05646	1.	1·90	1·76	0·01096
2.	4·66	4·18	0·05652	2.	2·50	2·32	0·01093
3.	5·00	4·50	0·05646	3.	3·60	3·34	0·01094
4.	5·66	5·08	0·05648	4.	4·40	4·08	0·01094
5.	6·86	6·16	0·05645	5.	5·00	4·62	0·01096
6.	1·46	1·31	0·05650	6.	5·50	5·20	0·01093
		Average	0·05648			Average	0·0194

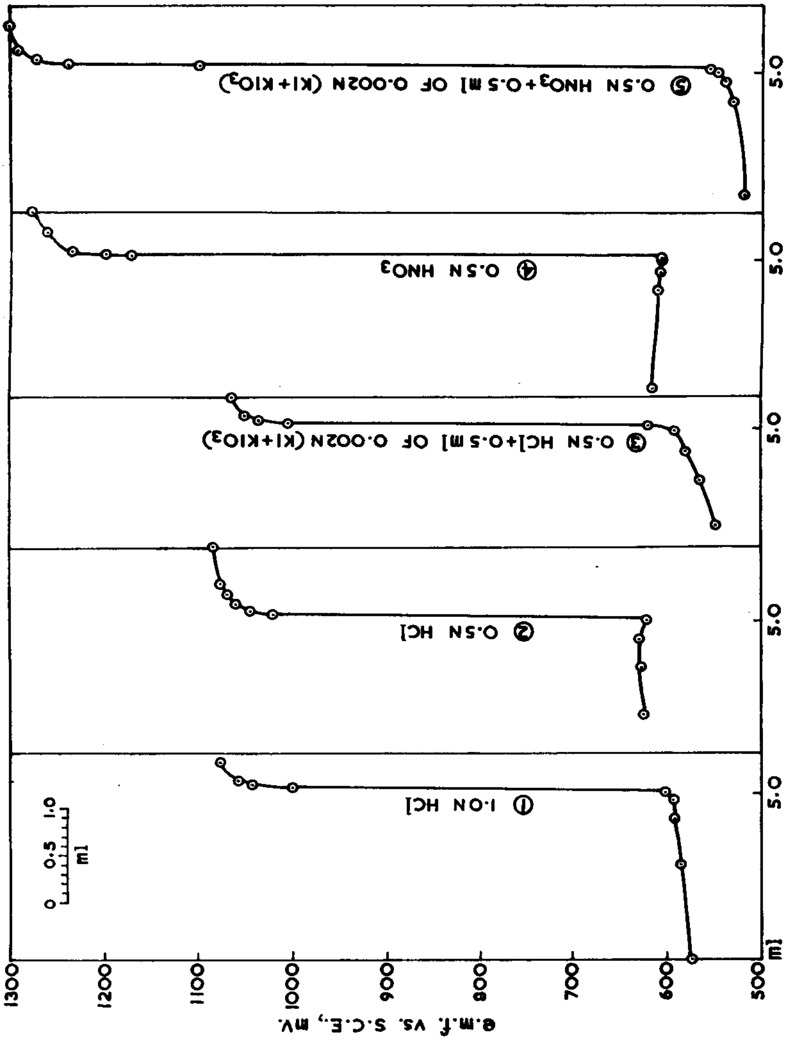


FIG. 1.—Potentiometric titration of oxalic acid.

Experiments have shown that reverse titrations of ammonium hexanitratocerate(IV) with oxalic acid are not possible in hydrochloric acid, because of the reaction between cerate and hydrochloric acid.

Titration of oxalic acid in a nitric acid medium

Sodium oxalate can also be titrated with ammonium hexanitratocerate(IV) solution to a potentiometric end-point in a medium containing nitric acid at concentrations ranging from 0·5*N* to 1·0*N*. As in a hydrochloric acid medium, the potentials attain steady values only 1 min after the addition of each portion of cerate. The addition of 0·5 ml of the potassium iodide-iodate catalyst mixture to 50 ml of the titration mixture, however, assists the attainment of steady potentials within 10–15 sec. The potential break at the equivalence point has been observed to be about 600–640 mV per 0·04 ml of 0·05*N* cerate solution, and about 400–450 mV per 0·04 ml of 0·01*N* cerate solution. From a large number of titrations carried out in this manner, it has been observed that ammonium hexanitratocerate(IV) solution can be standardised with sodium oxalate with an average error of not more than ±0·1% for 0·05*N* solutions and not more than ±0·04% for 0·01*N* solutions. It has also been observed that reverse titrations of ammonium hexanitratocerate(IV) in a nitric acid medium are possible with sodium oxalate.

Potentiometric Titration of Mandelic Acid with Ammonium Hexanitratocerate(IV)

Titrations in a hydrochloric acid medium

During the potentiometric titration of about 0·01*N* to 0.05*N* mandelic acid with about 0·1*N* to 0·05*N* ammonium hexanitratocerate(IV) in a hydrochloric acid medium at room temperature, it has been observed that the concentration of the hydrochloric acid is of great significance. When the concentration of hydrochloric acid is 1·0*N* or 0·5*N* the potential break at the end-point is about 320–400 mV per 0·04 ml of 0·1*N* cerate solution. In 0·1*N* hydrochloric acid medium, the potential break is about 420–470 mV for the same volume of the oxidant. The potentials attain steady values in about 4 min after the addition of each increment of cerate in 1·0*N* hydrochloric acid, in about 3 min in 0·5*N* hydrochloric acid and in about 2 min in 0·1*N* hydrochloric medium. It has also been observed that titrations of 0·01*N* mandelic acid can be carried out with 0·01*N* cerate solution in 0·5*N* hydrochloric acid with some difficulty and more easily in 0·1*N* hydrochloric acid; the titrations are not possible in 1·0*N* hydrochloric acid, because the potentials do not attain steady values even 5 min after the addition of each increment of the oxidant. The addition of 0·5 ml of the potassium iodide-iodate catalyst solution to 50 ml of the titration mixture, however, helps the potentials to attain steady values within 10 to 15 sec. While titrating 0·01*N* solutions of mandelic acid, 0·1 ml of the catalyst solution is sufficient.

Some typical potentiometric curves, obtained under different experimental conditions, are given in Fig. 2. A large number of titrations of mandelic acid have been made in this manner and some typical results are given below in Table III.

The amount of cerate consumed in these titrations corresponds stoichiometrically to the oxidation of mandelic acid to benzaldehyde:

$$C_6H_5CH(OH)COOH \rightarrow C_6H_5CHO + CO_2 + 2H^+ + 2e.$$

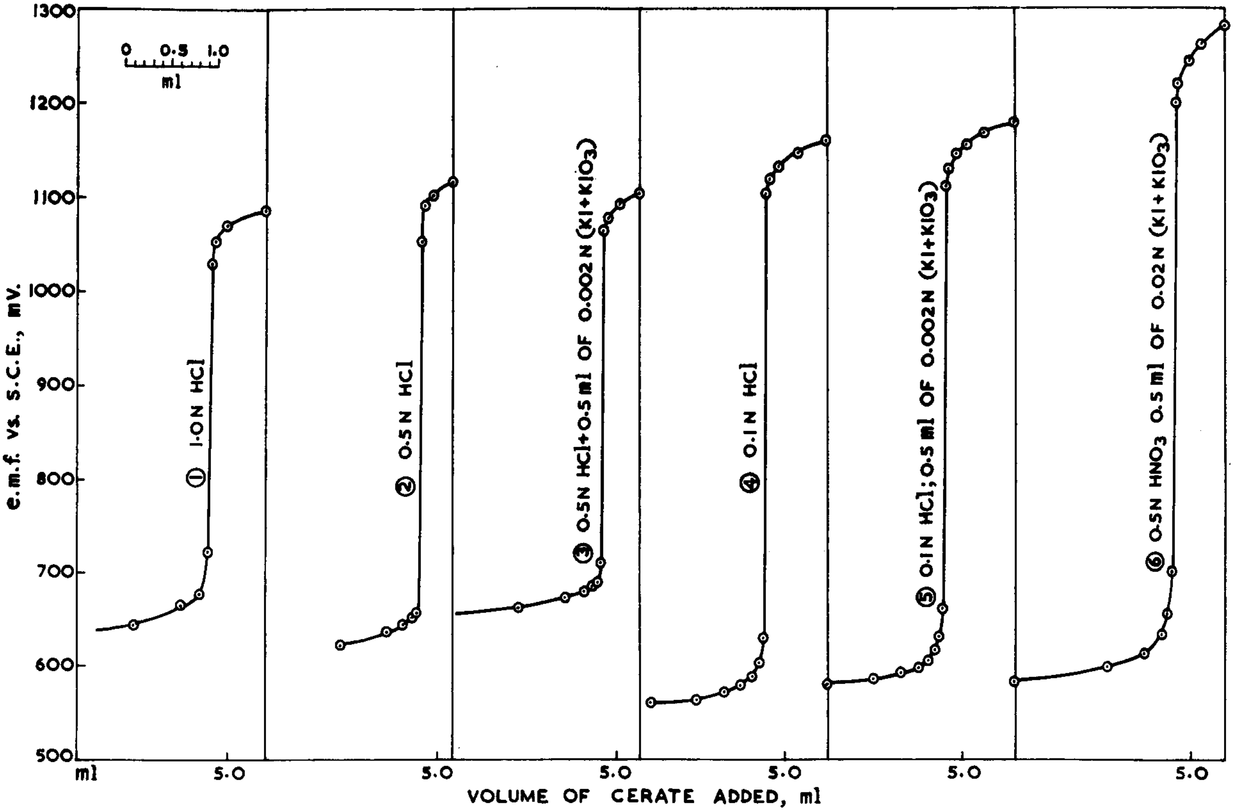


FIG. 2.—Potentiometric titration of mandelic acid.

TABLE III. POTENTIOMETRIC DETERMINATION OF MANDELIC ACID BY AMMONIUM HEXANITRATOCERATE(IV) IN A HYDROCHLORIC ACID MEDIUM

Mandelic acid, *mmoles*			
Taken	Found	Taken	Found
0·2375	0·2372	0·03500	0·03500
0·2225	0·2220	0·03000	0·03002
0·1900	0·1895	0·02500	0·02504
0·3026	0·3022	0·01500	0·01504

Reverse titrations of ammonium hexanitratocerate(IV) with mandelic acid could not be carried out because of the reaction between the cerate and hydrochloric acid.

Titration in a nitric acid medium

It has been observed that the potentiometric titration of 0·1*N* to 0·05*N* mandelic acid cannot be carried out with 0·1*N* or 0·05*N* cerate solution in 1·0*N* or 0·5*N* nitric acid, because the potentials do not attain steady values even 10 min after the addition of each portion of the cerate solution. However, it has been noted that when the concentration of nitric acid is 0·1*N* in the titration mixture, the potentials attain steady values in 1 min.

It has also been observed that the addition of 0·5–1·0 ml of a solution of potassium iodide-iodate mixture to 50 ml of the titration mixture facilitates the attainment of stable potentials within 15 sec, even when the concentration of nitric acid is 0·5*N*. The potential jump at the equivalence point is about 350–450 mV per 0·04 ml of the oxidant. Some typical results out of a large number of determinations of mandelic acid are given in Table IV.

TABLE IV. DETERMINATION OF MANDELIC ACID WITH AMMONIUM HEXANITRATOCERATE(IV) IN 0·5*N* NITRIC ACID.

Mandelic acid, *mmoles*			
Taken	Found	Taken	Found
0·3230	0·3228	0·03650	0·03640
0·3130	0·3132	0·03420	0·03410
0·2590	0·2590	0·02520	0·02516
0·2070	0·2072	0·02480	0·02480
0·1750	0·1752		
0·1270	0·1272	0·01250	0·01246

Reverse titrations of ammonium hexanitratocerate(IV) with mandelic acid have also been attempted. Although the potential quickly attains steady values even without the use of a catalyst, the titres are somewhat low, the error varying from 2·0 to 7·0%. The low consumption of mandelic acid is very likely because a part of the benzaldehyde is undergoing further oxidation when in contact with excess of ammonium hexanitratocerate(IV).

Zusammenfassung—Die Bedingungen zur genauen Titration von Oxal- und Mandelsäure mit Ammonium-hexanitratocerat(IV) bei Raumtemperatur in salpeter- oder salzsaurem Medium mit potentiometrischer Anzeige wurden ausgearbeitet. 0·1 oder 0.01 N Lösungen des Oxydationsmittels können leicht gegen Natriumoxalat als Urtiter eingestellt werden. Die sehr rasche Reaktion, die nun zwischen Cer und Oxalsäure in salzsaurem Medium beobachtet wurde (das Standardpotential von Cer ist hier etwa 1,28 V) is von fundamentaler Bedeutung, da gezeigt wird, dass die Leichtgkeit, mit der Cer und Oxalsäure in salpeter- und perchlorsaurer Lösung reagieren, entgegen der Anschauung von Smith und Mitarbeitern nicht auf das höhere Oxydationspotenial von Cer in diesen Medien zurück zuführen ist.

Résumé—Les conditions d'un dosage précis par virage potentiométrique des acides oxalique et mandélique sont bien connues. On utilise l'hexanitrate-cerate(N) d'ammonium, à température ordinaire et en milieu chlorhydrique ou nitrique. On a pu montrer que l'on pouvait standardiser des solutions à 0,1 N ou 0,01 N d'agent oxydant en utilisant l'oxalate de sodium comme référence standard. La réaction très rapide que l'on peut observer entre le cérate et l'acide oxalique en milieu chlorhydrique (ou le potentiel redox du cérate est d'environ 1,28 V) est d'une importance capitale: elle montre en effet d'une manière univoque que la facilité de réaction entre l'hexanitrate-cérate(IV) d'ammonium et l'acide oxalique en milieu chlorhydrique ou nitrique n'est pas dûe à l'élévation du potentiel d'oxydation du cérate dans ce milieu acide, comme l'affirme Smith et ses collaborateurs.

REFERENCES

[1] N. H. Furman, *J. Amer. Chem. Soc.*, 1928, **50,** 755.
[2] H. H. Willard and P. Young, *ibid.*, 1928, **50,** 1322.
[3] *Idem, ibid.*, 1933, **55,** 3260.
[4] G. F. Smith, *Cerate Oxidimetry*. The G. Frederick Smith Chemical Co., Columbus, Ohio, 1942, p. 39.
[5] G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Analyt.*, 1938, **10,** 304.
[6] G. F. Smith, *loc. cit.*, p. 31.
[7] V. Panduranga Rao and G. Gopala Rao, *Talanta*, 1959, **2,** 370
[8] G. Gopala Rao, P. V. Krishna Rao and K. S. Murty, *ibid.*, 1962, **9,** 835.
[9] V. H. Dodson and A. H. Black, *J. Amer. Chem. Soc.*, 1957, **79,** 3657.
[10] A. Benrath and H. Ruland, *Z. anorg. Chem.*, 1920, **114,** 267.
[11] G. F. Smith, V. R. Sullivan and G. Frank, *Ind. Eng. Chem., Analyt.*, 1936, **8,** 449.

Talanta, 1963, Vol. 10, pp. 667 to 672. Pergamon Press Ltd. Printed in Northern Ireland

A THERMOGRAVIMETRIC PYROLYSIS STUDY OF THE INTERACTION PRODUCTS OF DIHYDROGEN-DI(1,2,3-BENZOTRIAZOLATIUM) HEXACYANOFERRATE(II) WITH CERTAIN ORGANIC AMINES

R. F. WILSON and G. HENRY, JR.
Department of Chemistry, Texas Southern University, Houston 4, Texas, U.S.A.

(*Received* 4 *December* 1962. *Accepted* 1 *February* 1963)

Summary—Thermogravimetric pyrolyses of the interaction products of certain organic amines, tetramethylammonium chloride and piperidine with dihydrogen-di(1,2,3-benzotriazolatium) hexacyanoferrate(II) are reported.

THIS paper results from a thermogravimetric study of the complexed products formed in the interaction of dihydrogen-di(1,2,3-benzotriazolatium) hexacyanoferrate(II) with certain organic amines previously reported.[2] It was found that all of the compounds studied were stable up to at least 50° and that decomposition of the compounds occurred between 50° and 325°. Thermogravimetric analyses of the complexed compounds gave support to the proposed formulae of the products formed in the interaction of tetramethylammonium chloride, piperidine and certain amines with dihydrogen-di(1,2,3,-benzotriazolatium) hexacyanoferrate(II).

EXPERIMENTAL

Apparatus

The thermobalance employed in this study was assembled as described by Wendlandt.[1] Temperature measurements of the furnace were obtained employing an iron-constantan thermocouple using an ice bath as reference junction. The thermocouple was calibrated against the boiling point of water and the melting points of water, tin, lead and antimony; these materials were of 99·98% or greater purity. A double-range portable millivolt potentiometer was used to measure the voltage of the thermocouple. A synchronous motor-driven powerstat was used to vary the voltage.

Procedure

All precipitates were freshly prepared according to the procedure of Wilson and James[2] and they were dried over magnesium perchlorate at room temperature for 24 hr in a vacuum desiccator before being pyrolysed in the furnace of the thermobalance. Decomposition of the compounds was carried out by placing between 20 and 45 mg of each dried precipitate in a platinum boat and suspending the boat in the furnace. The output of the motor-driven powerstat connected directly to the heating elements of the furnace was set initially at 20 V and the input voltage of this powerstat was adjusted to 110 V by means of a second powerstat. The furnace temperature was increased at an average rate of 2°/min. In all pyrolyses, readings on the balance and on the potentiometer were taken at short intervals until a temperature of 500° was obtained.

RESULTS

The pyrolysis curves of compounds 1–10 with the respective formulae: $[CH_3NH_3]_4Fe(CN)_6$, $[(CH_3)_3NH]_4Fe(CN)_6$, $[(C_2H_5)_2NH_2]_4Fe(CN)_6$, $[(CH_3)_2NH_2]_4Fe(CN)_6$, $[(CH_3)_4N]_4Fe(CN)_6$, $[C_6H_4(NH_3)_2]_2(C_6H_4N_2NH)_2Fe(CN)_6$, $[C_6H_4(NH_3)_2]_2Fe(CN)_6$, $[C_2H_5NH_3]_4Fe(CN)_6$, $[C_6H_5NH_3]_2(C_6H_4N_2NH_2)_2Fe(CN)_6$, and $H_2[(CH_2)_5NH_2]_2Fe(CN)_6$, are presented graphically in Figs. 1, 2 and 3, and the analysis of these curves

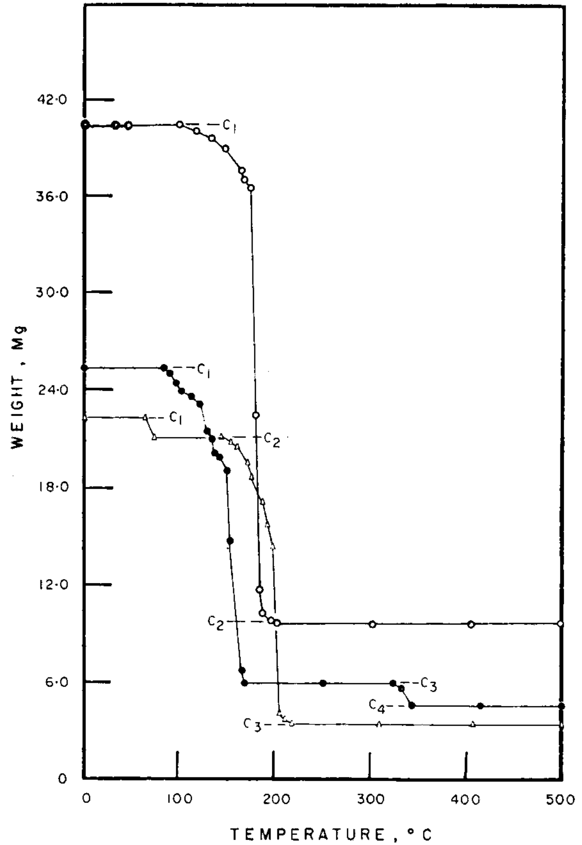


Fig. 1—Thermogravimetric analysis of compounds 1-3:
1. $[CH_3NH_3]_4Fe(CN)_6$, —○—
2. $[(CH_3)_3NH]_4Fe(CN)_6$, —●—
3. $[(C_2H_5)_2NH_2]_4Fe(CN)_6$. —△—

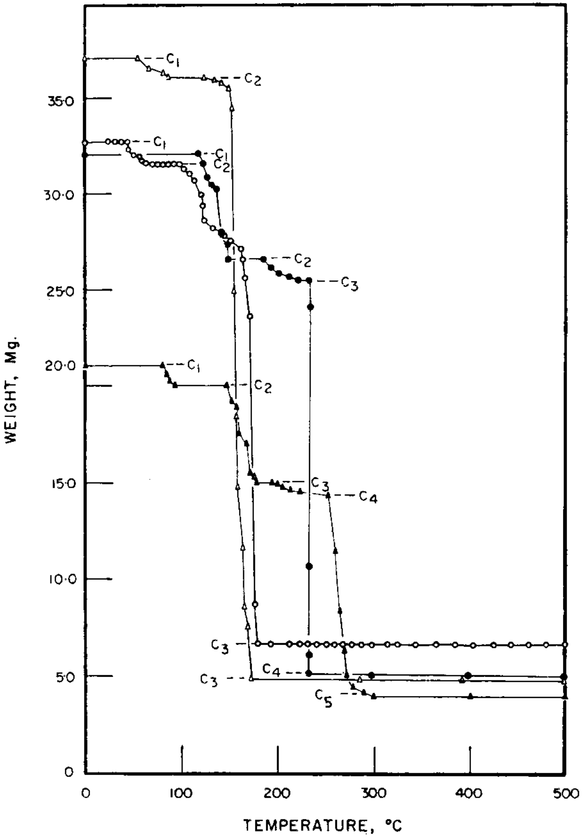


Fig. 2—Thermogravimetric analysis of compounds 4-7:
4. $[(CH_3)_2NH_2]_4Fe(CN)_6$, —○—
5. $[(CH_3)_4N]_4Fe(CN)_6$, —●—
6. $[C_6H_4(NH_3)_2]_2(C_6H_4N_2NH)_2Fe(CN)_6$, —△—
7. $[C_6H_4(NH_3)_2]_2Fe(CN)_6$. —▲—

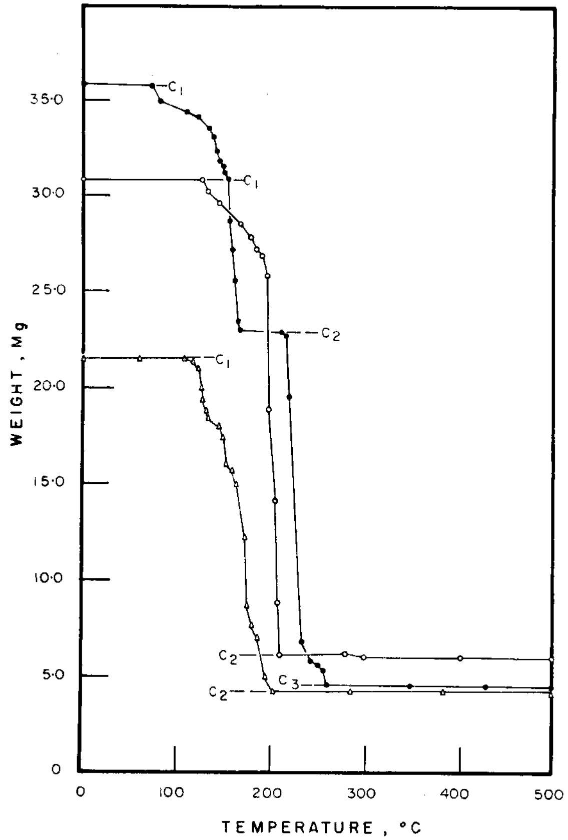


Fig. 3—Thermogravimetric analysis of compounds 8–10:
8. $[C_2H_5NH_3]_4Fe(CN)_6$, ——○——
9. $[C_6H_5NH_3]_2(C_6H_4N_2NH_2)_2Fe(CN)_6$, ——●——
10. $H_2[(CH_2)_5NH_2]_2Fe(CN)_6$. ——△——

is given in Table I. For each compound the weights at plateaus C_2, C_3, C_4 and C_5 were calculated on the basis of the following reactions:

Compound 1

C_2: $4[CH_3NH_3]_4Fe(CN)_6 + 3O_2 \xrightarrow[\Delta]{(100\text{–}190)^\circ}$

$$16CH_3NH_2\uparrow + 16HCN\uparrow + 4(CN)_2 + 2Fe_2O_3$$

Compound 2

C_3 $4[(CH_3)_3NH]_4Fe(CN)_6 \xrightarrow[\Delta]{(85\text{–}170)^\circ} 16(CH_3)_3N\uparrow + 16HCN\uparrow + 4Fe(CN)_2$

C_4: $4Fe(CN)_2 + 3O_2 \xrightarrow[\Delta]{(170\text{–}325)^\circ} 4(CN)_2\uparrow + 2Fe_2O_3$

Compound 3

C_2: $4[(C_2H_5)_2NH_2]_4Fe(CN)_6 \xrightarrow[\Delta]{(65\text{–}75)^\circ}$

$$4HCN\uparrow + 4[(C_2H_5)_2NH][(C_2H_5)_2HN_2]_3Fe(CN)_5$$

C_3: $4[(C_2H_5)_2NH][(C_2H_5)_2NH_2]_3Fe(CN)_5 + 3O_2 \xrightarrow[\Delta]{(145\text{–}210)^\circ}$

$$16(C_2H_5)_2NH\uparrow + 12HCN\uparrow + 4(CN)_2\uparrow + 2Fe_2O_3$$

TABLE I.—PLATEAUS

Compound	C1		C2			C3			C4			C5		
	Initial weight, *mg*	**Temp.** range, °*C*	Weight, *mg*		**Temp.** range, °*C*	Weight, *mg*		Temp. range, °*C*	Weight, *mg*		**Temp.** range, °*C*	Weight, *mg*		**Temp.** range, °*C*
			Calc.	Meas.		Calc.	Meas.		Calc.	Meas.		Calc.	Meas.	
1. $[CH_3NH_3]_4Fe(CN)_6$	40.6	>100	9.5	9.6	<190									
2. $[(CH_3)_3NH]_4Fe(CN)_6$	25.4	> 85				6.1	6.0	170–325	4.5	4.5	<325			
3. $[(C_2H_5)_2NH_2]_4Fe(CN)_6$	22.1	> 65	20.9	20.9	75–145	3.5	3.4	<210						
4. $[(CH_3)_2NH_2]_4Fe(CN)_6$	32.8	> 55				6.6	6.6	<180						
5. $[(CH_3)_4N]_4Fe(CN)_6$	32.1	>120				25.7	25.7	225–235	5.0	5.0	<235			
6. $[C_6H_4(NH_3)_2]_2(C_6H_4N_2NH)_2Fe(CN)_6$	37.2	> 60				4.4	4.5	<150						
7. $[C_6H_4(NH_3)_2]_2Fe(CN)_6$	21.0	> 80						80–245	14.4	14.4	250–300	3.9	3.9	<300
8. $[C_2H_5NH_3]_4Fe(CN)_6$	30.8	>130	6.2	6.3	<210									
9. $[C_6H_5NH_3]_2(C_6H_4N_2NH_2)_2Fe(CN)_6$	35.8	> 75	23.1	23.0	<170	4.5	4.4	215–260						
10. $H_2[(CH_2)_5NH_2]_2Fe(CN)_6$	21.4	>115	4.4	4.4	<205									

Compound 4

$$C_3\text{: } 4[(CH_3)_2NH_2]_4Fe(CN)_6 + 3O_2 \xrightarrow[\Delta]{(55\text{–}180)^\circ}$$
$$16(CH_3)_2NH\uparrow + 16HCN\uparrow + 4(CN)_2\uparrow + 2Fe_2O_3$$

Compound 5

$$C_3\text{: } 4[(CH_3)_4N]_4Fe(CN)_6 \xrightarrow[\Delta]{(120\text{–}225)^\circ} 4(CH_3)_4NCN\uparrow + 4[(CH_3)_4N]_3Fe(CN)_5$$

$$C_4\text{: } 4[(CH_3)_4N]_3Fe(CN)_5 + 3O_2 \xrightarrow[\Delta]{(225\text{–}235)^\circ} 12(CH_3)_4NCN\uparrow + 4(CN)_2\uparrow + 2Fe_2O_3$$

Compound 6

$$C_3\text{: } 4[C_6H_4(NH_3)_2]_2(C_6H_4N_2NH)_2Fe(CN)_6 + 3O_2 \xrightarrow[\Delta]{(60\text{–}150)^\circ}$$
$$16HCN\uparrow + 8C_6H_4(NH_2)_2\uparrow + 8C_6H_4N_2NH\uparrow + 4(CN)_2\uparrow + 2Fe_2O_3$$

Compound 7

$$C_4\text{: } 4[C_6H_4(NH_3)_2]_2Fe(CN)_6 \xrightarrow[\Delta]{(80\text{–}245)^\circ}$$
$$4C_6H_4(NH_2)_2\uparrow + 4HCN\uparrow + 4H[C_6H_4(NH_3)_2]Fe(CN)_5$$

$$C_5\text{: } 4H[C_6H_4(NH_3)_2]Fe(CN)_5 + 3O_2 \xrightarrow[\Delta]{(250\text{–}300)^\circ}$$
$$12HCN\uparrow + 4(CN)_2\uparrow + 4C_6H_4(NH_2)_2\uparrow + 2Fe_2O_3$$

Compound 8

$$C_2\text{: } 4[C_2H_5NH_3]_4Fe(CN)_6\ 3O_2 \xrightarrow[\Delta]{(130\text{–}210)^\circ}$$
$$16C_2H_5NH_2\uparrow + 16HCN\uparrow + 4(CN)_2\uparrow + 2Fe_2O_3$$

Compound 9

$$C_2\text{: } 4[C_6H_5NH_3]_2(C_6H_4N_2NH_2)_2Fe(CN)_6 \xrightarrow[\Delta]{(75\text{–}170)^\circ}$$
$$16HCN\uparrow + 4C_6H_4N_2NH\uparrow + 4[(C_6H_5NH_2)_2(C_6H_4N_2NH)]Fe(CN)_2$$

$$C_3\text{: } 4[(C_6H_5NH_2)_2(C_6H_4N_2NH)]Fe(CN)_2 + 3O_2 \xrightarrow[\Delta]{(215\text{–}260)^\circ}$$
$$4C_6H_4N_2NH\uparrow + 8C_6H_5NH_2\uparrow + 4(CN)_2\uparrow + 2Fe_2O_3$$

Compound 10

$$C_2\text{: } 4H_2[(CH_2)_5NH_2]_2Fe(CN)_6 + 3O_2 \xrightarrow[\Delta]{(115\text{–}205)^\circ}$$
$$16HCN\uparrow + 8(CH_2)_5NH\uparrow + 4(CN)_2\uparrow + 2Fe_2O_3$$

DISCUSSION

During the course of study of the products resulting from the interaction of dihydrogen-di(1,2,3-benzotriazolatium) hexacyanoferrate (II) with certain aliphatic and aromatic organic amines, piperidine and tetramethylammonium chloride, thermogravimetric pyrolyses of several of these complexed compounds have been carried out. Final decomposition of the complexed amine compounds in the temperature range of 50° to 325°, gave iron^{III} oxide, hydrogen cyanide, cyanogen, the respective amine and in two instances 1,2,3-benzotriazole.

A general reaction for compounds 1–4 and 8 may be written as

$$4[(R)_xNH_y]_4Fe(CN)_6 + 3O_2 \xrightarrow[\Delta]{(55\text{–}325)^\circ}$$
$$16[(R)_xNH_{y-1})]\uparrow + 16HCN\uparrow + 4(CN)_2\uparrow + 2Fe_2O_3$$

where $[(R)_xNH_{(y-1)}]$ is used in place of the amines in compounds 1–4 and 8, and x and y may each assume positive integral values of 1, 2 or 3.

A general reaction for compounds 6,7,9 and 10 may be written as

$$4H_x[(R)_y(NH_z)_s]_2(R'H_t)_uFe(CN)_6 + 3O_2 \xrightarrow[\Delta]{(60-300)^\circ}$$
$$16HCN\uparrow + 4(CN)_2\uparrow + 2Fe_2O_3 + 8H_x[(R)_y[NH_{(z-1)}]_s]\uparrow + 4u([R'H)_{(t-1)}]$$

where R is used in place of $C_6H_4<$, C_6H_5- and the $(CH_2)_5$- groups, R′ is used in place of the 1,2,3-benzotriazole molecule, and $R'H^+$ is used in place of the 1,2,3-benzotriazolatium ion. The respective values that the subscriptions x, y, z, s, t and u may assume are: 0 or 2, 1 or 5, 2 or 3, 1 or 2, 0 or 1 and 0 or 2.

Acknowledgment—The authors wish to express their sincere thanks to the Robert A. Welch Foundation for a grant, which supported this thermogravimetric study.

Zusammenfassung—Die thermogravimetrische Pyrolyse der Reaktion von gewissen organischen Aminen, Tetramethylammoniumchloride und Piperidin mit Dihydrogen-di(1,2,3-beztriazolatium)-hexacyanoferrat(II) wird studiert.

Résumé—On donne les résultats concernant les pyrolyses thermogravimétriques et les produits obtenus par interaction de l'hexacyanoferrate(II) de dihydrogeno-(benzo-1,2,3-triazolatium) avec certaines amines organiques, le chlorure de tétraméthylammonium, et la pipéridine.

REFERENCES

[1] W. W. Wendlandt, *Analyt. Chem.*, 1955, **27,** 1277.

[2] R. F. Wilson and J. James, *Z. anorg. Chem.*, 1962, **315,** 236.

Talanta, 1963, Vol. 10, pp. 673 to 678. Pergamon Press Ltd. Printed in Northern Ireland

ANION EXCHANGE OF URANIUM, THORIUM, IRON AND ALUMINIUM IN MINERAL ACID-ETHER SOLUTIONS

SEPARATION OF URANIUM FROM THORIUM, ALUMINIUM AND IRON

S. URUBAY, J. KORKISCH and G. E. JANAUER*
Analytical Institute of the University of Vienna, Austria

(*Received* 14 *December* 1962. *Accepted* 2 *February* 1963)

Summary—The adsorption behaviour is described of uranium, thorium, iron^{III} and aluminium on the strongly basic anion exchanger Dowex 1 in mixtures of ethers with hydrochloric or nitric acid. The distribution coefficients of these elements have been determined in diethyl and di-isopropyl ether as well as in dioxan. Based on these results separation methods for uranium, thorium, iron and aluminium have been developed.

DIETHYL ETHER together with nitric acid has been extensively employed as a solvent for the chromatographic separation and isolation of uranium and thorium by means of paper strips,[1] thick filter paper[2] and cellulose columns.[3–9] Better separation is claimed when substituting part of the cellulose by activated aluminium oxide[10–11] or part of the ether by light petroleum.[12] Some workers in this field recommend a silicon dioxide column[13] whereas others use methyl isobutyl ketone or isobutyl acetate as a solvent.[14] All of these methods have in common that nitric acid is used as the aqueous portion of the solvent because of the high solubility of uranyl nitrate in the solvents employed. In the present work the distribution between uranium, thorium, aluminium and iron dissolved in ether-mineral acid mixtures and the strongly basic anion exchanger Dowex 1 has been investigated. From the results obtained in mixtures of diethyl ether or dioxan with nitric acid two column methods for the quantitative separation of these elements were developed.

EXPERIMENTAL

Reagents

Anion-exchange resin: The strongly basic resin Dowex 1, X8 (100–200 mesh, chloride or nitrate form) was used. After washing with 1*M* hydrochloric or 6*M* nitric acid and removal of acid by washing with water and methanol, it was dried by exposure to the air.

Standard uranium solution: Prepared by dissolving an exactly weighed amount of $(UO_2)(NO_3)_2 \cdot 6H_2O$ in 6*M* nitric acid so that the solution contained 10 mg of uranium/ml.

Standard thorium solutions: Prepared as previously described.[15]

Solutions containing 1 mg of uranium or thorium/ml were prepared from the standard solutions by dilution with water. Standard solutions of iron^{III} and aluminium in nitric or hydrochloric acid solution were employed. Reagent grade diethyl ether, di-isopropyl ether and dioxan were used.

Methods of quantitative determination and apparatus

For the quantitative determination of thorium, iron and aluminium spectrophotometric methods using the azo dye Solochromate Fast Red[16] were employed using a Beckman spectrophotometer model B. Uranium determinations were either performed polarographically or fluorimetrically.[17] For this purpose a Polarecord 216, Metrohm AG polarograph and a Galvanek Morrison, Mark V fluorimeter were employed. The ion-exchange columns used for the separation experiments were of the same type and dimensions as earlier reported.[17]

---

* Present address: Clarkson College of Technology, Potsdam, N.Y., U.S.A.

Determination of distribution coefficients

The distribution coefficients of uranium, thorium, iron and aluminium were measured in hydrochloric and nitric acid–ether mixtures of varying composition. For the preparation of these mixtures either one or other of the two ethers which are immiscible with water (i.e., diethyl or di-isopropyl ether) were mixed in different ratios with 12*M* hydrochloric or 10*M* nitric acid and shaken until equilibrium was attained. For the determination of the distribution coefficients an aliquot portion (usually 10 ml) of the ether phase saturated with acid was employed. Aliquot portions of the solutions containing 1 mg of uranium or thorium/ml were evaporated to dryness on a water bath (Erlenmeyer flask with ground stopper). To the residue 10 ml of the ether phase of a certain acidity were added and the solution equilibrated with 0·5 g of the resin (either chloride or nitrate form, depending on the acid used) for 15 hr (shaking machine). Thereafter the resin was filtered off and uranium or thorium determined in an aliquot portion of the filtrate. From the results thus obtained the distribution coefficients[17] and separation factors were calculated. The results shown in Figs. 1 and 2 were obtained by applying this working procedure. Because dioxan is completely miscible in many ratios with

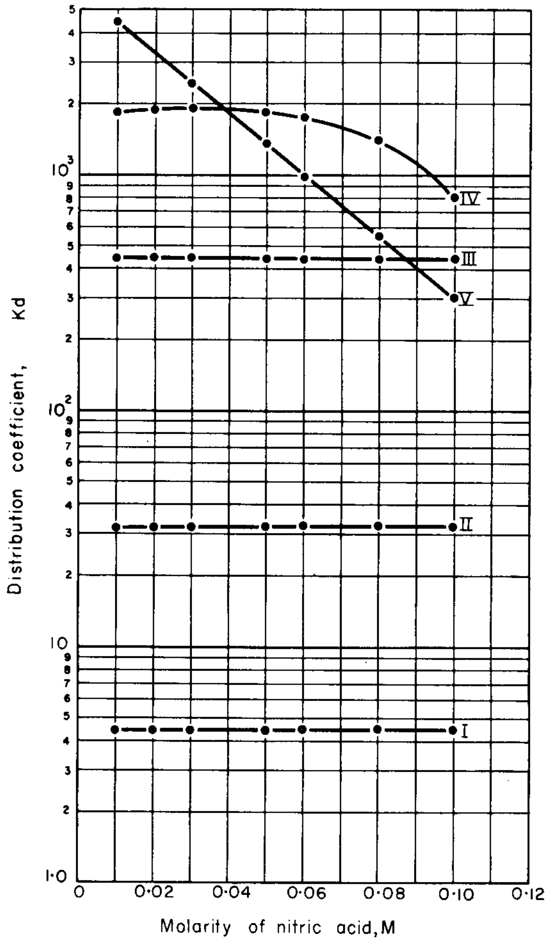


FIG. 1.—Effect of acidity on Kd in ether–nitric acid mixtures:
I—Uranium in diethyl ether,
II—Uranium in di-isopropyl ether,
III—Thorium in diethyl ether,
IV—Aluminium in diethyl ether,
V—Iron in diethyl ether.

aqueous hydrochloric or nitric acid the distribution coefficients were determined in the same way as has been described earlier for aliphatic alcohols.[17]

Column operations

Based on the results shown in Figs. 3 and 4, the following separation procedures were developed:

1. *In diethyl ether-nitric acid medium* (separation of uranium from thorium, iron and aluminium). After washing the resin bed with 50 ml of 1*M* nitric acid the resin was pretreated with 50 ml of ether 0.03*M* in nitric acid. As the sorption solution 50 ml of an ether-nitric acid mixture of the same acidity containing uranium, thorium, iron and aluminium were employed. This solution was passed through the column at a flow rate of 0.5 ml/min. During this operation iron, aluminium and thorium were quantitatively adsorbed by the resin whereas uranium passed into the effluent. After washing the resin with 50 ml of ether-nitric acid mixture of the same composition as that used for pretreatment, the combined effluents were evaporated to dryness on a water bath (because ether-nitric acid mixtures easily explode on heating, prior removal of ether at room temperature is advisable). Uranium in the residue was then determined fluorimetrically. For the elution of thorium, aluminium and iron, 50 ml of 1*M* nitric acid were employed. In Table I the results of a series of such ion-exchange separations are shown.

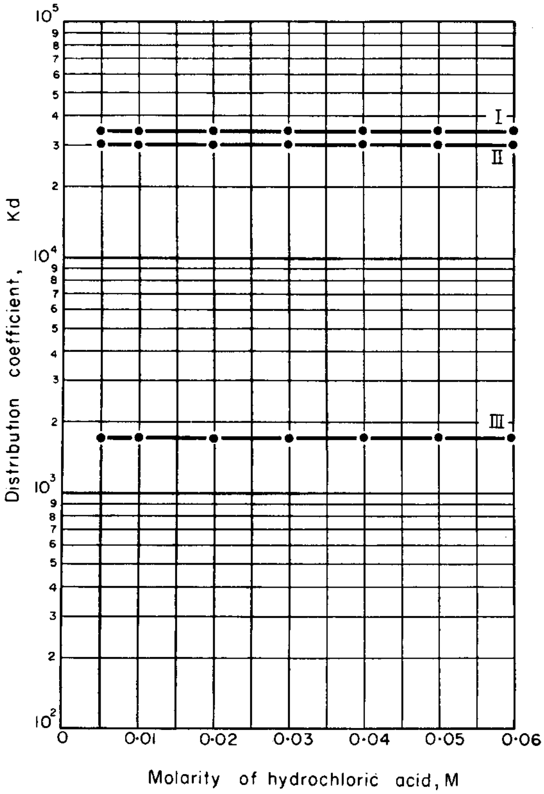


FIG. 2.—Effect of acidity on Kd in ether-hydrochloric acid mixtures:
I—Uranium in diethyl ether,
II—Uranium in di-isopropyl ether,
III—Iron in diethyl ether,

2. *In dioxan-nitric acid medium* (separation of uranium from thorium). After washing the resin with 50 ml of 1*M* nitric acid, the resin was pretreated with 50 ml of a mixture consisting of 90% of dioxan and 10% of 6*M* nitric acid, then the sorption solution (45 ml of dioxan + 5 ml of 6*M* nitric acid) containing uranium and thorium was passed through the column at a flow rate of 0.5 ml/min. During this process thorium is adsorbed by the resin whereas uranium passes into the effluent. After washing the resin with 50 ml of dioxan-nitric acid mixture of the same composition as that used for pretreatment, the thorium was eluted with 100 ml of 1*M* nitric acid. In Table II the results of a series of such ion-exchange separations are shown.

TABLE I—SEPARATION OF URANIUM FROM THORIUM, IRON AND ALUMINIUM IN DIETHYL ETHER–NITRIC ACID MEDIUM

Amounts used, *μg*		Amounts used, *mg*		Amounts recovered, *μg*		Amounts recovered, *mg*	
U	Th	Fe	Al	U	Th	Fe	Al
10	50	10	10	10	49·5	10·1	10
10	50	10	10	10	48·0	10·2	10
10		10	10	9·9		9·9	10
10		10	10	9·8		10·0	10·1
10		10		10·1		9·9	
10		10		10·1		9·8	
10			10	9·8			9·9
10			10	10·0			10·0
100	50	10	10	98·5	51·5	10·1	9·9
1,000	100	10	10	995·4	98·3	9·8	10·1

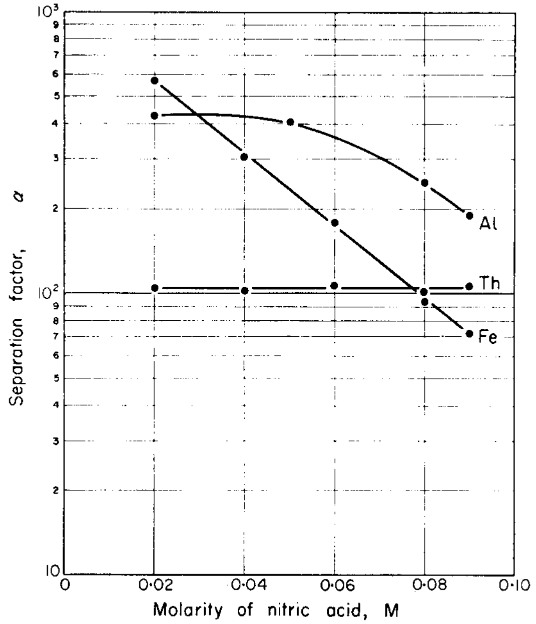


Fig. 3—Separation factors in diethyl ether–nitric acid mixtures.

RESULTS

Figs. 1 and 2 show the effect of acidity on the distribution coefficients of uranium, thorium, iron and aluminium. From these figures it can be seen that the distribution coefficients of uranium and thorium are independent of the acidity which is not the case, however, when aliphatic alcohols are used.[17]

Because the chlorides of thorium* and aluminium are only slightly soluble in hydrochloric acid–ether mixtures no curves could be obtained in such media. Also, because of solubility reasons the Kd-measurements in di-isopropyl ether had to be confined to uranium only.

---

* At a ratio of 1:1 of diethyl ether to 12*M* hydrochloric acid the solubility is higher whereas the adsorption is negligible.

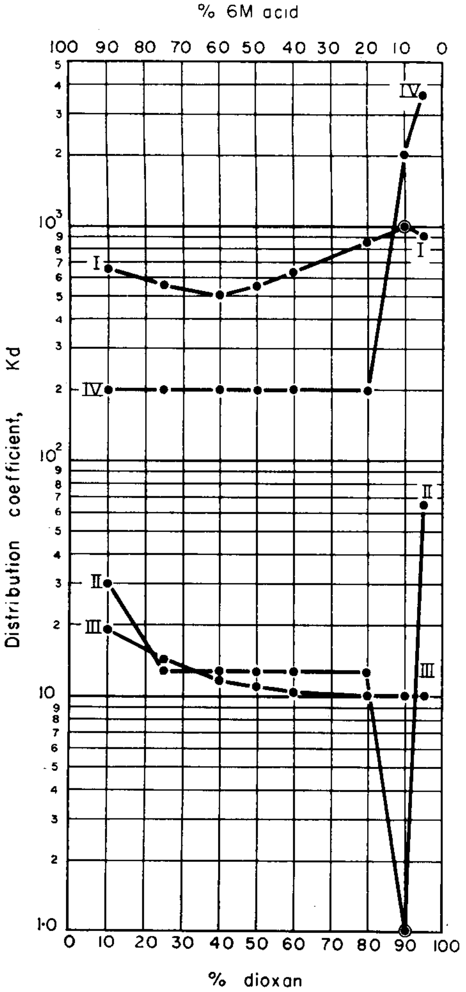


Fig. 4—Effect of dioxan concentration:
I—Uranium in hydrochloric acid,
II—Thorium in hydrochloric acid,
III—Uranium in nitric acid,
IV—Thorium in nitric acid.

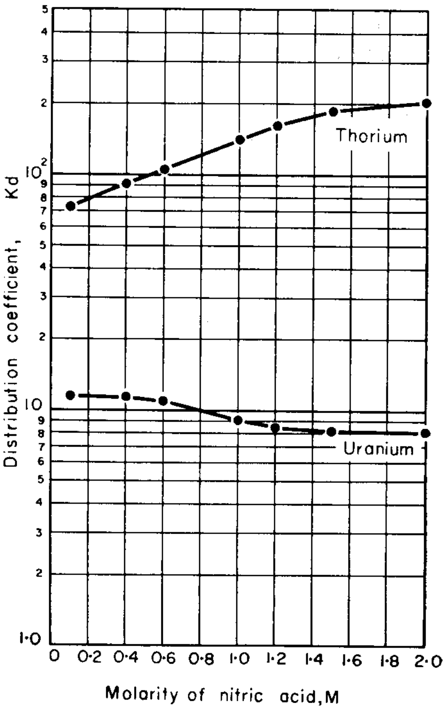


FIG. 5—Effect of acidity in 80% dioxan–20% 6*M* nitric acid mixtures.

TABLE II—SEPARATION OF URANIUM FROM THORIUM IN DIOXAN–NITRIC ACID MEDIUM

Amounts used, µg		Amounts recovered, µg	
U	Th	U	Th
10	50	9·8	49
10	100	9·7	98
100	100	97·6	102·3
1,000	100	1,021·5	101·8

From the Kd-values obtained in diethyl ether–nitric acid media the separation factors (α = Kd Element/Kd Uranium) were calculated and the results are represented in Fig. 3, from which it is seen that a separation of uranium from thorium, iron and aluminium can easily be carried out because the α-values are very much different from 1. This is the basis for the first separation method outlined above.

In Fig. 4 the effect of dioxan concentration on the distribution coefficients of uranium and thorium is shown. From these results it is evident that for the purpose of separating thorium from uranium, a mixture consisting of 90% of dioxan and 10% of $6M$ nitric acid is most suitable. Because the separation factor α in this medium is 65, the second separation method can successfully be applied for the quantitative separation of these two elements.

Fig. 5 shows the effect of acidity on the distribution coefficients of uranium and thorium in mixtures containing 80% of dioxan and 20% of nitric acid. From the curves it is seen that the effect of acidity is not very pronounced.

It can be said conclusively that quantitative separations of uranium in ether-nitric acid mixtures can also be performed by using an anion exchanger instead of cellulose or other adsorbents hitherto employed for this purpose.

Acknowledgments—This research was sponsored by the International Atomic Energy Agency acting through the United States Atomic Energy Commission under Agency Research Contract No. 67/US, renewal No. 1. The generous support from these agencies is gratefully acknowledged.

Zusammenfassung—In der vorliegenden Arbeit wird das Adsorptionsverhalten von Uran, Thorium, Eisen und Aluminium am stark basichen Anionenaustauscher Dowex 1 in Mischungen von Salz- und Salpetersäure und Äthern beschrieben. Verteilungskoeffizienten für diese Elemente in Diäthyläther, Diisopropyläther und Dioxan werden angegeben. Diese Resultate dienen als Grundlage für Trennungen des Urans von Thorium, Eisen und Aluminium.

Résumé—Phénomènes d'absorption, de l'uranium, du thorium, du fer(III) et de l'aluminium sur l'échangeur anionique Dowex 1 basique en solution dans les éthers et en milieu chlorhydrique ou nitrique. Détermination des coefficients de distribution de ces éléments dans l'éther ordinaire, l'oxyde d'isopropyle et le dioxane. Description d'une méthode de séparation de l'uranium du thorium, du fer et de l'aluminium basée sur ces résultats.

REFERENCES

[1] T. V. Arden, F. H. Burstall and P. Linstead, *J. Chem. Soc.*, 1949, 311.
[2] W. J. Frierson, P. F. Thomason and H. P. Raaen, *Analyt. Chem.*, 1954, **26**, 1210.
[3] F. H. Burstall and R. A. Wells, *Analyst*, 1951, **76**, 396.
[4] F. T. Rabbits, *Can. Mining Met. Bull.*, 1952, No. 477, 29.
[5] N. F. Kember, *Analyst*, 1952, **77**, 78.
[6] J. Szonntagh, L. Farády and A. Janosi, *Magyar Kem. Foly.*, 1955, **61**, 312.
[7] D. Lebez and M. Ostanek, Proc. Int. Conf. in Geneva on the Peaceful Uses of Atomic Energy (UN, New York), 1956, **8**, 289.
[8] R. H. Kennedy, USAEC., Tech. Inform. Service AECD–3187 1950.
[9] J. Walkden, Rep. AERE–AM 35.
[10] A. F. Williams, *Analyst*, 1952, **77**, 297.
[11] W. Ryan and A. F. Williams, *ibid.*, 1952, **77**, 293.
[12] D. Lebez and M. Ostanek, *J. Stefan Inst. (Ljubljana) Rep.*, 1955, **2**, 9.
[13] Tadashi Hara, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78**, 337.
[14] T. Palágyi, *Acta Chim. Acad. Sci. Hung.*, 1960, **22**, 239.
[15] J. Korkisch and F. Tera, *J. Inorg. Nuclear Chem.*, 1960, **15**, 177.
[16] G. E. Janauer and J. Korkisch, *Talanta*, 1962, **9**, 427.
[17] *Idem*, *ibid.*, 1962, **9**, 957.

Talanta, 1963, Vol. 10, pp. 679 to 684. Pergamon Press Ltd. Printed in Northern Ireland

APPLICATION OF FEIGL'S REACTIONS IN BIOCHEMISTRY AND AGRICULTURAL CHEMISTRY*

A. BONDI
Faculty of Agriculture, Hebrew University, Rehovot, Israel

(*Received* 10 *January* 1963. *Accepted* 21 *January* 1963)

Summary—A review is presented of applications of Feigl's reactions in biochemistry and agricultural chemistry.

A LARGE number of reactions discovered by Feigl or used by him for purposes of spot test analyses have been applied by other authors for the solution of complicated problems in biochemistry and agricultural chemistry.

Various qualitative tests have been adapted for quantitative purposes and have made possible studies on the action of certain enzymes. Thus, derivatives of carboxylic acids, such as esters, amides and anhydrides, can be readily converted to hydroxamic acids. Hydroxamic acids form a highly coloured chelate complex with iron^{III} chloride in weak acid solution. This reaction has been used by Feigl[1] in spot tests for acid derivatives and by later authors for investigations of acetylcholine esterase,[2] phosphotransacetylase[3] and glutamyl transferase.[4] Nerve tissue contains the enzyme acetylcholine esterase which catalyses the hydrolysis of acetylcholine and plays an important role in the transmission of nerve impulses. Hestrin[2] used Feigl's iron^{III}-hydroxamic acid test for studying the activity of this enzyme. Free choline and acetic acid do not give the colour reaction and therefore the colour intensity obtained by the addition of an iron^{III} salt and hydroxylamine to samples taken from incubates of substrate and enzyme after different intervals serves as a measure of the activity of this enzyme.

The high activity of phosphorus-containing insecticides, such as Parathion, is caused by the inhibition of choline esterase which is a vital enzyme in insects. Therefore its influence on the activity of choline esterase can be determined by the described procedure which represents an easy way for studying the action of such insecticides.[5]

The same reaction has been applied successfully to the quantitative determination of other biological substances. Lipman and Tuttle[3] used it for the determination of acetylphosphate, a metabolic intermediate formed from pyruvate by bacteria. Glutamyltransferase, an enzyme discovered by Waelsch *et al.*,[4] catalyses the reaction glutamine + hydroxylamine → glutamohydroxamic acid + ammonia. Considerable knowledge about the mechanism of this enzymatic reaction was gained by a quantitative procedure based on the colour reaction of the resulting glutamohydroxamic acid with an iron^{III} salt. Again, the same principle has been applied to the determination of total esterified fatty acids in plasma,[6] and recently also to the determination of methoxyl groups in pectins.[7] The commercial evaluation of pectins is based on their content of methoxyl group, the determination consisting of the liberation of these groups by saponification, conversion to methyl formate, distillation of the methyl formate into an alcoholic hydroxylamine solution and determination as iron^{III} hydroxamate.

---

* Presented before the Fourth Annual Meeting of the Chemical Society of Brazil in Rio de Janeiro, November, 1962.

An interesting enzyme, nitroarylreductase, causing the reduction of nitro groups was discovered in Neurospora bacteria and in extracts of animal organs. With *m*-dinitrobenzene as substrate, both nitrophenylhydroxylamine and nitroaniline have been formed as products of the reduction *in vivo*. Feigl's test for nitrophenylhydroxylamine by reaction with sodium pentacyanoammineferrate could be used very successfully for investigating the kinetics of nitroarylreductase; the purple colour of the soluble complex formed can be evaluated quantitatively.[8]

Feigl demonstrated convincingly that the presence of certain functional groups in the molecule of organic reagents is responsible for their specific activity towards certain inorganic ions. For instance, the presence of the dioxime group is specific for nickel. Conversely, he used inorganic reagents to detect functional groups in organic compounds, in this case solutions of nickel salts and hydroxylamine for the detection of the diketo group. This principle has been used by different biochemists for the detection and determination of biacetyl,[9] pyruvic aldehyde,[10] or acetoin,[9] the latter after oxidation to biacetyl. These compounds are precipitated as nickel dioximes, the nickel content of which can be determined colorimetrically as the soluble diacetyldioxime compound of quadrivalent nickel according to Feigl. The above mentioned organic compounds are products of bacterial fermentations and their separation and determination as complex nickel salts has helped to elucidate the mechanism of the corresponding bacterial reactions.

Many analytical procedures generally accepted and used are based on principles first proposed by Feigl, a fact which is seldom remembered. The tremendous development of the biochemistry of phosphorus is due in part to the colorimetric determination involving reduction of phosphomolybdic acid. According to Feigl, this reaction is due to the enhanced reactivity of molybdenum trioxide complexed by phosphoric acid; this enhanced activity of phosphomolybdic acid towards benzidine was applied first in Feigl's spot test for phosphoric acid and later to numerous procedures for its colorimetric determination. Feigl's theory about the enhanced reactivity of molybdenum trioxide because of the formation of a complex compound has been confirmed by physical investigations and is now generally accepted.

The opening of the pyridine ring by irradiation or by the action of bromcyanogen, with the formation of glutamic aldehyde, the so-called Koenig reaction, was first applied by Feigl[11] for analytical purposes; the aldehyde formed condenses with aromatic amines and yields coloured bases.[5] The formation of such dyes constitutes the basis of the most common chemical method for the determination of the vitamin niacin.[12]

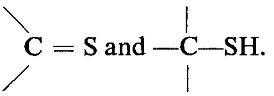
The formation of the very stable red iron^{II} bipyridyl ion for analytical purposes was first introduced in 1931 independently by Feigl[13] and Hill.[14] Natural antioxidants like vitamin E or synthetic phenolic antioxidants such as BHA or BHT can be detected and determined easily by the action on the light yellow solution of iron^{III} chloride and bipyridyl, which is reduced to the red iron^{II} bipyridyl ion. Synthetic antioxidants are widely used for stabilising fats and oils as well as vitamin A, and the general importance of vitamin E in cell metabolism is beginning to be recognised. The analytical determination of these antioxidants can be carried out by this reaction after separation of interfering lipids and pigments. This vitamin E test is known as the Emmerle-Engel reaction.[15]

Spot tests for glycolic acid and phenoxyacetic acid recommended by Feigl are based on the release of formaldehyde by acid treatment and its detection by chromotropic acid. Quantitative methods for the determination of biologically important substances, such as papaverine,[16] the herbicide 2,4-D[17] or the mucopolysaccharide sialic acid,[18] are based on the same principle combined with the determination of the violet colour formed by the addition of chromotropic acid to formaldehyde in the presence of concentrated sulphuric acid.

It was spot test analysis which first made use of capillarity and adsorptive effects on filter paper for the simultaneous detection of different ions. The same principles have been applied most successfully in paper chromatography. On the other hand, various specific reagents developed by Feigl also serve as spray reagents in paper chromatography. It can be said that paper chromatography has been inspired in many respects by spot test analysis. Therefore, the success of paper chromatography in solving biochemical problems is due to a great extent to Feigl.

Chargaff *et al.*[19] used the iodine-azide reaction for the detection of cysteine by paper chromatography. According to Feigl, the reaction

$$2NaN_3 + I_2 \rightarrow 2NaI + 3N_2$$

is catalysed by inorganic sulphides and by organic compounds containing the groups  $>C=S$ and $-\overset{|}{\underset{|}{C}}-SH$. Compounds belonging to these groups can be separated on paper as a result of their different R_F values and are recognised after spraying with a starch-containing iodine-azide solution. The reaction between sodium azide and iodine takes place only in the area occupied by a compound capable of catalysing the reaction between these two compounds. Elsewhere, an excess of iodine remains; the starch reacts with the excess iodine to produce the blue starch-iodine complex leaving white spots in those areas occupied by the reacting sulphur compounds. A good contrast between the deep-blue background and the white spots is obtained.

Hasson[19a] and Macek *et al.*[20] used as a spray reagent for paper chromatography of certain alkaloids a reagent recommended by Feigl for spot test identification of secondary aliphatic amines: a mixture of sodium nitroprusside and acetaldehyde. The amines form blue soluble compounds when they react with sodium nitroprusside and aldehydes in an alkaline medium.

The same reagent has been used successfully by Hasson[21] for developing paper chromatograms of sympathomimetic amines. Alternately, such amines, containing also phenolic hydroxyl groups, can be recognised on the chromatograms with the help of a reagent recommended by Feigl for the identification of phenols; this test is based on the conversion of phenols to complex cobalt^{III} salts of *o*-nitrosophenols.

Feigl's very elegant spot test for coumarin has been applied successfully to the paper chromatography of this group of compounds in extracts obtained from plant materials.[22] This test is based on the cleavage of the pyrone ring by alkali and formation of *o*-hydroxycinnamic acid which gives a yellow-green fluorescence in ultraviolet light. A very sensitive test for selenium discovered by Feigl has been used recently by Schwarz and Stesney[22a] for determining selenite-selenium on paper chromatograms at levels below 0·001 μg. This test is based on the observation that traces of selenium catalytically accelerate the reduction of methylene blue by sulphide ions, Schwarz refers to the analogy between the catalytic effect of selenium used for its detection and the biological mode of action of this element, one of the most potent bioelements known.

Various elements or compounds contained in natural products have been characterised by using Feigl's specific reactions. This has been the case, for instance, for zinc and magnesium as the active constituents of proteases. It is very surprising that a vitamin such as vitamin B_{12} contains the very toxic cyanide radical complexed with cobalt. Folkers *et al.*[23] established the presence of the cyanide radical in this vitamin by the sensitive copper acetate-benzidine test of Feigl. Many histochemical procedures[24] for the detection of inorganic compounds in tissues have been developed from Feigl's specific reaction.

In agricultural chemistry Feigl's specific reactions have been used very successfully for the detection and determination of residues of chemicals in foods and feeds. Because the use of chemicals such as pesticides or herbicides in modern agriculture is essential, especially in tropical and subtropical countries, it is the task of the analyst to ascertain the absence of their residues in agricultural products or at least to establish that their concentrations do not exceed certain limits.

An assay first described by Feigl and used for the detection of amines could be modified and applied to the detection of chlorine-containing insecticides. According to the original reaction, the dried sample to be tested for amines is melted with colourless fluorescein chloride and anhydrous zinc chloride; fluorescein chloride and the amine react with liberation of hydrogen chloride and formation of rhodamine dyes. The intense colour of the rhodamine dyes is probably because of their carbonium salt structure.

In our case an amine, diphenylamine, together with zinc chloride is used for detecting chlorine-containing organic compounds. The function of fluorescein chloride is taken over by the chlorine-containing substance to be detected. This reaction is positive for Aldrin, Dieldrin, Toxaphene and DDT, but Lindane gives negative results.[25] After the fusion has been made and the products taken up in water, different colours are obtained according to the samples used: Toxaphene, greenish-blue; Aldrin and Dieldrin, purple; DDT, orange-red. The intensity of the colours can be determined in the usual way. These methods have been applied for the exact determination of micro quantities of Dieldrin[26] and Toxaphene[27].

Maleic hydrazide has been used successfully for retarding plant growth and preventing sprouting. Residues of this compound can be determined readily by hydrolysis and coupling of the liberated hydrazine with *p*-dimethylaminobenzaldehyde.[28] The colour reaction involves a condensation of aldehyde and hydrazine and the aldazine formed is dissolved in acid with the production of a coloured quinonoid cation. This colour reaction used by Feigl for qualitative purposes has been converted into a quantitative procedure.

A method for the determination of the herbicide 2,4-D by release of formaldehyde and its colorimetric determination has been mentioned before.

The use of the above mentioned iodine-azide solution as a spray reagent for detecting dithiocarbamates on paper chromatograms enables a comparatively simple identification of residues of these insecticides.[29]

A problem of great significance in Israel is the determination of traces of biphenyl in citrus fruits. The oranges are wrapped in paper treated with biphenyl in order to prevent rotting of the fruit during transport. Because most of the importer countries have fixed limits for the permissible amounts of biphenyl residues, exact quantitative determinations of traces present in the fruits have to be carried out. Rajzman[30] solved this complicated analytical problem by using a reaction recommended by Feigl as a general test for aromatic hydrocarbons. The biphenyl is removed by vapour distillation and determined by the reaction with formaldehyde and concentrated sulphuric acid, resulting in coloured *p*-quinonoid compounds.

Fluorides or derivatives of fluorine are very toxic and in certain cases their absence has to be established. The Association of Official Agricultural Chemists of the United States (AOAC)[31] has adopted as an official method for this purpose Feigl's test[32] based on the prevention of the fluorescence of aluminium oxinate. Aluminium oxide and various aluminium salts form highly fluorescent salts with oxine. Fluorides cannot be transformed into fluorescent oxinates and this causes a quenching of the fluorescence of aluminium oxinate.

With the increasing use of thallium compounds as rodenticides there is a danger of thallium poisoning in man or animals as a result of careless handling of these compounds. The detection and determination of thallium in urine is needed for confirmation of the clinical diagnosis. Methods used for these purposes have hitherto been very complicated and time consuming. Rappaport[33] developed a much simpler method based on the reaction of thallium with rhodamine B discovered by Feigl. The lengthy removal of accompanying organic material is superfluous. Thallium can be determined by formation of a coloured complex of thallium$^{\text{III}}$ salt and rhodamine B which is extracted by benzene.

Zusammenfassung—Eine Übersicht der Anwendung der Methoden von Feigl im Gebiet der Biochemie und Landwirschaftschemie wird dargelegt.

Resume—Une revue est présentée de l'application des méthodes de Feigl dans la chemie biologique et agricole.

REFERENCES

[1] F. Feigl, V. Anger and O. Frehden, *Mikrochemie*, 1934, **15**, 12.
[2] S. Hestrin, *J. Biol. Chem.*, 1949, **130**, 249.
[3] F. Lipman and L. C. Tuttle, *ibid.*, 1945, **159**, 21.
[4] N. Grossowicz, E. Wainfan, E. Borek and H. Waelsch, *ibid.*, 1950, **187**, 111.
[5] I. W. Cook, *J. Assoc. Offic. Agric. Chemists*, 1954, **37**, 561.
[6] D. M. Morgan and K. J. Kingsbury, *Analyst*, 1959, **84**, 409.
[7] O. A. Guagnini, E. E. Vonesch and M. H. C. K. de Riverós, *Mikrochim. Acta*, 1961, 408.
[8] M. Zucker and A. Nason, in S. P. Colowick and N. O. Kaplan, *Methods in Enzymology*, Vol. 2. Academic Press, New York, 1955, p. 406.
[9] E. Stotz and J. Raborg, *J. Biol. Chem.*, 1943, **150**, 25.
[10] C. Neuberg and M. Scheuer, *Monatsh.*, 1929, **53/54**, 1031.
[11] F. Feigl, V. Anger and R. Zappert, *Mikrochemie*, 1934, **16**, 71.
[12] Association of Vitamin Chemists, Inc., *Methods of Vitamin Assay*. Interscience Publish. Inc., New York, 1951, p. 178.
[13] F. Feigl and H. Hamburg, *Z. analyt. Chem.*, 1931, **86**, 1.
[14] R. Hill, *Proc. Roy. Soc.*, 1931, **107**, 205.
[15] A. Emmerle and C. Engel, *Rec. Trav. Chim.*, 1938, **57**, 1351.
[16] M. Largejahn, *Pharm. Weekblad*, 1957, **92**, 693.
[17] L. C. Erickson and B. L. Brannaman, *Hilgardia*, 1954, **23**, 175.
[18] E. Klenk, *Z. physiol. Chem.*, 1961, **307**, 266.
[19] E. Chargaff, C. Levine and Ch. Green, *J. Biol. Chem.*, 1948, **175**, 67; see W. Awe, *Naturwiss.*, 1954, **41**, 528.
[19a] Hasson, *Anas Academ. Brasil. Ciencias*, 1955, **27**, 285.
[20] K. Macek, I. Hacaperkova and B. Kakac, *Pharmazie*, 1956, **11**, 533.

[21] A. Hasson, *Anas Academ. Brasil. Ciencias*, 1957, **29**, 27.

[22] I. M. Hais and K. Macek, *Handbuch der Papierchromatographie*. G. Fischer Verl., Jena, 1958, p. 335.

[22a] K. Schwart; in R. S. Harris and T. G. Wool, *Vitamins and Hormones*, Vol. 20. Academic Press, New York and London, 1962, p. 480.

[23] N. G. Brink, F. A. Kuchl and K. Folkers, *Science*, 1950, **112**, 354.

[24] A. G. E. Pearse, *Histochemistry, Theoretical and Applied*. I. and A. Churchill, Ltd., London, 2nd Ed., 1960, p. 681 ff.

[25] A. Bondi, *Proceedings of Feigl Symposium*. Elsevier Publishing Co., Amsterdam, 1962, in press.

[26] C. Cueto, Jr., *J. Agric. Food Chem.*, 1960, **8**, 273.

[27] A. J. Graupner and C. L. Dunn, *ibid.*, 1960, **8**, 286.

[28] C. Anglin and J. H. Mahon, *J. Assoc. Offic. Agric. Chemists*, 1958, **41**, 177.

[29] W. P. McKinley and S. A. Margarvey, *ibid.*, 1960, **43**, 718.

[30] A. Rajzman, *Analyst*, 1960, **85**, 116.

[31] *Official Methods of Analysis of the Association of Official Agricultural Chemists*. Washington, 9th Ed., 1960, p. 388.

[32] F. Feigl, H. W. Zocher and C. Török; see F. Feigl, *Chemistry of Specific, Selective and Sensitive Reactions*. Academic Press Inc. New York, 1949, p. 184.

[33] F. Rappaport and F. Eichborn, *Clinica Chim. Acta*, 1957, **2**, 16.

Talanta, 1963, Vol. 10, pp. 685 to 689. Pergamon Press Ltd. Printed in Northern Ireland

A NEW PRINCIPLE OF ACTIVATION ANALYSIS SEPARATIONS—II*

SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF ZINC AND COPPER IN GERMANIUM DIOXIDE

ADOLF ZEMAN, JAROMÍR RŮŽIČKA and JIŘÍ STARÝ
Department of Nuclear Chemistry, Faculty of Nuclear Physics
Praha 1, Břehová 7, Czechoslovakia

(*Received* 10 *November* 1962. *Accepted* 9 *January* 1963)

Summary—A substoichiometric determination of zinc and copper in germanium dioxide is based on dissolution of the irradiated sample in sodium hydroxide followed by addition of known amounts of carriers for the metals to be determined, then adjustment to suitable conditions for extraction. An irradiated standard sample is treated simultaneously in exactly the same way. The solutions thus prepared are extracted with substoichiometric amounts of dithizone in carbon tetrachloride and the amounts of zinc and copper in the germanium dioxide calculated from the activities of the extracts obtained. The present procedure is far more simple and rapid than previously published methods. It eliminates not only distillation but also many separation steps commonly used, thus shortening the time of analysis to 20 min.

INTRODUCTION

In a previous paper[1] the general theory of substoichiometric determination in activation analysis was presented. From this theory conditions for the determination of many elements were predicted. In the present work verification of this principle is provided by the determination of traces of zinc and copper in germanium dioxide.

EXPERIMENTAL

Apparatus

Gamma spectrometer: One-channel, with strip-chart recorder.
Scintillation counter: With well-type NaI(Tl)-crystal.
pH-meter: pHM-2, Radiometer, Copenhagen, Denmark.
Mechanical shaker.
Glass test-tubes: With ground stopper, 60-ml volume.

Reagents

Carrier solutions: 0·0100*M* zinc sulphide in 0·001*N* sulphuric acid; 0·0100*M* copper sulphate in 0·001*N* sulphuric acid.

Diethanoldithiocarbamate [*bis-(2-hydroxyethyl)dithiocarbamate*]*:* Prepared by mixing 3·0 g of AnalaR diethanolamine and 1·75 g of AnalaR carbon disulphide in 60 ml of AnalaR absolute methanol. *Buffer-masking solution* (*for determination of zinc*)*:* Prepared by mixing 30 ml of diethanoldithiocarbamate solution and 60 ml of 0·05*M* ammonium oxalate in 0·1*M* ammonium chloride. The pH of this solution was adjusted to 8·5 ± 0·5 by aqueous ammonia (purified by isothermal distillation in the presence of EDTA).

Masking solution (*for determination of copper*)*:* 15% potassium iodide solution.

Dithizone solution: $8{\cdot}0 \times 10^{-4}M$ dithizone (AnalaR) in AnalaR carbon tetrachloride (twice distilled)

Qualitative analysis

At first a qualitative analysis of the germanium dioxide was carried out with the gamma spectrometer. For this purpose the test sample (0·1 g of GeO_2) was irradiated with a neutron flux of 5×10^{12} neutrons.cm^{-2}.sec^{-1} for 20 hr in a pile.

---

* Part I—see reference 1.

After irradiation, the sample was dissolved in 30 ml of concentrated hydrochloric acid under the oxidising action of nitric acid. The hold-back carriers for Cu, Zn, Sn, Mo, As, Te and Sb were added. From this mixture the germanium tetrachloride was twice distilled. After adding 0·2 g of non-active germanium tetrachloride (as a carrier), the distillation was twice repeated.[2] The residue was transferred to the measuring cell and the gamma spectrum registered. A peak at the energy of 0·48 MeV corresponds to a mixture of nuclides ^{64}Cu ($t_{1/2}$ = 12·8 hr) and ^{69m}Zn ($t_{1/2}$ = 13·8 hr). The half-life measured at the energy 0·48 MeV corresponds approximately to 13 hr. For this reason the quantitative analysis of zinc and copper must be provided by radiochemical methods.

Quantitative analysis

Quantitative analysis has been carried out by substoichiometric determination[1] using solvent extraction with dithizone. The principle of this method is as follows: To the simultaneously irradiated standard and test samples known *exactly equal* amounts of carriers for the metals to be determined are added. After isotopic equilibrium is reached and the conditions are suitably adjusted (pH, masking agent), both solutions are simultaneously extracted with the same dithizone solution in carbon tetrachloride. The amounts of dithizone must be always less than stoichiometrically corresponds to the amount of carrier added. The amount of metal (y) to be determined is calculated from

$$y = y_s \frac{a}{a_s} \tag{1}$$

where y_s = the amount of metal in the irradiated standard sample, and a and a_s = the activities of the same amounts of the organic extract from the test and standard samples, respectively.

Selective determination of traces of zinc and copper

The conditions for the determination are based on the results of the determination of traces of zinc[3] and copper[4] by isotopic dilution analysis with dithizone extraction and on the theory of substoichiometric determination. For equation (1) to be valid, it is necessary to isolate always exactly the same amount of the metal to be determined from the standard and test samples. Preliminary experiments showed that this condition for the determination of zinc is fulfilled at pH 7–10 (in the presence of oxalate and diethanoldithiocarbamate as a masking agent) and for the determination of copper at pH 0·5–2·0 (in the presence of potassium iodide as a masking agent). The dithizone concentration in carbon tetrachloride was $8 \times 10^{-4}M$.

Procedure

Dissolve 0·1 g of irradiated GeO_2 in 3 ml of 8N sodium hydroxide solution. Carefully acidify this solution with drops of 8N sulphuric acid until a white precipitate appears. Redissolve this precipitate with drops of acid. The pH of the thus prepared solution is approximately 2–4. Add 1·00 ml of 0·0100M zinc sulphate carrier solution and 1·00 ml of 0·0100M copper sulphate carrier solution. Dilute with distilled water to 50 ml and transfer two 25-ml aliquots into 60-ml glass test tubes.

*Determination of zinc**. Neutralise the aliquot of solution with aqueous ammonia and add 5 ml of buffer-masking solution for selective determination of zinc. Extract this solution (pH 8·5 ± 0·5) with 5 ml of $8 \times 10^{-4}M$ dithizone solution in carbon tetrachlordie. Transfer 4 ml of the extract to a well-type scintillation counter and measure the activity (a). Treat a known part of the standard sample of zinc† (y_s) simultaneously and in exactly the same way as the test sample and measure the activity of 4 ml of the organic extract under the same conditions (a_s). For verification of the results extract the remaining aqueous phases once more with 5 ml of $8 \times 10^{-4}M$ dithizone in carbon tetrachloride (activities a' and a_s'). Calculate the amount of zinc (y) present in the germanium dioxide from equation (1). In our experiments the mean values of a and a' and of a_s and a_s' were used for calculation as practically $a = a'$ and $a_s = a_s'$.

Determination of copper. Adjust the pH of the second aliquot to 1·0 ± 0·5 with sulphuric acid. Add 2 ml of 15% potassium iodide solution and extract the solution with 5 ml of $8 \times 10^{-4}M$ dithizone in carbon tetrachloride. Measure the activity of 4 ml of the extract in a well-type scintillation counter

---

* Possible interference as a result of the nuclear reaction ^{72}Ge(n, α)^{69}Zn, which might be brought about by fast neutrons in the irradiation flux, was considered to be negligible (*cf.* references 2 and 5). A preliminary spectrographic determination of zinc gave results of the same order as those obtained by the present activation analysis method.

† 3.22 mg of zinc oxide and 0·365 mg of copper oxide were sealed in quartz ampoules as standard samples for irradiation. A systematic study of the possible influence of self-shielding differences between test and standard samples was not carried out because of the relatively small amount of germanium dioxide irradiated.

(*a*). Treat the standard sample of copper (y_s) simultaneously and in exactly the same way as the test sample (a_s). Calculate the amount of copper (y) present in the germanium dioxide from equation (1).

The radiochemical purity was checked by discriminated gamma-scintillation determination of the half-lives of the dithizone extracts (see Fig. 1.) Cross-contamination is not to be expected from theory.[3,4]

TABLE I.—SUBSTOICHIOMETRIC DETERMINATION OF ZINC AND COPPER

	Direct extraction		Distillation followed by extraction	
	Cu	Zn	Cu	Zn
GeO_2 taken, *g*	0·1206	0·1206	0·1240	0·1240
Amounts (y_s) of standard added, μg	0·1165	1·288	0·1165	1·288
Activity* obtained from sample, *a*	345	4348	417	4864
Activity* obtained from standard sample, a_s	13771	15083	13771	15083
Amount of metal found in GeO_2, μg	0·00292	0·370	0·00352	0·416
%	$2{\cdot}4 \times 10^{-6}$	$3{\cdot}1 \times 10^{-4}$	$2{\cdot}8 \times 10^{-6}$	$3{\cdot}3 \times 10^{-4}$

* All activities are expressed in cpm and are the mean values from three measurements corrected for background and decay.

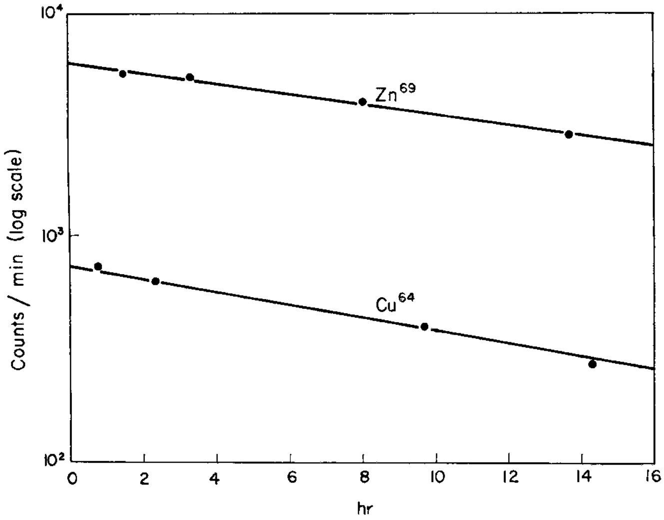


FIG. 1.—The decay curves of dithizone extracts of copper and zinc.

RESULTS AND DISCUSSION

Results obtained by the method described above are summarised in Table I (columns 1 and 2). For verification of the great efficiency of the substoichiometric extraction separations the germanium was also separated from the test samples by the classical method (distillation of germanium tetrachloride). The procedure was as follows:

Dissolve the irradiated sample of germanium dioxide (about 0·1 g) in 30 ml of concentrated hydrochloric acid, then add the carrier solutions for zinc and copper (1·00 ml of 0·0100*M* solutions). Distil until the residual solution is 2–3 ml. Add 30 ml of concentrated hydrochloric acid and repeat the distillation, then evaporate the solution to dryness after addition of 2–3 drops of concentrated sulphuric acid. Take up the residue in 50 ml of 0·01*N* sulphuric acid and treat two 25-ml aliquots as described above (see Determination of zinc and copper).

Comparing the results obtained by this procedure (columns 3 and 4, Table I) with those obtained by the direct extraction (columns 1 and 2), an excellent agreement of results is to be seen. It is evident that the distillation can be avoided.

The main advantage of the proposed method is its great speed and simplicity. The classical scheme for determination of zinc,[5] for example, consists of (1) triple distillation of germanium tetrachloride, (2) precipitation of tellurium after reduction by sulphur dioxide, (3) precipitation of zinc sulphide, (4) precipitation of $Zn[Hg(CNS)_4]$, (5) removal of mercury as HgS, (6) scavenging steps consisting of precipitation of Bi_2S_3 and $Fe(OH)_3$, and (7) weighing the $Zn[Hg(CNS)_4]$ precipitate and measuring its activity.

The classical procedure for determination of copper[5,6] is more simple than that for zinc, but it is also time consuming.

CONCLUSION

A new rapid and simple method for traces of zinc and copper based on substoichiometric determination has been developed. The time of analysis is shortened from some hours to 20 min.

An analysed sample of germanium dioxide contained $3{\cdot}1 \times 10^{-4}\%$ of zinc and $2{\cdot}4 \times 10^{-6}\%$ of copper. The procedure described can undoubtedly be used with little adaptation for the determination of traces of zinc and copper in various other materials of high purity, *e.g.* metallic germanium, silicon, aluminium, *etc.*

Acknowledgement—The authors thank Dr. V. Majer and Dr. R. Přibil for their interest in this work.

Zusammenfassung—Zink und Kupfer können in Germaniumdioxyd bestimmt werden, indem man die Probe nach Bestrahlung in Natronlauge löst, bekannte Trägermengen für die zu bestimmenden Metalle zusetzt und dann mit substöchiometrischen Mengen Dithizon in Tetrachlorkohlenstoff extrahiert. Eine bestrahlte Probe bekannter Zusammensetzung wird ebenso behandelt. Die Mengen von Zink und Kupfer im Germaniumdioxyd wurden aus den Aktivitäten der Extrakte berechnet. Diese Methode is viel einfacher und zeitsparender als früher veröffentlichte; sie erspart nicht nur die Destillation, sondern auch viele der üblichen Trennungsoperationen. So dauert die Analyse nur noch 20 Minuten.

Résumé—Une méthode de détermination sub-stoéchiométrique du zinc et du cuivre dans le bioxyde de germanium est basée sur la dissolution dans la soude de l'échantillon irradié, suivie de l'addition de quantités connues d'entraîner pour les métaux envisagés, et enfin de la mise au point de conditions d'extraction favorables. Simultané un échantillon de composition connue ast irradié et traité de la même façon. Les solutions ainsi préparées sont extraites par des quantités sub-stoéchiométriques de dithizone dans le tétrachlorure de carbone, et les quantités de zinc et de cuivre présentes dans le bioxyde de germanium calculées à partir des activités des extraits obtenus.

Ce procédé est beaucoup plus simple et plus rapide que les méthodes antérieures, et il permet d'éliminer la distillation et de nombreuses étapes rencontrées dans la séparation par les voies habituelles; le temps de l'analyse est ainsi ramené à 20 minutes.

REFERENCES

[1] J. Růžička and J. Starý, *Talanta*, 1963, **10**, 287.
[2] G. H. Morrison and J. F. Cosgrove, *Analyt. Chem.*, 1956, **28**, 320.
[3] J. Starý and J. Růžička, *Talanta*, 1961, **8**, 296.
[4] *Idem, ibid.*, 1962, **9**, 617.
[5] I. P. Alimarin, Ju. V. Jakovlev and A. I. Zhabin, *The Application of Labelled Atoms in Analytical Chemistry*. USSR Academy of Sciences, Moscow, 1955, p. 58,
[6] G. Szekely, *Analyt. Chem.*, 1954, **26**, 1500.

Talanta, 1963, Vol. 10, pp. 691 to 692. Pergamon Press Ltd. Printed in Northern Ireland

PRELIMINARY COMMUNICATION

Applications of infra-red spectroscopy—XI*
The determination of 1,2-diols by modified Zeisel reactions

(*Received* 11 *February* 1963. *Accepted* 12 *February* 1963)

DERIVATIVES of 1,2-diols, and compounds made by condensations with ethylene or propylene oxides, are becoming increasingly important as solvents, plasticisers, detergents and emulsifiers.

Specialised methods have been developed for the analysis of ethylene oxide condensates,[1] and for the separation, by azeotropic distillation[2] and by chromatographic methods,[3-5] of aqueous solutions of simple glycols and their derivatives. For quantitative determinations, the Malaprade[6] periodate oxidation involves the determination of formaldehyde[7,8] or silver iodate.[9] Other investigators have used an acetylation method,[10] cerate oxidation[11] (which releases formic acid), and dichromate oxidation[12] (which produces carbon dioxide).

A more general method, however, involves the well-known Zeisel reaction, in which 1,2-diols yield an olefine and an alkyl iodide. The method has been used on the micro scale.[13] Although early attempts to use this reaction quantitatively were unsuccessful, it has been claimed[14-16] that reasonable results are obtained if the sum of the molar yields of both the volatile products is taken: the relative yields of the two reaction products appear to be dependent on the compound under study and on the precise reaction conditions. Although Etienne[16] found that iodine chloride was more satisfactory than bromine as an absorbant for ethylene, all attempts[14] to simplify the analysis, by introducing a single chemical absorption system for both volatile products, have failed. A method[17] based on determination of the iodine liberated in the reaction medium through decomposition of the primarily formed di-iodo alkanes has been adapted to the micro scale.[18]

Vapour-phase infra-red spectroscopy gives a simple, sensitive and specific method for the simultaneous determination of ethylene, or propylene, together with alkyl iodides. For ethane-diol, calibration is based on the absorption by ethylene at 955 cm^{-1} and by ethyl iodide at 1215 cm^{-1}. Routine analyses can be made without difficulty on 5-mg samples. The analytical apparatus required has been described (see Fig. I, ref. 19): details of the simple gas-cells,[20] construction of calibration curves,[21] and a procedure for the measurement of infra-red absorptions[21] have been given.

Part X: D. M. W. Anderson, S. Garbutt, M. A. Herbich and S. S. H. Zaidi, *Analyst*, 1963, **88**, in press.

Under our standard conditions[22] for Zeisel determinations, [*i.e.*, 5-mg samples refluxed with 6 ml of hydriodic acid (55%) using nitrogen as flow-gas at 6–8 ml per min] ethanediol gives 85 moles per cent of ethylene and 15 moles per cent of ethyl iodide. This agrees well with the observations of Kaintz[13] but not with those of Morgan.[14] The evolution of ethylene is extremely rapid. From start of reflux, the evolution of ethylene is complete within 10 min; evolution of ethyl iodide is slower, being complete in 30 min, a time slightly less than is usual in determinations on ethoxy compounds (*cf.* ref. 13).

A pure sample of 1,2-di-iodoethane decomposed rapidly (*a*) in boiling water, giving a quantitative molar yield of ethylene, (*b*) in hydriodic acid, giving 90 moles per cent of ethylene and 10 moles per cent of ethyl iodide. In agreement with Etienne,[16] the formation of 1,2-di-iodoethane may therefore be the essential reaction intermediate (*cf.* ref. 14). The suggestion[16] that low results may be caused by the loss of traces of 1,2-di-iodoethane from the reaction flask must be questioned, however; the decomposition of 1,2-di-iodoethane in boiling aqueous solutions is so rapid that its existence as a reaction intermediate must be very short under the analytical reaction conditions. Further experiments are in progress to investigate all aspects of the determination of 1,2-diols and their derivatives in an attempt to improve the sensitivity, reproducibility and accuracy of this modified Zeisel method: the results will be published in due course.

Recently, constant-boiling hydrochloric[23] and hydrobromic[24] acids have been used to advantage in modified Zeisel reactions. Because both 1,2-dibromo- and 1,2-dichloroethane are relatively more stable than 1,2-di-iodoethane, it was suggested[25] that reaction of 1,2-diols with hydrochloric or hydrobromic acids might lead to the formation of a single volatile reaction product. Unfortunately, this does not occur. Ethanediol does not react to any significant extent with constant-boiling hydrochloric acid. Reaction with constant-boiling hydrobromic acid gives 1,2-dibromoethane, ethyl bromide and ethylene: furthermore, the total molar yield of these products is only about 50% after reflux for 2 hr. Hydrobromic acid is therefore less satisfactory than hydriodic acid as an analytical reagent. When 1,2-dibromoethane is treated with constant-boiling hydrobromic acid, some dibromoethane distils unchanged, and some is decomposed to ethylene, a small proportion of which (as shown in separate experiments) is converted to ethyl bromide.

Department of Chemistry
The University
Edinburgh 9, *Scotland*

D. M. W. ANDERSON ®
S. S. H. ZAIDI

Summary—Vapour-phase infrared spectroscopy offers a simple, sensitive and specific method for simultaneous determinations of the olefines and alkyl iodides liberated in Zeisel determinations on 1,2-diols.

Zusammenfassung—Die Infrarotspektroskopie in der Dampfphase bietet eine einfache, empfindliche und spezifische Methode für die gleichzeitige Bestimmung der bei Zeisel-Bestimmungen an 1,2-Diolen gebildeten Olefine und Alkyljodide.

Résumé—La spectroscopie infra-rouge en phase vapeur constitue une méthode simple, sensible et spécifique du dosage simultané des oléfines et des iodures d'alcoyle formés dans le dosage des diols-1,2 par la méthode de Zeisel.

REFERENCES

[1] L. E. Weeks, J. T. Lewis and M. E. Ginn, *J. Amer. Oil Chem. Soc.*, 1958, **35**, 149.
[2] H. M. Rosenberger and C. J. Shoemaker, *Analyt. Chem.*, 1957, **29**, 100.
[3] R. N. Sargent and W. Rieman, *Analyt. Chim. Acta*, 1957, **16**, 144.
[4] H. G. Nadeau and D. M. Oakes, *Analyt. Chem.*, 1960, **32**, 1760.
[5] G. J. Papariello, S. Chulkaratana, J. Higuchi, J. E. Martin and V. P. Kuceski, *J. Amer. Oil Chem. Soc.*, 1960, **37**, 396.
[6] L. Malaprade, *Bull. Soc. chim. France*, 1928, **43**, 683.
[7] L. Maros and E. Schulek, *Acta Chim. Acad. Sci. Hung.*, 1959, **20**, 359.
[8] R. N. Harger and R. B. Forney, *J. Forensic Sci.*, 1959, **4**, 136.
[9] E. R. Hess, C. B. Jordan and H. K. Ross, *Analyt. Chem.*, 1956, **28**, 134.
[10] I. M. Yurist and Y. F. Firsova, *Zhur. analit. Khim.*, 1956, **11**, 205.
[11] N. N. Sharma and R. C. Mehrotra, *Analyt. Chim. Acta*, 1955, **13**, 419.
[12] C. L. Whitman, G. W. Roecker and C. F. McNervey, *Analyt. Chem.*, 1961, **33**, 781.
[13] G. Kainz, *Mikrochim. Acta*, 1960, 254.
[14] P. W. Morgan, *Ind. Eng. Chem., Analyt.*, 1946, **18**, 500.
[15] H. J. Lortz, *Analyt. Chem.*, 1956, **28**, 892.
[16] H. Etienne, *Ind. Chim. Belge*, 1957, **22**, 1175, 1287.
[17] S. Siggia, A. C. Starke, J. J. Garis and C. R. Stahl, *Analyt. Chem.*, 1958, **30**, 115.
[18] K. Oruba, *Mikrochim. Acta*, 1961, 801.
[19] D. M. W. Anderson and J. L. Duncan, *Talanta*, 1960, **7**, 70.
[20] *Idem*, *Chem. and Ind.*, 1958, 1662.
[21] D. M. W. Anderson, *Analyst*, 1959, **84**, 50.
[22] D. M. W. Anderson and J. L. Duncan, *Talanta*, 1961, **8**, 1.
[23] *Idem*, *ibid.*, 1962, **9**, 661.
[24] D. M. W. Anderson, S. Garbutt, M. A. Herbich and S. S. H. Zaidi, *Analyst*, 1963, **88**, in press.
[25] G. F. Longman, *personal communication.*

Talanta, 1963, Vol. 10, pp. 693 to 710. Pergamon Press Ltd. Printed in Northern Ireland

SHORT COMMUNICATIONS

Zerstörungsfreie spektrochemische Analyse archäologischer Bronzefunde

(*Eingegangen am* 21 *August* 1962. *Angenommen am* 12 *Dezember* 1962)

Bei den bisher zur quantitativen Spektralanalyse archäologischer Bronzen angewandten Verfahren entnimmt man dem Fundstück 20–400 mg Bohrspäne. Diese werden entweder lösungsspektralanalytisch untersucht,[2,3] oder man erschmilzt einen kleinen Regulus, den man abfunkt,[5] oder die Späne werden in eine gebohrte Spektralkohle gestopft und darin der Analyse unterworfen.[9,11] Bei den von uns untersuchten Proben handelte es sich meist um kleine Fundstücke, die eine Entnahme von Spänen nicht erlaubten. Die Analyse mußte deshalb unmittelbar am Fundstück erfolgen.

Ein direktes Abfunken der Proben führte nur dann zu annehmbaren Ergebnissen, wenn der Funkenfleck bei allen Proben gleich groß war. Diese Forderung ließ sich bei der sehr unterschiedlichen Gestalt der kleinen Fundstücke nur durch eine Begrenzung des Funkenfleckes auf einen Durchmesser von maximal 2 mm. erreichen. Hierfür wandten wir das früher zur spektrochemischen Lokalanalyse von Geyer, Doerffel und Kirst[4] ausgearbeitete Verfahren an, ohne allerdings die damals benötigten extrem kleinen Flächenelemente anzustreben. Durch Überziehen der Probe mit einer Schicht von Hochspannungsisolierlack und Durchbohren dieser Lackschicht kann man die gewünschten Funkenflecken von begrenzten Abmessungen mit guter Reproduzierbarkeit herstellen. Die Größe des Funkenfleckes ist abhängig vom Durchmesser des gebohrten Loches, von der Hitzebeständigkeit des Lackes und von der Dauer des Funkenüberganges. Durch diese Begrenzung des Funkenfleckes auf einen Durchmesser von maximal 2 mm gelingt es, die sonst unvermeidbaren Einflüsse der Probenform zu eliminieren. Man kann nunmehr Fundstücke der verschiedensten Gestalt durch direktes Abfunken quantitativ analysieren.

TABELLE I.—AUFNAHMEBEDINGUNGEN ZUR ANALYSE DER BRONZEFUNDSTÜCKE

Gegenelektrode:	Angespitzter Kohlestift, Durchmesser 5 mm, $\measuredangle = 90°$
Elektrodenabstand:	2 mm
Anregung:	Feußner–Funkenerzeuger, $C = 3000$ pF, $L = 0{,}02$ mH, $U = 10{,}6$ kv.
Vorfunk:	30 sek.
Belichtung:	120 sek. (bei Plattenmaterial Agfa Spektral blau hart)
Zwischenblende:	O
Spaltbreite:	0,02 mm
Spektrograph:	Mittlerer Quarzspektrograph

Arbeitsvorschrift

Nach vorsichtigem Entfernen der Patinaschicht an der zu untersuchenden Stelle überzieht man die Probe mit lufttrocknendem Hochspannungsisolierlack. Nach dem Trocknen wird die Lackschicht an der gewünschten Stelle mit einem Spiralbohrer von 0,5 mm Durchmesser vorsichtig durchbohrt. Die so vorbereiteten Proben werden auf dem Funkentisch mit einem angespitzten Kohlestift als Gegenelektrode abgefunkt (Aufnahmebedingungen siehe Tabelle I). Voraussetzung für ein brauchbares Analysenergebnis ist die einwandfreie Justierung der Funkenstrecke in die optische Achse des Zwischenabbildungssystems (Einzelheiten hierzu vgl.[4]) Außerdem muß die vom Funken getroffene Stelle horizontal liegen, andernfalls kann in den Spektren ein erhöhter Untergrund auftreten.

Nach der Aufnahme des Spektrums wird die Lackschicht mit Azeton abgewaschen, der Funkenfleck wird durch Nachpolieren entfernt und die untersuchte Stelle durch Nachpatinieren wieder unsichtbar gemacht.

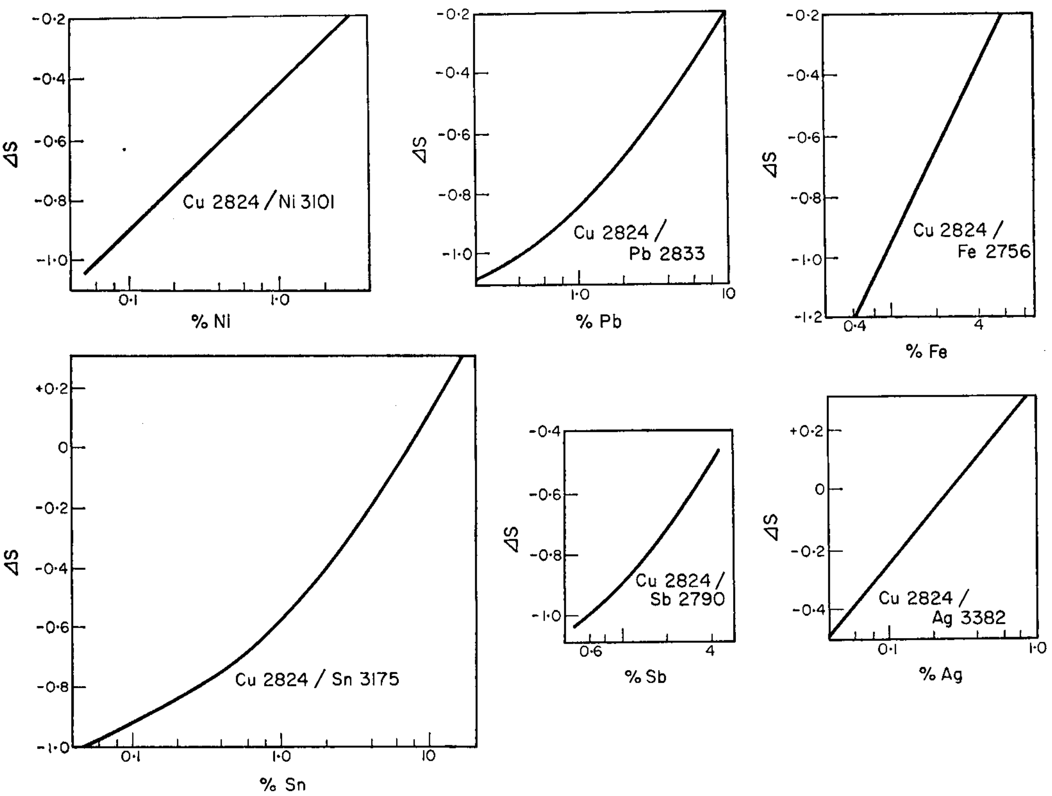


Abb. 1.—Eichkurven für die quantitative Auswertung

Zur quantitativen Auswertung werden die Schwärzungen der in Tabelle II angegebenen Linien unter dem Schnellphotometer ausgemessen. Die benutzten Eichkurven zeigt Abb. 1. Hierin sind die auf Cu = 100% bezogenen Relativprozente angegeben. Die auf die Summe aller Bestandteile = 100% bezogenen Absolutprozente erhält man in bekannter Weise durch Proportionsbildung.[7,8]

Bewertung

Einige mit dem beschriebenen Verfahren gewonnene Analysenergebnisse zeigt Tabelle III. Die angegebenen Parallelbestimmungen entstammen verschiedenen Stellen der untersuchten Probe. In Tabelle IV sind die ermittelten relativen Standardabweichungen (vgl.(11)) zusammengestellt. Diese geben zwar wegen der bereits früher[5] festgestellten Probeninhomogenitäten kein charakteristisches

Tabelle II.—Zur quantitativen Analyse benutzte Linien (teilweise nach[10]). Intensitäten und Anregungsenergien entnommen.[6]

Element	Analysen-linie, [Å]	Intensität		Anreg.-energie, eV
		Bogen	Funken	
Ag	3382,9	1000	700	3,66
Cu	2824,4	1000	300	5,78
Fe	2756,3	300	100	4,60
Ni	3101,6	1000	150	4,11
Pb	2833,1	500	80	4,4
Sb	2790,4			
Sn	3175,0	500	400	4,33

TABELLE III.—ANALYSENWERTE EINIGER UNTERSUCHTER BRONZEFUNDE

	Ag	Fe	Ni	Pb	Sb	Sn
Ring	0,76	0,22	0,49	0,62	0,22	0,29
	0,78	0,23	0,54	0,60	0,26	0,39
geometr. Mittel	0,77	0,22	0,51	0,61	0,24	0,34
Abs.—%	0,75	0,21	0,50	0,59	0,23	0,33
Ring	1,00	0,13	0,12	0,15	0,02	0,08
	1,06	0,17	0,21	0,29	0,06	0,08
geometr. Mittel	1,03	0,15	0,16	0,21	0,04	0,08
Abs.—%	1,01	0,15	0,16	0,21	0,04	0,08
Speerspitze.	0,36	0,17	0,27	0,39	0,06	3,4
	0,38	0,17	0,33	0,27	0,06	4,4
geometr. Mittel	0,37	0,17	0,30	0,32	0,06	3,9
Abs.—%	0,35	0,16	0,28	0,30	0,06	3,7

TABELLE IV.—STANDARDABWEICHUNGEN BEI DER EETIMMUNG DER EINZELNEN ELEMENTE

Element	Standardabweichung Rel.-Proz.	
Ag	+16 ...	−14
Fe	+13 ...	−12
Ni	+15 ...	−13
Pb	+18 ...	−15
Sb	+18 ...	−15
Sn	+16 ...	−14

Bild für die Leistungsfähigkeit des Verfahrens, sie ermöglichen jedoch Rückschlüsse auf die Aussagekraft der Analysenergebnisse. Der Zeitbedarf des Analysenverfahrens ist wegen seiner einfachen Probenvorbereitung viel geringer als beiden bis her bekannten Methoden. Da die Probe bei der Analyse nicht beschädigt wird, kann man sie an mehreren verschiedenen Stellen abfunken und dadurch einen besseren Durchschnittswert erzielen.

K. DOERFFEL
R. WAGNER

*Institut für analytische Chemie der Technischen Hochschule für Chemie Leuna-Merseburg, **Merseburg** (Deutsche Demokratische Republik) Geusaer Strasse*

Zusammenfassung—Es wird ein spektralanalytisches Verfahren zur zerstörungsfreien Untersuchung archäologischer Bronzefunde beschrieben. Es können Proben beliebiger Form und Größe quantitativ analysiert werden, sofern sie ein ebenes Flächenelement von etwa 2 mm Durchmesser besitzen. Das Verfahren erfordert wenig Arbeit für die Probenvorbeitung. Es gestattet, die Fundstücke zur besseren Durchschnittsbildung an verschiedenen Stellen abzufunken. Der entstehende Funkenfleck läßt sich nach der Analyse leicht wieder beseitigen.

Summary—A spectrochemical method of analysis for the non-destructive investigation of archaeological bronzes is described. Samples of any size or shape can be analysed quantitatively if any planar area 2 mm in diameter is available, Little work is required to prepare the samples.

By using several locations a better average analysis can be obtained. The spots caused by the operation of the arc can readily be removed after the analysis.

Résumé—Les auteurs décrivent une méthode spectroanalytique pour l'étude non destructive des bronzes archéologiques. Des échantillons de toutes dimensions et de toutes formes peuvent être analysées quantitativement, tant qu'il y a une surface plane de 2 mm de diamètre. Un petit travail est nécessaire pour préparer les échantillons. Il est possible d'utiliser différentes positions pour l'analyse afin d'obtenir une meilleure moyenne. Les spotes dus à l'impact de l'arc peuvent facilement être éliminés quand l'analyse a été effectuée.

LITERATUR

[1] K. Doerffel, *Z. analyt. Chem.*, 1962, **185,** 1.
[2] M. van Doorselaer, *Mikrochim Acta,* 1951, **36/37,** 513.
[3] J. Gillis, M. van Doorselaer und J. Ramirez-Munos, *Anal. Real. Soc. Espan. Fis. Quim., Ser. B.*, 1951, **47,** 609.
[4] R. Geyer, K. Doerffel und H. Kirst, *Z. analyt. Chem.*, 1960, **172,** 326.
[5] H. Otto, *Spectrochim Acta,* 1940, **1,** 381.
[6] A. N. Saidel, W. K. Prokoffiew und S. M. Raiski, *Spektraltabellen.* (Übersetzung aus den Russischen), VEB Verlag Technik, Berlin, 1955.
[7] H. Scheller, *Einführung in die angewandte spektrochemische Analyse.* VEB Verlag Technik, Berlin, 1961.
[8] W. Seith, *Metall u. Erz,* 1944, **41,** 35.
[9] I. R. Sselimchanow, *Ber. Akad. Wiss. Aserbeidschan,* 1957, **13,** 967.
[10] C. Zeiss, *Arbeitsvorschriften für die quantitative spektrochemische Bestimmung von Metallen.*
[11] K. Zimmer, Z. L. Szabó und P. Patay, *Magyar Kem. Folyóirat,* 1962, **68,** 515.

Determination of small amounts of zirconium—I: Gravimetric procedures using mandelic acid and its derivatives

(*Received* 23 *October* 1962. *Accepted* 29 *January* 1963)

THE use of mandelic acid and related glycolic acid derivatives[1] to precipitate zirconium^{IV} has been reviewed by Hahn.[2] The selectivity of this group of reagents for zirconium has ensured their use; the reagent most favoured for general use has been *p*-bromomandelic acid.

In connection with the gravimetric determination of small amounts of zirconium in refractory samples, such as alloys, glasses and minerals,[3] the optimum and limiting conditions have been investigated for mandelic acid, *p*-bromomandelic acid and a heretofore only briefly studied reagent, *m*-nitromandelic acid.

EXPERIMENTAL

After washing with acetone and ethanol, dissolve 1-g quantities of pure zirconium metal in concentrated acid, with heating, and dilute to 1 litre:

Solution A: Dissolve in 25 ml of HNO_3 + 1 ml of HF, then evaporate with 30–35 ml of H_2SO_4.
Solution B: Dissolve in 25 ml of HNO_3 + 25 ml of H_2SO_4, then evaporate with 25 ml of H_2SO_4.

Solution C: Dissolve in 50 ml of H_2SO_4.
Solution D: Dissolve in 25 ml of HCl + 25 ml of H_2SO_4.

These solutions were dispensed with calibrated pipettes (accurate to 1 % or better).

Precipitation was generally made by adding the reagent solution dropwise from a burette with constant stirring of the test solution. Filtration was made through No. 40 Whatman filter paper. Weighings of the ignited crucible, empty/or containing ignited precipitate and filter paper ash, were reproducible to ±0·01 mg. The filter ash was 0·02–0·03 mg.

Recommended procedures are given following discussion of the data; procedures used in studying the reagents follow.

TABLE I.—FACTORS IN PRECIPITATION OF ZIRCONIUM WITH MANDELIC ACID:
(A) Effect of original zirconium solution composition[a]

Stock solution	Zirconium found for amount taken, *mg*		
	1·00	3·00	10·00
A	1·04	2·96	9·81
B	0·98	3·03	9·98
C	1·00	2·96	8·88
D	0·99	3·00	10·06

[a] Total volume: 50 ml. Concentrations: Zr 0·22, 0·66 and 2·19 *mM*; MA 0·33*M*; acid 2·0–2·2*M*.

(B) Zirconium concentration (10% MA precipitant)[c]

Zirconium		
Taken, *mg*	Found, *mg*	Deviation, %
0·10[a]	0·05$_9$, 0·06$_0$ 0·06$_7$, 0·07$_0$ 0·08$_9$, 0·10$_3$	+3 to −41
0·30[b]	0·28$_5$, 0·29$_0$	−8, −3
0·50[a]	0·48$_6$, 0·50$_2$	−3, ±0
0·70[b]	0·70$_0$	±0
1·00[b]	0·99, 1·03	−1, +3

[a] Zirconium stock solution C.

[b] Zirconium stock solution D.

[c] Total volume: 20 ml. Concentrations: Zr 0·055 to 0·548 *mM*; acid 1·9*M*; MA 0·33*M*.

(C) Added hydrochloric acid (10% MA as precipitant)[b]

HCl,[a] *M*	Zirconium		
	Taken, *mg*	Found, *mg*	Deviation, %
1·9	1·00	0·98	−2
2·6	1·00	1·03	+3
3·2	1·00	1·00	±0
3·8	1·00	0·99	−1

[a] Concentration in the test solution.

[b] Total volume: 20 ml. Concentrations: Zr 0·548 *mM*; MA 0·33*M*.

(D) Mandelic acid concentration and digestion time[a]

Mandelic acid reagent %	Digestion time, *min*	Zirconium		
		Taken, *mg*	Found, *mg*	Deviation, %
2	20	1·0	No ppt.	−100
3	20	1·0	No ppt.	−100
4	20	1·0	0·45	—55
4	40	1·0	0·51	−49
4	60	1·0	0·59	−41
6	20	1·0	0·74	−26
6	40	1·0	0·84	−16
6	60	1·0	0·85	−15

[a] Total volume: 50 ml. Concentrations: Zr 0·219 *mM*; acid 2*M*; MA 0·066, 0·10, 0·13 and 0·20*M*.

Mandelic acid. Dissolve 10 g of mandelic acid (MA) in warm water and dilute to 100 ml.
(1) Transfer zirconium solution and 8 ml of HCl to a 150-ml beaker, dilute to 25 ml, heat to 50–60°, add 25 ml of MA solution and digest for 20 min at 80–85°. Filter precipitate, wash with 25–30 ml of warm solution (2 ml of HCl + 5 g of MA per 100 ml), slowly char paper and precipitate in a porcelain crucible, ignite, cool and weigh as ZrO_2.
(2) Transfer zirconium solution and 3 ml of HCl to a 50-ml beaker, dilute to 10 ml, heat to 50–60°, add 10 ml of MA solution and digest for 20 min at 80–85°. Filter precipitate, wash with 10 ml of warm solution as before, but ignite in a platinum crucible.

p-*Bromomandelic acid.* Dissolve 1·5 g of *p*-bromomandelic acid (BMA) in warm water, filter and dilute to 100 ml.

Transfer zirconium solution and 3 ml of HCl to a 50-ml beaker, dilute to 10 ml, heat to 50–60°, add 10 ml of BMA solution and digest for 15 min at 80–85°. Filter precipitate, wash with 10–25 ml of hot water, char slowly in a platinum crucible and ignite at 900–1000°.

m-*Nitromandelic acid.* Dissolve requisite amount of *m*-nitromandelic acid (NMA) in warm water, filter and dilute to 100 ml.
(1) Transfer zirconium solution to a 50-ml beaker, dilute to 10 ml, heat to 45–60°, add 10 ml of 5% or 4% NMA solution and digest for 10–15 min at 60–70°. Filter precipitate, wash with 10–15 ml of warm 5% NMA and ignite in a platinum crucible.
(2) Transfer 1 ml of zirconium solution D and 10 ml of water to a 50-ml beaker, heat to 50–60°, add 10 ml of 15% NMA solution and digest for 10–15 min at 60–70°. Filter precipitate, wash with 10 ml of warm 5% NMA solution and ignite in a platinum crucible.

RESULTS AND INTERPRETATION

Mandelic acid

Zirconium was determined at the 1 to 10-mg level by procedure (1) [Table I(A)] and at the 0·1 to 1-mg level by procedure (2) [Table I(B)]. Procedure (2) was also applied at varying concentrations of hydrochloric acid and mandelic acid (MA), and for varying digestion times [Tables I(C) and I(D)]. The following conclusions can be drawn:
(1) Zirconium level: 10% MA is satisfactory for the determination of small amounts ($\geqslant$ 0·5 mg); results are low for $<$ 0·3 mg.
(2) Precipitant concentration: 10% MA is adequate for quantitative precipitation at the 0·3-mg zirconium level and above; it is difficult to obtain quantitative results at the 1-mg level with lower MA concentrations.
(3) Acid concentration: No difference was found in the range of 3–6*M* hydrochloric acid (sometimes augmented by free sulphuric acid from the zirconium solution).
(4) Digestion and washing: To obtain a good precipitate, heating for 20 min at 80–85° is necessary; longer periods give no improvement. Use of a wash solution containing 2 ml of concentrated hydrochloric acid and 5 g of MA per 100 ml are necessary because of the appreciable solubility of zirconium tetramandelate in water.

p-*Bromomandelic acid*

The following conclusions can be drawn from the results of determining zirconium under various conditions (Table II):
(1) Zirconium level: 1·5% BMA is adequate for quantitative precipitation down to the 0·1-mg level. Excellent precision and accuracy are attainable at the 1-mg level.
(2) Precipitant concentration: 1·5% and 2% BMA are equally good for precipitating zirconium from 1–4*M* hydrochloric acid; less than 1·5% BMA is unsatisfactory at the 0·1-mg level.
(3) Digestion and washing: Because of the slow reaction between BMA and zirconium at room temperature, it is necessary to warm the solution. Temperatures near the boiling point of water apparently result in decomposition of BMA. A good crystalline precipitate is obtained by heating to 50–60°, adding BMA dropwise with constant stirring and digesting for about 15 min at 80–85°; longer times are unnecessary. Hot water is suitable for washing.

m-*Nitromandelic acid*

The following conclusions are evident from the use of 4% to 15% NMA as precipitant (Table III):
(1) Zirconium level and acid concentration: In less acidic media zirconium quantitatively forms a brown precipitate. However, results are low at low NMA concentrations; 15% NMA is suitable for the determination of amounts of zirconium as low as 0·1 mg.
(2) Digestion period and temperature: It is helpful in obtaining a good precipitate to warm the solution and to add NMA dropwise, stirring constantly. For complete precipitation, it is necessary to digest the solution for 10–15 min at 60–70°.

TABLE II.—FACTORS IN THE PRECIPITATION OF ZIRCONIUM WITH *p*-BROMOMANDELIC ACID[a]

Reagent concn., %	No. of runs	Zirconium Taken, *mg*	Found, *mg*	Average, *mg*	Standard deviation, *mg*
1·0	4	0·10	0·03–0·07		
1·5	6	0·10	0·090–0·105	0·10	0·006
1·5	6	1·00	0·987–1·028	1·002	0·015
1·5	2	2·00	2·04, 1·98		
1·5	2	3·00	3·04, 3·00		
1·5	2	4·00	4·02, 4·06		
1·5	1	5·00	4·98		
2·0	4	1·00	0·992–1·021	1·00	0·013

[a] Total volume: 20 ml. Concentrations: Zr 0·055 (0·1 mg), 0·55 (1 mg) to 2·75 (5 mg) *mM*; acid 1·9-2·1*M*.

TABLE III.—FACTORS IN THE PRECIPITATION OF ZIRCONIUM WITH *m*-NITROMANDELIC ACID[d]

Zr soln.	HCl added, *ml*	Reagent concn., %	Zirconium Taken, *mg*	Found, *mg*
A	0	5	2·00	0·99[a]
	1	5	2·00	No ppt.
B	0 and 1	4	2·00	No ppt.
C	0 and 1	5	2·00	No ppt.
D	0	4	2·00	0·89
D	0	5	2·00	1·07
	1 and 2	5	2·00	No ppt.
A	0	10	1·00	0·69
	1	10	1·00	No ppt.
B	0	10	1·00	0·63
	1	10	1·00	No ppt.
C	0	10	1·00	0·50
	1	10	1·00	No ppt.
D	0	10	1·00	0·89
	1	10	1·00	No ppt.
D	0	15[e]	0·100	0·099[b]
			1·00	0·93, 1·00
	0[c]	15[e]	1·00	0·98, 1·00
	1 and 2	15[e]	1·00	No ppt.

[a] Precipitate washed with hot water; all other precipitates washed with warm 2% *m*-nitromandelic acid, except as noted.

[b] Washed with 5% *m*-nitromandelic acid.

[c] Without added HCl, the pH is about 1·6; with added HCl, it is between 0·0 and 0·2.

[d] Total volume: 20 ml. Zr concentration: 0·55*mM* for 1 mg; 1·10*mM* for 2 mg.

[e] Total acid concentration in these experiments: <0·05*M*, *ca.* 0·05*M*, *ca.* 0·05*M*, <0·7*M*.

(3) Wash solution: Because of the appreciable solubility of the precipitate in water, a warm wash solution containing 5% NMA is recommended.

DISCUSSION

To obtain satisfactory precipitation within a reasonable time, a large excess of reagent must be used; the weight ratios of reagent to zirconium (molar ratios in parentheses) are 250–10,000 (150–6,000) for MA, 30–1,500 (12–600) for BMA and 750–1,500 (350–700) for NMA.

Although MA is adequate for the gravimetric determination of zirconium at the 1-mg level in a highly acidic medium, BMA is generally preferable because it avoids the use of a wash solution containing the reagent and gives better results at low zirconium levels. NMA is not satisfactory as a precipitant in highly acidic media; however, at pH 1·3 or greater, it seems preferable to MA because of more rapid precipitation and better accuracy at low zirconium levels, *e.g.*, 0·1 mg.; MA was not investigated at as low acidities as was NMA. NMA also gives more rapid precipitation than BMA. A wash solution containing reagent is necessary in the case of MA and NMA.

Sensitivity

Satisfactory results were obtained with BMA for solutions as dilute as 0·1 mg of zirconium in a final volume of 20 ml; 0·05 mg of zirconium (20-ml volume; 1·9*M* hydrochloric acid; final BMA concentration 0·75%; filtered after 3 hr) gave a residue corresponding to 0·04 ± 0·01 mg.

Interferences

Anions which form complexes with zirconium, *e.g.*, fluoride and sulphate, interfere in some zirconium methods; no such interference was indicated for the mandelate reagents by the use of the different zirconium solutions. Nevertheless, it is probably best to use hydrochloric acid to maintain a high acidity level. In general, 2–4*M* hydrochloric acid solutions seem satisfactory in allowing complete precipitation of zirconium by glycolic acid derivatives while at the same time assuring the selectivity of the method by minimising the precipitation of other cations. The need to use a lower acidity in the case of NMA is a distinct disadvantage.

In 4–6*M* hydrochloric acid, zirconium forms precipitates of the theoretical composition with MA; at a lower acidity, basic salts may be formed. The latter, is, however, of no consequence because the precipitate is finally ignited to zirconium dioxide.

Hafnium, of course, interferes quantitatively in all precipitation methods for zirconium and, if present, will be measured along with it. The general selectivity of the method is indicated by the successful determination of small amounts of zirconium in complex samples.[3]

Recommended procedures

The following procedures are recommended for the determination of zirconium at the milligram level, using the precipitants indicated:

Mandelic acid (for 1 mg or more of zirconium in 3–6*M* HCl): Heat the 10-ml sample solution to 50–60° in a 50-ml beaker, then add 10 ml of 10% MA solution dropwise with constant stirring. Digest for 20 min at 80–85°. Filter and wash with a warm solution (2 ml of HCl + 5 g of MA per 100 ml). Char paper and precipitate in a platinum crucible; ignite to ZrO_2 at 900–1000°.

p-*Bromomandelic acid* (for 0·1 mg or more of zirconium in 1–4*M* HCl): Heat the 10-ml sample solution to 50–60°, then add dropwise 10 ml of 1·5% BMA with constant stirring. Digest for 15 min at 80–85°. Filter, wash with 15–25 ml of hot water; char and ignite in platinum crucible.

m-*Nitromandelic acid* (for 0·1 mg or more of zirconium at pH 1·3): Heat the 10-ml sample solution to 50–60°, then add dropwise 10 ml of 15% NMA solution with constant stirring. Digest for 10–15 min at 60–70°. Filter, wash with 10 ml of 5% warm NMA solution; char and ignite in platinum crucible.

Acknowledgement—One of the authors (MR) wishes to thank the International Atomic Energy Agency for a fellowship, which enabled this work to be carried out.

Mohammed Rafiq*
Charles L. Rulfs
Philip J. Elving

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

Summary—The limiting factors have been investigated for precipitation of zirconium at the milligram level by mandelic acid, *p*-bromomandelic acid and *m*-nitromandelic acid; the latter has only been briefly studied previously. Optimum conditions have been determined for quantitatively precipitating zirconium at 0·1- and 1-mg levels.

---

* Present address: University of Kabul, Kabul, Afghanistan.

Zusammenfassung—Die Empfindlichkeitsgrenzen für die Fällung von Zirkonium mit Mandelsäure, p-Brom- und m-Nitromandelsäure im Milligrammbereich wurden ermittelt; die Fällung mit m-Nitromandelsäure war vorher nur oberflächlich untersucht. Die optimalen Bedingungen für die quantitative Fällung von Zirkonium in Bereich von 0,1–1 mg wurden ermittelt.

Résumé—Voici une étude des facteurs limites de la précipitation du zirconium en quantités de l'ordre du milligramme par les acides mandélique, p-bromomandélique et m-nitromandélique, ce dernier n'ayantété précédemment étudiés que d'une manière superficielle. Les conditions optima de la précipitation quantitative du zirconium pour des teneurs variant de 0,I à I mg. sont déterminées.

REFERENCES

[1] R. E. Oesper and J. J. Klingenberg, *Analyt. Chem.*, 1949, **21,** 1509.

[2] R. B. Hahn, in I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry.* Interscience Publishers, New York, 1961, Part II, Vol. 5, pp. 61–138.

[3] M. Rafiq, C. L. Rulfs and P. J. Elving, *Talanta*, 1963, **10,** in press

---

Precipitation from homogeneous solution with *N*-benzoylphenylhydroxylamine acetate

(*Received* 9 *November* 1962. *Accepted* 14 *January* 1963)

In 1950, *N*-benzoylphenylhydroxylamine (BPHA) was introduced by Shome[1] as a precipitant for aluminium$^{\mathrm{III}}$, copper$^{\mathrm{II}}$, iron$^{\mathrm{III}}$ and titanium$^{\mathrm{IV}}$. Since that time it has also been used to precipitate beryllium$^{\mathrm{II}}$,[2] cobalt$^{\mathrm{II}}$,[3] nickel$^{\mathrm{II}}$,[3] molybdenum$^{\mathrm{VI}}$,[4] niobium$^{\mathrm{V}}$ [5,6] tantalum$^{\mathrm{II}}$,[5,6] tin$^{\mathrm{IV}}$,[7] zirconium$^{\mathrm{IV}}$,[8,9] scandium$^{\mathrm{III}}$,[10] thorium$^{\mathrm{IV}}$ and cerium$^{\mathrm{III}}$.[11]

BPHA has three important characteristics which make it preferable to cupferron which it resembles. It is a stable compound, more effective separations can be achieved and it forms stoichiometric compounds with most ions, so enabling the complex to be weighed directly instead of necessitating ignition to the oxide.

The present investigation was undertaken to explore the usefulness of *N*-benzoylphenylhydroxylamine acetate (BPHAA) as a reagent for the *in situ* generation of BPHA. Copper was arbitrarily chosen as a model ion with which to test the new reagent.

EXPERIMENTAL

Reagents

Copper solution: Copper metal (99·9%) was dissolved in nitric-hydrochloric acid. The concentration of copper in the solution was determined by electrolysis, by precipitation with BPHA and by iodometric titration.

BPHA: Eastman Organic Chemicals, Distillation Products Industries, Rochester 3, New York, U.S.A.

BPHAA: This is a new PFHS compound manufactured by Burdick and Jackson Laboratories, Muskegon, Michigan, U.S.A.

All other chemicals used were reagent grade.

RESULTS AND DISCUSSION

As a result of preliminary investigations, the following procedure was devised:

Solutions containing 1 to 25 mg of copper in a 400-ml volume were buffered at pH 4·5 with 0·1M acetic acid-0.1M sodium acetate buffer. The solutions were heated nearly to boiling and 19 ml of an ethanolic solution, containing twice the theoretical amount of BPHAA required to precipitate the copper present, were added with stirring. The beakers were then immersed in a constant temperature bath (65°). After 24 hr, one tenth of the theoretical amount of BPHA* in 1 ml of ethanol was added

---

* This is a precautionary measure to make certain of the removal of final traces of copper, especially if there is doubt as to the full maintenance of the proper temperature throughout the period of precipitation (*cf.* Gordon, Salutsky and Willard[12]).

TABLE I.—PRECIPITATION OF COPPER ALONE

Method of precipitation	CONVEN-TIONAL	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS
Cu taken, *mg*	24·4	24·4	20·4	14·3	10·2	5·84	4.08	2·04	1·02
Difference in Cu found, *mg*	0·0 0·0	0·0 0·0	0·0 0·0	−0·1 −0·1	−0·2 −0·2	−0·1 −0·1	−0·3 −0·2	−0·3 −0·5	−0·4 −0·3
Cu in filtrate, *mg*	a	0·04 0·06	a	0·13 0·18	0·22 0·26	a	a	a	a

[a] not determined

TABLE II.—SEPARATION OF COPPER FROM DIVERSE IONS

Method of precipitation	CONVEN-TIONAL	PFHS	CONV.	PFHS	CONV.	PFHS	CONV.	PFHS	CONV.	PFHS
Diverse ion, *mg*	Cd 75	Cd 75	Cd 75	Cd 75	Cd 25	Cd 25	Co 75	Co 75	Co 25	Co 25
Cu taken, *mg*	25·0	25·0	14·3	14·3	20·4	20·4	20·4	20·4	20·4	20·4
Difference in Cu found, *mg*	+0·4 +0·5	0·0 0·0	+0·4 +0·3	0·0 −0·1	0·0 +0·3	0·0 0·0	+1·0 +1·1	+0·1 +0·1	+0·6 +0·8	0·0 0·0

and 30 min later the hot solutions were filtered. The precipitates were washed with hot water and dried at 110°.

Low results were obtained when temperatures above 65° were used during the 24-hr reaction time. Although a shorter precipitation period could be obtained by utilising the faster hydrolysis rate of BPHAA at higher temperatures, reagent decomposition was a limiting factor. The decomposition of BPHAA seemed highly dependent on pH, becoming negligible in acidic solution. However, the hydrolysis rate of the reagent becomes slower in more acidic media. These are factors which could be considered in developing methods for the precipitation of other metals. Low results were also obtained if the reaction mixture contained more than 20 ml of ethanol.

As Table I shows, between 10 and 25 mg of copper could be quantitatively precipitated by means of BPHAA. Low results were obtained when less than 10 mg of copper were precipitated. Quantities of copper greater than 25 mg were not used because of the restriction imposed by the solubility of BPHAA, *i.e.*, this upper amount of copper was equivalent to the maximum quantity of BPHAA (twice the theoretical) which the reaction medium described in the procedure was capable of dissolving. As shown in Table I also, copper in several of the filtrates was determined with dithizone with the results confirming the gravimetric data.

Table II demonstrates the superior separations which BPHAA affords over BPHA when copper is precipitated in the presence of cobalt or cadium. Much better physical characteristics were also obtained by the method of PFHS.

Acknowledgement—Two of the authors (Paul Ellefsen and Louis Gordon) wish to acknowledge the partial support of the United States Atomic Energy Commission under Contract AT(11–1)–582.

Summary—A preliminary study has been made of the use of *N*-benzoylphenylhydroxylamine acetate as a source of *N*-benzoylphenylhydroxylamine in precipitation from homogeneous solution. Initial experiments with a model system in which the separation of copper from cobalt and cadmium was studied have demonstrated the superior applicability of *N*-benzoylphenylhydroxylamine acetate over *N*-benzoylphenylhydroxylamine as a precipitant.

Zusammenfassung—*N*-Benzoyl-phenylhydroxylamin-acetat wurde zur Erzeugung von *N*-Benzoyl-phenylhydroxylamin bei der Fällung aus homogener Lösung verwendet. Erste Experimente, bei denen als Beispiel Kupfer von Kobalt und Cadmium zu trennen war, zeigten die Uberlegenheit des Acetats gegenüber *N*-Benzoyl-phenylhydroxylamin als Fällungsreagens.

Résumé—On présente une etude préliminaire de l'usage du *N*-benzoylphenylhydroxylamino acétate comme source de *N*-benzoyl-phénylhydroxylamine utilisée comme agent de précipitation dans les solutions homogènes. Les essais préliminaires sur une solution de référence en vue d'étudier la séparation du cuivre dans un système contenant aussi du cuivre et du cobalt, montre la superiorité du *N*-benzoylphénylhydroxylamino acétate sur la *N*-benzoylphénylhydroxylamine comme agent précipitant.

Department of Chemistry
Case Institute of Technology
Cleveland 6, *Ohio, U.S.A.*
PAUL R. ELLEFSEN
LOUIS GORDON®

Department of Chemistry
University of Birmingham
Birmingham 15, *England*
R. BELCHER

Burdick and Jackson Laboratories
Muskegon, Michigan, U.S.A.
WILLIAM G. JACKSON

REFERENCES

[1] S. C. Shome, *Analyst*, 1950, **75**, 27.
[2] J. Das and S. C. Shome, *Analyt. Chim. Acta*, 1961, **24**, 37.
[3] S. K. Sinha and S. C. Shome, *ibid.*, 1959, **21**, 459.

[4] *Idem*, *ibid.*, 1961, **24**, 33.
[5] F. J. Langmer and T. Hongslo, *ibid.*, 1960, **22**, 301.
[6] A. K. Majumdar and A. K. Mukherjee, *ibid.*, 1958, **19**, 23.
[7] D. E. Ryan and G. D. Lutwick, *Canad. J. Chem.*, 1953, **31**, 9.
[8] I. P. Alimarin and T. Yun'-Syan, *Zhur. Anal. Khim.*, 1959, **14**, 574.
[9] D. E. Ryan, *Canad. J. Chem.*, 1960, **38**, 2488.
[10] I. P. Alimarin and T. Yun'-Syan, *Zavodskaya Lab.*, 1959, **12**, 1435.
[11] S. K. Sinha and S. C. Shome, *Analyt. Chim. Acta*, 1959, **21**, 415.
[12] L. Gordon, M. L. Salutsky and H. H. Willard, *Precipitation from Homogeneous Solution.* John Wiley & Sons, Inc., New York, 1959, p. 60.

New *o-o′*-dihydroxyazo dyes from 8-hydroxyquinoline

(*Received* 27 *November* 1962. *Accepted* 25 *January* 1963)

INTRODUCTION

8-HYDROXYQUINOLINE (oxine) is able to couple with some diazo compounds, originating a series of dyes named "azoxines".[1] So far "azoxines" have only been described with the azo group in position 5 of 8-hydroxyquinoline.[2,3] Such compounds, although they form chelates of considerable stability with copper^{II} and other heavy metal ions, in general have a poor affinity for the alkaline earth metals. Therefore the possibility of preparing dyes with the azo group in the 7-position of 8-hydroxyquinoline has been studied in order to obtain *o-o′*-dihydroxy compounds, which are known[4] to form chelates of great stability with almost all metal ions.

This work was started fundamentally with the hope of finding with some of these dyes a fluorescent reaction, especially for aluminium and magnesium. 8-Hydroxyquinoline was selected as the coupling component because of its giving out fluorescence with these and other metallic ions, although with very little specificity.[5]

It has been found that almost all *o-o′*-dihydroxy dyes synthesised from 8-hydroxyquinoline give out a pink fluorescence exclusively with aluminium and magnesium, which can be specific and of extreme sensitivity in certain circumstances.[6]

Synthesis

When one tries to couple diazotised 1-amino-2-hydroxynaphthalene-4-sulphonic acid with 8-hydroxyquinoline in an aqueous medium at an alkaline pH (about 8), coupling takes place slowly in position 5 with formation of a purple dye. However, if the reaction is carried out in a 1:1 water-alcohol medium above 80°, coupling takes place in positions 5 and 7. The dye mixture thus obtained is purplish-blue in colour. This latter type of synthesis offered the desired results with regard to a dye with a specific reaction for magnesium.

Several attempts were made to obtain a maximum yield of the compound coupled in the 7-position; optimal results were reached at pH values about 10 and at temperatures near to 80°. At room temperature the purple compound was formed almost exclusively. Several other media were tried, but the above mentioned one was found to give the best performance.

EXPERIMENTAL

Diazotisation of 1-*amino*-2-*hydroxynaphthalene*-4-*sulphonic acid*

Disperse 25 g of 1-amino-2-hydroxynaphthalene-4-sulphonic acid in 50 ml of water, then add 0·2 g of hydrated copper sulphate and 9 g of sodium nitrite dissolved in the minimum amount of distilled water. Leave the solution in the dark for 1–2 hr, after which the diazotisation is complete. Add an excess of concentrated hydrochloric acid, filter off the hydrochloride through a sintered-glass funnel and wash with two portions of 10 ml of 1:1 hydrochloric acid.

Coupling with 8-*hydroxyquinoline*

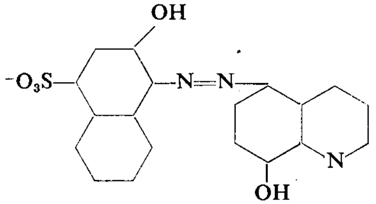
Dissolve 16 g of 8-hydroxyquinoline in 100 ml of a 1:1 mixture of water and alcohol, then add the solid diazo compound and when complete solution is obtained add 2*M* sodium hydroxide slowly and with constant stirring until the pH is 10. Heat the mixture to 60–70° (the liquid immediately takes up a purplish-blue tint), and continue to heat for a further 0·5 hr, then eliminate the alcohol as much as possible. Acidify the solution with acetic acid to pH 5–6, thus precipitating the greater part of the azo dye. Filter the precipitate and wash several times with water and finally with acetone. About 11 g of raw dye is obtained whose water solution at pH 10 is purplish-blue in colour.

By means of paper chromatography it was possible to show that the product was a mixture of two compounds with very similar R_f values; one compound is blue and the other purple. If the synthesis was made under similar conditions but in the cold, the resulting dye gave almost exclusively the purple fraction when chromatographed.

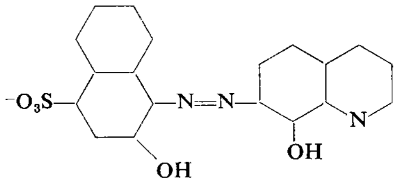
Dye composition

Elementary analysis of the two dye samples gave very similar results, although not very reliable ones because of the difficulty of obtaining pure samples of them.

The product is considered to consist almost exclusively of the two isomers coupled in the 5- and 7-positions of the 8-hydroxyquinoline:



(1)



(2)

As can be seen, (2) is an *o-o′*-dihydroxyazo dye and it should therefore form chelates of a greater stability.

Chromatographic purification

Unsuccessful attempts were made to separate the two dye compounds by paper chromatography with different solvents. The chromatograms appeared with continuous tails which did not show any separation, and at the same time the original purplish shade changed to pink, probably because of the presence of traces of metal ions in the paper or in the solvent.

By means of Whatman No. 1 paper, previously washed with 0·1*N* EDTA solution (as disodium salt), and with a solvent made up of butanol-ethanol-water-aqueous ammonia (1:1:0·5:0·05), separations were obtained which were good enough to allow an individual elution of both compounds.

In the separation on a preparative scale, much greater difficulty was experienced because the normal chromatographic systems worked only in the 0·1 to 1-mg range, but not at the 100 to 200-mg level.

Among the recommended methods in the literature for similar separations, only that of column chromatography with cellulose powder enabled a preparative-scale separation to be achieved. A column was prepared from cellulose powder Binzer No. 221 and washed with 0·02*N* EDTA solution (about 1 litre), then with distilled water and finally with 1 litre of butanol-ethanol-water-aqueous ammonia solution.

Procedure. Dissolve 0·1 g of the dye sample in about 25 ml of the butanol-ethanol-water-aqueous ammonia solvent, filter through a Whatman No. 1 paper previously washed with EDTA and pass the resulting solution through the column of cellulose powder. When all of the solution has been introduced, pass fresh solvent slowly (at about 1 ml/min) through the column.

After some hr separation into two well defined bands is observed, the first one purple and the second one blue, with an intermediate zone of a mixture of these also apparent. Elute the three fractions, the the first and the last, corresponding to the two components under study being in a greater amount. Evaporate (temperature not above 40–50°) each fraction until dry, leaving a dark black or brown solid.

From the final amounts collected it was not possible to deduce the percentage of each of the two compounds in the original sample, because of losses through adsorption in the column and the intermediate fractions which could not be further fractionated. Fig. 1 shows the absorption spectrum in the visible range of the blue and purple fractions at pH 10.

RESULTS AND DISCUSSION

At pH 10 the dye (2) is pure blue, but if a trace of a metal ion is added, the colour immediately changes to a shade ranging from pink to purple. In the case of magnesium^{II} a carmine red hue with an intense pink fluorescence under ultraviolet light was observed, visible even in diffuse light. It is essential that the pH be 10–11·5 as a maximum; a pH higher than 10 gives a fluorescence intensity somewhat lower. With aluminium^{III} the fluorescence obtained is also of a pink hue, the maximum intensity of which is reached at pH 6–6·5.

The dye (2) forms chelates with the following metals: copper^{II}, zinc^{II}, cadmium^{II}, aluminium^{III}, iron^{III}, thorium^{IV}, nickel^{II} and cobalt^{II}, irreversibly with regard to EDTA but some of them reversible to cyanide. In the case of the zinc and cadmium chelates, after several tests the conclusion has been reached that they are or are not reversible to EDTA according to the reaction conditions, depending especially on the ratio of the amount of metal ion to that of dye, possibly because of a 2:1 complex which would be of a higher stability than the EDTA complex.

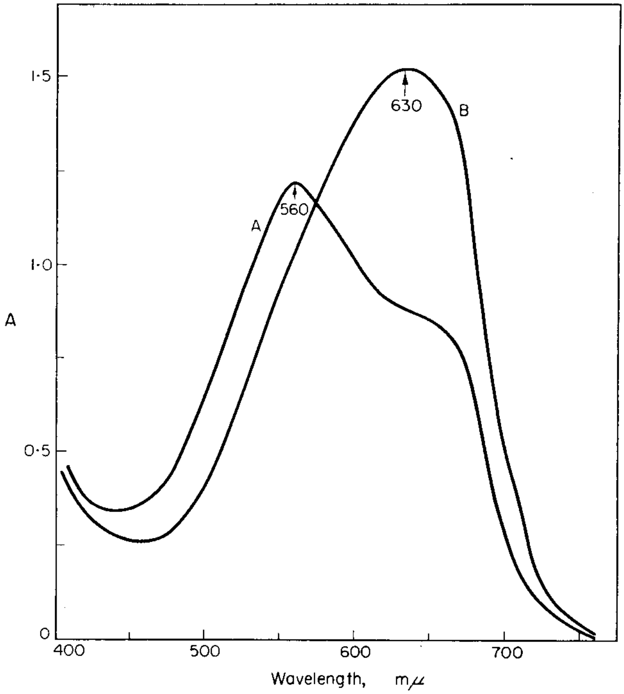


Fig. 1.—Absorption spectra at pH 10:
(A) Blue fraction, (B) Purple fraction.

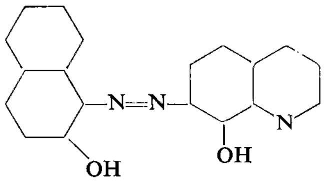
The reaction with magnesium has been studied, the pink fluorescence being specific at pH 10 in the presence of a masking agent, such as cyanide, triethanolamine, ascorbic acid, *etc.*, because heavy metals would otherwise interfere. Calcium does not interfere provided it is present in amounts not higher than 250 times that of magnesium. The sensitivity limit for magnesium alone is 1 μg in 10 ml (0·1 ppm).

The possibility has been studied of using the dye as an indicator in chelometric titrations. In the titration of calcium and magnesium with EDTA it changes from carmine to blue, with an equal or superior contrast to Eriochrome Black T, and it has the advantage of being more stable in solution.

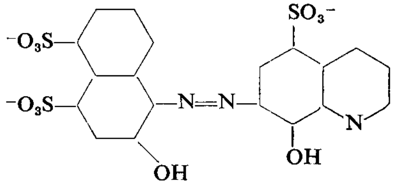
The chelometric titration of calcium with this indicator at pH 10 is not satisfactory because of the small stability of the calcium complex at this pH. However, at pH 11·5 (concentrated aqueous ammonia) the indicator works very well and titrations can be carried out with a very strong contrast (magnesium interferes).

The dye (1) behaves like "azoxines" coupled in position 5, forming chelates of remarkable stability with copper^{II} which are reversible to EDTA. Also it acts as a redox indicator. Thus, in the presence of a trace of copper^{II} and cyanide at pH 8 it changes from violet to colourless. On the addition of ascorbic acid the original colour is restored. With this reaction it has been possible to detect copper^{II} at a level of 1 μg in 10 ml. The mechanism of the reaction is unknown, but it might arise from the oxidising power of the CN_2 formed between the copper^{II} and the cyanide.[7]

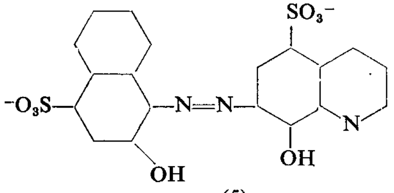
The following dyes which are similar to (2) have been synthesised and they have been found to have the same properties as (2):



(3)

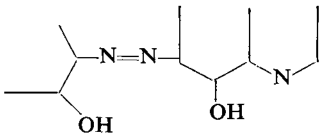


(4)



(5)

It seems, therefore, that the characteristic group giving rise to fluorescence with magnesium is:



The dye (3) is somewhat soluble in non-polar solvents, which confers on it a potential interest for solvent extraction of cations.

Instituto de Biología Aplicada C.S.I.C.
Departmento de Fisiología Vegetal
Universidad de Barcelona, Spain

A. BADRINAS

Summary—The preparation and characteristics of a series of *o-o′*-dihydroxyazo dyes of 8-hydroxyquinoline have been studied. The colour and fluorescent reactions of these dyes with several cations are given, especially specific reactions for aluminium and magnesium.

Zusammenfassung—Die Darstellung und Eigenschaften einer Serie von *o-o′*-dihydroxi Azo-Farbstoffen von dem 8-Oxychinolin werden hier studiert und zwar angesichts ihrer analytischen Anwendung. Die farbigen und fluoreszenten Verhalten der vorgenannten Farbstoffe gegenüber verschiedenen anderen Kationen werden erwähnt, wobei eine besondere Aufmerksamkeit den spezifischen Verhalten von Aluminium und Magnesium geschenkt wird.

Résumé—L'obtention et les caractéristiques d'une série d'azo-colorants *o-o′*-dihydroxy de la 8-oxyquinoléine sont étudiées ici en vue de leur application analytique. On mentione les réactions colorées et fluorescentes des colorants indiqués avec divers cations, en insistant spécialement sur les réactions spécifiques de l'aluminium et du magnesium.

REFERENCES

[1] J. S. Fritz, W. J. Lane and A. S. Bystroff, *Analyt. Chem.*, 1957, **29**, 821.
[2] G. Gutzeit and R. Monier, *Helv. Chim. Acta*, 1933, **16**, 233.

[3] K. J. Matsumura, *J. Amer. Chem. Soc.*, 1927, **49,** 810.
[4] A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds.* Prentice Hall Inc., 1952, p. 2.
[5] J. A. Radley and J. Grant, *Fluorescence Analysis in Ultraviolet Light.* Chapman Hall Ltd., 1954, p. 401.
[6] F. Bermejo, A. Badrinas and A. Prieto, *Inf. Quim. Anal.*, 1960, **14,** 151.
[7] F. Feigl, *Spot Tests in Organic Analysis.* Elsevier, 1956, p. 330.

Selective spot test for europium in the presence of other rare earths

(*Received* 8 *January* 1963. *Accepted* 6 *February* 1963)

ONE of the separations of europium from the other rare earths is based on the exceptional stability of europium^{II} sulphate.[1–6] Unlike bivalent samarium and ytterbium, europium^{II} is relatively stable even in aqueous solution. Bivalent europium is especially stable in a sulphate-containing medium, as its precipitate resembles that of strontium sulphate. This behaviour was used for the specific detection of europium in the redox reaction with cacotheline.[7] This method is highly sensitive and specific, but the coloured reaction product faded quickly.

In the course of studies on the thermal decomposition of europium oxalate the problem of specific detection of europium arose, and it was found that a selective and efficient agent for the reduction of tervalent europium to its stable bivalent state is magnesium strips in sulphuric acid. The resulting bivalent europium readily reduces phosphomolybdic acid to molybdenum blue. As is known, this colour is highly stable.

Procedure

Minute quantities of the sample are taken in a micro test tube. A few strips of magnesium and about 1 ml of 2*N* sulphuric acid are added. After approximately 5 min, 1 drop of the solution is deposited on filter paper, and the stain is treated dropwise with a 5% aqueous solution of phosphomolybdic acid. The presence of europium is indicated by the appearance of an intense blue colour.

The test was found to be specific in the presence of all other rare earth elements.

Identification limit: 5 μg.

Concentration limit: 1:10,000.

Department of Inorganic and Analytical Chemistry
Hebrew University, Jerusalem, Israel

ERVIN JUNGREIS
EZRA LEVY

Summary—A new spot test for the detection of europium is described, based on the redox reaction between Eu^{II} and phosphomolybdic acid. The test is specific for europium in the presence of all other rare earth elements.

Zusammenfassung—Eine neue Tüpfelmethode für den Nachweis Europiums wurde beschrieben. Der Nachweis beruht auf die Redox-Reaktion zwischen zweiwertigem Europium und phosphomolybdischer Säure. Die Methode ist spezifisch für Europium in der Anwesenheit aller anderen seltenen Erden.

Résumé—Une nouvelle réaction à gouttes pour l'identification de l'Europium, basée sur la réaction d'oxyréduction entre Eu(II) et l'acide phosphomolybdique est proposée. La réaction est spécifique pour l'Europium en présence de tous les autres éléments des terres rares.

REFERENCES

[1] L. F. Yntema, *J. Amer. Chem. Soc.*, 1930, **52**, 2782.
[2] D. V. Pearce, *Chem. Revs.*, 1935, **16,** 131.
[3] H. N. McCoy, *J. Amer. Chem. Soc.*, 1935, **57,** 1756; 1936, **58,** 1577; 1941, **63,** 3432.
[4] A. Brukl, *Angew. Chem.*, 1936, **49,** 159.
[5] L. Holleck and W. Noddack, *ibid.*, 1937, **50,** 819.
[6] E. I. Onstot, *J. Amer. Chem. Soc.*, 1955, **77,** 2129.
[7] G. Beck, *Microchim. Acta*, 1938, **3,** 141.

An improved preparation of ammonium hexanitratocerate(IV) and routine analytical testing procedure to prove primary reference standard purity

(*Received* 22 *January* 1963. *Accepted* 7 *February* 1963)

INTRODUCTION

Ammonium nitratocerate was first proposed as a primary standard of reference in oxidimetry by Smith, Sullivan and Frank.[1] An exhaustive and extended study by Smith and Fly[2] substantiated the merits of the new proposed standard. Primary standards sodium oxalate and arsenic trioxide served as comparison standards. Both react stoichiometrically in the reduction of the cerate when perchloric acid is employed in the reacting solutions. Nitroferroïn serves as indicator with the reactants at ambient temperature. The single electrode potential of the couple $Ce^{IV} \longleftrightarrow Ce^{III}$ in formal perchloric acid solution is 1·71 V. The potential "break" at the equivalence point is approximately 0·8 V.[3]

PREPARATION OF 98·5% NITRATOCERATE

Hydrated ceric oxide, $CeO_2{\cdot}H_2O$, is dissolved in hot concentrated nitric acid. The solution thus obtained is filtered using glass cloth and reduced pressure. The filtrate is then treated with an excess of ammonium nitrate to form the ammonium derivative of nitratoceric acid, insoluble in concentrated nitric acid. The orange-yellow crystals are filtered with reduced pressure, and are air dried to give 98·5–99% pure nitratocerate. More complete directions in these manipulations are described in references[1,2] previously cited.

FINAL PURIFICATION OF AMMONIUM NITRATOCERATE

The former procedure[1,2] for the purification of 98·5–99·0% pure nitratocerate involved recrystallisation from concentrated nitric acid. The improved procedure involves recrystallisation from aqueous solution. When ammonium nitratocerate is dissolved in distilled water to make a saturated solution, the pH developed is approximately unity. No hydrolysis of the standard Ce^{IV} results. Even on heating to boiling point, such solutions still do not hydrolyse. The temperature coefficient of reduction in solubility with lowering temperature is very favourable to the production of finely divided crystal aggregates. These are filtered in commercial-size Buchner-type filters with reduced pressure applied. The crystals are washed with a limited amount of water, and are finally dried at 85°. The product, tested as hereinafter outlined, from two separate 50-pound batches of purified material prepared for commercial distribution,* gave purity of 100·0% and 99·95%. The accuracy is approximately ±0·02%.

ROUTINE QUALITY TEST PROCEDURE

Reagents

Perchloric acid: Formal, sp. gr. 1·055 at 25°/4°.

Sodium Oxalate: U.S. Bureau of Standards, primary standard.

Nitro-ferroïn indicator solution: 0·001825*N*; 1 ml is equivalent to 0·0010 g of ammonium nitratocerate.

Ammonium nitratocerate solution: 1 mg of nitratocerate in 1 ml of 1*F* perchloric acid (0·001825*N* nitratocerate).

Ammonium nitratocerate to be tested for purity: Dried to constant weight at 85° (Mol. Wt. $548{\cdot}25_8$).

Apparatus

400-*ml beakers:* Freed from the least trace of adsorbed organic matter by rinsing with hot perchloric acid containing ammonium nitratocerate, followed by rinsing with distilled water.

Transfer pipette: 1·0-ml capacity.

Calibrated 1·0-*ml pipette:* marked in 0·1-ml graduations.

Procedure

Weigh accurately 2·1938 g of ammonium nitratocerate. Transfer the weighed sample to a 400-ml beaker. Dissolve the sample in 125–130 ml of 1*F* perchloric acid. The solution will be light yellow. This weight of sample is equivalent to 40 ml of 0·1000*N* reagent for test (with a 0·0008-g vacuum weighing correction applied).

Weigh accurately 0·2680 g of standard reference sodium oxalate. Transfer the weighed sample to a 400-ml beaker. Dissolve the oxalate in 125–130 ml of 1*F* perchloric acid. This weight is equivalent to 40 ml of 0·1000*N* reagent solution (any vacuum weighing correction is negligible).

---

* By The G. Frederick Smith Chemical Co. of Columbus, Ohio, U.S.A.

With thorough stirring (preferably by a magnetic device with accompanying beaker rotor) transfer the cerate solution to the oxalate solution, slowly, over an interval of 15–20 sec. The interaction is instantaneous at ambient temperature.

Now add 1 ml of indicator. With nitratocerate of 100% purity, the indicator will give a pink solution because of its own colour. If the nitratocerate is somewhat less than 100% pure, the colour of the solution at this point will be produced by the indicator in the presence of a minute excess of unoxidised oxalate.

Using the calibrated 1-ml pipette, now add the volume of 0·001825*N* nitratocerate solution just necessary to decolorise the indicator. If 1·0 ml only of this nitratocerate solution is required, the standard of reference oxidant being tested is 100·00% pure. Each 0·1 ml of the titrant over 1·0 ml corresponds to 0·0001 g of additional nitratocerate which must be added, to be exactly equivalent to the weight of sodium oxalate oxidised. By subtracting 1·0 ml from the required addition of back-titrant, and multiplying the result by 0·0010 g/ml, the correction weight of ammonium nitratocerate is found. This value subtracted from 2·1930, and the result divided by 2·1930 will give the purity of the test sample under standardisation.

PRECAUTIONS

Do not dry ammonium nitratocerate above 85°.

The reaction beakers must be completely devoid of adsorbed organic material on their inner walls. The redox potential of the $Ce^{IV} \leftrightarrow Ce^{III}$ system in 1*F* perchloric acid, as previously stated, is 1·71 V. Almost all forms of organic matter are rapidly oxidised, exhibiting high equivalency factors.

The indicator is added in minimal amounts because of low solubility in perchloric acid solution (less than sufficient to form a 0·001*N* solution).

The redox colour change at the equivalence point is not permanent. In bright daylight, or on exposure to direct sunlight, it is quite rapidly reduced from the ferric to the ferrous form with return of the red colour (4–5 min).

For each ml of 0·1000*N* solution, 54·4825 mg of $(NH_4)_2Ce(NO_4)_2$ are required.

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

G. Frederick Smith

Summary—Ammonium nitratocerate, $(NH_4)_2Ce(NO_3)_6$, has been employed over a period of years as a primary standard in oxidimetry. An improved method for its preparation is described. Practical routine control laboratory directions are given for proving the purity of the finished product.

Zusammenfassung—Ammoniumnitratocerat $(NH_4)_2Ce(NO_3)_6$ wird schon seit vielen Jahren als Urtitersubstanz in der Oxydimetrie verwendet. Es wird hier eine verbesserte Reinigungsmethode für das Salz beschrieben und für den routinemäßigen Laboratoriumsbetrieb geeignete Methoden zur Reinheitsprüfung des Endproduktes werden angegeben.

Résumé—Le nitratocérate d'ammonium, $(NH_4)_2Ce(NO_3)_6$, a été utilisé pendant des années comme échantillon standard en oxydimetrie. Amélioration de la méthode de purification, et contrôle de pureté dans le produit élaboré.

REFERENCES

[1] G. F. Smith, V. R. Sullivan and G. Frank, *Ind. Eng. Chem., Analyt.*, 1936 **8** 449.
[2] G. F. Smith and W. H. Fly, *Analyt. Chem.*, 1949, **21,** 1233.
[3] G. F. Smith and J. S. Fritz, *ibid.*, 1948, **20,** 874.

Talanta, 1963, Vol. 10, p. 711. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

Sorption of ferroïn on silica and its analytical use

SIR:

In a previous paper[1] dealing with the sorption of ferroïn on silica and its utilisation for the determination of trace amounts of iron, an alkaline solution of potassium iodide was recommended as desorption reagent. This reagent forms with ferroïn an ion-association complex $[Fe(Phen)_3{}^{2+}2\ I^-]$ insoluble in water but very soluble in a water-methanol mixture.

Recently we have observed that the complexes of 1,10-phenanthroline with metals (including iron^{II}) which are sorbed on silica can be easily desorbed in the form of their complexes $[Fe(Phen)_3{}^{2+},2X^-]$, where X is an anion of certain monobasic acids, *e.g.*, monochloroacetic, trichloroacetic, acetic or formic acid. Ferroïn sorbed on a silica column (5 cm high and 1·5 cm in diameter) is completely desorbed with 10–15 ml of 1*M* solutions of the acids mentioned, of which the pH has been adjusted to 9–10. Particularly when the sorption is carried out in the presence of EDTA it is appropriate to use water-methanol mixtures for the desorption. We find it quite satisfactory to use a mixture with methanol of an aqueous solution of the composition described in the ratio 1:1.

It appears probable that the substitution of commoner salts for the relatively expensive potassium iodide could be of value for industrial laboratories where the economic factor in a series of analyses plays an important role.

F. VYDRA
M. MARKOVÁ

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

5 *March* 1963

REFERENCE

[1] F. Vydra and V. Marková, *Talanta*, 1963 **10**, 339.

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

EDITORIAL NOTE

Some of the papers in this issue have been held over for one month because of the publication of the Hungarian Honour Issue in May.

The Editorial Board of Talanta would like to apologise to those authors whose papers have suffered this delay.

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

NOTICES

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

BUNDESREPUBLIK DEUTSCHLAND

Anläßlich der Hauptversammlung der Gesellschaft Deutscher Chemiker, die dieses Jahr vom 9 bis 14. September in Heidelberg stattfindet, lädt die Fachgruppe "Analytische Chemie" zu einer 1 1/2-tägigen Vortragsveranstaltung ein. Sie steht unter dem Rahmenthema

"Analytische Methoden in der medizinisch-biologischen Praxis und Forschung",

dessen erster Teil am 9. und 10. September Vorträge über "*Moderne analytische Methoden und Probleme auf dem Gebiet der Eiweisschemie*" bringen wird. Im nächsten Jahr sind zwei Fortsetzungen dieser Vortragsveranstaltung in Form von Arbeitstagungen über die klinische Analyse organischer Substanzen sowie anorganischer Ionen, die im Rahmen von größeren Fachgruppen-Tagungen stattfinden sollen, vorgesehen.

Für die Heidelberger Vortragesveranstaltung sind folgende Hauptvorträge vorgesehen:

Prof. Dr. ZAHN, Aachen:
"*Zum heutigen Stand der Proteinchemie*"

Prof. Dr. SCHREIER, Heidelberg:
"*Analytische Probleme bei angeborenen Anomalien des Eiweissstoffwechsels*"

Prof. Dr. TURBA, Dr. FASOLD, Dr. GUNDLACH, Würzburg:
"*Neuere Methoden zur Trennung und Reinigung von Proteinen*"

Dr. BARANDUM, Bern:
Beispiele für die klinische Bedeutung immunochemischer Untersuchungen"

Dr. HEß, Heidelberg:
"*Grundlagen der Bestimmung von Enzymaktivitäten*"

Dr. RICHTERICH, Bern:
"*Zuverlässigkeit von Laboratoriumsmethoden in der Eiweiss- und Enzymanalytik*"

Dr. SCHÖN, Erlangen:
"*Klinische Analyse, ihre Aufgaben und Probleme*".

Die Hauptvorträgesollen durch kurzeOriginalberichte, die sich mit dem Themenkreis "*Analytische Methoden der Eiweißchemie*" befassen, ergänzt werden.

CZECHOSLOVAKIA

Thursday 6 *June* 1963: **National Conference on Modern Methods of Analysis of Fats and Similar Products:** *Czechoslovak Chemical Society:* Prague. There will be a discussion on statistical treatment of the results, accuracy and sensitivity of new analytical methods recommended by the Division of Fats and Oils, I.U.P.A.C.

Wednesday-Monday 12–24 *June* 1963: **Seminary on Spectral Analysis:** *Czechoslovak Chemical Society:* Brno.

DEUTSCHE DEMOKRATISCHE REPUBLIK

Die Technische Hochschule für Chemie Leuna-Merseburg veranstaltet unter Mitwirkung der Chemischen Gesellschaft in der Deutschen Demokratischen Republik, Fachgruppe Analytische Chemie, eine Hochschultagung über

Moderne Methoden der analytischen Chemie

Diese Tagung hat die Aufgabe, die Verbindung von Wissenschaft und Praxis auf dem Gebiet der analytischen Chemie zu vertiefen. Es sollen einige besonders interessante Beispiele neuerer Analysenmethoden und ihrer Anwendung behandelt werden. Die Tagung umfaßt 3 Themengruppen:

I. *Neue Analysenmethoden,*
II. *Analytik spezieller Stoffgruppen,*
III. *Bedeutung der modernen analytischen Chemie in der Technik.*

Zur Übernahme von Vorträgen haben sich u.a. folgende namhafte Wissenschaftler aus Hochschule und Industrie bereit erklärt: Prof. Dr. J. Bognár, Miscolc, Prof. Dr. I. A. Busev, Moskau, Hüttendirektor Dr. H. Eckstein, Eisleben, Prof. L. Erdey, Budapest, Prof. Dr. Günther, Merseberg, Prof. Dr. M. Jureček, Pardubice, Dr. R. Kalvoda, Prag, Dr. S. Rennhak, Leuna, Prof. Dr. E. Rexer, Dresden Prof. Dr.-Ing. K. Schwabe, Dresden.

Die Leitung liegt in den Händen von Herrn Prof. Dr. R. Geyer, Direktor des Instituts für Analytische Chemie der Technischen Hochschule für Chemie Leuna-Merseburg, DDR.

NIEDERLANDE

Symposium über "**Moderne Methoden der Analyse organischer Verbindungen**", organisiert von der Fachgruppe "Analytische Chemie" der Gesellschaft Deutscher Chemiker und von der Sectie voor Analytische Chemie van de Koninklijke Nederlandse Chemische Vereniging vom 20.–23. Mai 1964 in Eindhoven (Holland). Das Symposium stellt die Fortsetzung der Münchener Analytikertagung von 1960 dar und steht unter der Patenschaft der Analytischen Sektion der IUPAC. Als Unterthemen für das Symposium wurden geplant:

1. *Elementaranalyse, funktionelle Gruppen*
2. *Konstitution organischer Verbindungen Molekülspektroskopie*
3. *Trennverfahren Wanderungsverfahren, chromatographische Verfahren*
4. *Analyse von Hochpolymeren*
5. *Analyse von Naturstoffen, klinische Analyse*

Das Programm der Tagung wird voraussichtlich Anfang 1964 zur Verfügung stehen. Auskünfte gibt die GDCh-Geschäftsstelle, 6000 Frankfurt (Main), Postfach 9075.

SWITZERLAND

Tuesday 27 *August–Wednesday* 4 *September* 1963: **Second World IFAC Congress on Automatic Control:** *Swiss Federation of Automatic Control:* Basle. The programme will cover the theory, applications and components of automatic control. Further information may be obtained from the Congress Secretary: Dr. ANTON VON SCHULTHESS, Wasserwerkstrasse 53, Zürich 6, Switzerland.

From Monday–Saturday 2–7 September 1963, the Swiss Industries Fair at Basle is organising an international exhibition "INEL-63" on Industrial Electronics where the newest developments and applications will be shown.

UNITED KINGDOM

Thursday 13 *June* 1963: **Summer Meeting:** *Society for Analtyical Chemistry, Biological Methods Group:* United Dairies Ltd., Wood Lane, London W. 12. During the morning the following papers will be delivered: **Aspects of the Natural Composition and Hygenic Quality Schemes**—Dr. R. C. WRIGHT, **Antibiotics in Milk**—Dr. J. TRAMER; a conducted tour of the Laboratories will take place during the afternoon.

Wednesday–Wednesday 10–17 *July* 1963: **XIXth International Congress of Pure and Applied Chemistry:** London (see *Talanta*, 1962, **9**, 955).

Wednesday–Friday 17–19 *July* 1963: **Microchemistry Group Summer Meeting:** *Society for Analytical Chemistry:* School of Pharmacy, Brunswick Square, London W.C. 1 [see *Talanta*, 1963 **10**, vi (April)].

Wednesday–Tuesday 17–23 *July* 1963: **Fifth International Pesticides Congress:** Friends House, London W.C. (see *Talanta*, 1962, **9**, 1073).

Monday–Friday 22–26 *July* 1963: **Microscopy Symposium:** *McCrone Research Institute:* Brighton.

Thursday–Friday 5–6 *September* 1963: Meeting on **Modern Aspects of Chromatography:** *Society for Analytical Chemistry, Scottish Section* and *Institute of Chemistry of Ireland:* Rupert Guiness Hall, Dublin.

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

B.S. 1121*: Methods for the analysis of iron and steel: Part* 43*:* 1963*: Alumina in iron ores and slags.* This specifies a method applicable to all iron ores, iron ore sinter, blast furnace and steel making slags containing more than 0·5% alumina, which are substantially acid-soluble. (*Price* 3s.)

B.S. 1747*: Measurement of air pollution: Part* 3*:* 1963*: Determination of sulphur dioxide.* This covers the construction and use of apparatus for the determination of atmospheric sulphur dioxide (*Price* 4s.)

UNITED STATES OF AMERICA

June 1963: **Second Annual Thermoanalysis Institute:** Florham-Madison campus, Fairleigh Dickinson University, New Jersey.

The Institute will cover the fundamentals of the theory and applications of thermoanalytical research techniques that are rapidly finding increasing applications in the study of diverse chemical systems. The programme will consist of intensive lectures and laboratory sessions. Lecturers will be scientists who are actively engaged in research programmes utilising differential thermal analysis, thermogravimetry and effluent gas analysis to avaluate a wide variety of organic, inorganic and metallo-organic compounds that are of both natural and synthetic origin. Specific fields in which these approaches are providing new and improved physicochemical data include polymer chemistry, pharmaceuticals, cosmetics, space age propellants and minerology.

The Institute will be comprised of a one-week introductory session, 10–14 June, followed by a three-day advanced session, 17–19 June. A second introductory session is scheduled for 24–28 June. Further information can be obtained from Dr. Saul Gordon, Director, Thermoanalysis Institute, Fairleigh Dickinson University, Madison, New Jersey.

Sunday–Friday 23–28 *June* 1963: **66th Annual Meeting of A.S.T.M.:** Chalfonte-Haddon Hall. Alantic City, N.J.

The programme for the **Symposium on X-ray and Electron Probe Analysis** is as follows:

Thursday, 27 *June*, *Morning*

Production of X-rays in X-ray Emission Spectrography.	P. D. Zemany
X-ray Optics in Electron Micro Analysis.	R. E. Ogilvie
X-ray Detectors and Electronic Systems.	W. R. Kiley

Thursday, 27 *June*, *Afternoon*

X-ray Spectrographic Analysis of Metals and Minerals: Scope and Limitations of Quantitative Analysis.	J. W. Kemp
Fluorescent X-ray Spectrographic Analysis of Trace Constituents, including Thin Films.	W. J. Campbell
X-ray Spectrographic Analysis of Liquids and Solutions.	E. L. Gunn

Thursday, 27 *June*, *Evening*

Electron Optical Design of Microprobe Analysers.	R. M. Fisher
Methods of Quantitative Electron Probe Analysis.	D. B. Wittry
Comparison of X-ray Fluorescence and Electron Probe Methods: Future Trends.	L. S. Birks

Friday, 28 *June*, *Morning*

Applications of the Electron Probe Microanalyser to Metallurgical Research.	K. F. J. Heinrich
Microprobe Analysis of Minerals and Segregates.	I. Adler
Electron Probe Applications to Biology.	A. J. Tousimis

Tuesday–Thurdsay 8–10 *October* 1963: **Seventh Conference on Analytical Chemistry in Nuclear Technology:** Oak Ridge National Laboratory, Gatlinburg, Tennesse.

The scope of the subject matter of the Conference this year will differ somewhat from that which was generally followed in the past in that all sessions will be devoted exclusively to different aspects of a single subject: **Analytical Instrumentation, covering the Design, Development and Utilisation of Manual and Automatic Methods of Analysis.**

It is intended that the Conference will be composed of six sessions embracing the following subtitles:

1. *Instrumental Methods for the Analysis of Molten Salt Systems.*
2. *Instrumentation for the Remote Controlled Analysis of Radioactive Materials.*
3. *Electroanalytical Instrumentation.*
4. *A Round-Table Discussion of Recent Developments in Analytical Instrumentation.*
5. *Analytical Spectroscopy and Gas Chromatography.*
6. *Instrumentation in Radiochemistry and Nuclear Analysis.*

Participation in the Conference either as a speaker or as a panelist will be on the basis of invited contributions; however, a limited number of papers, up to 25 min in length, are solicited and will be accepted provided the subject matter fits in with the over-all objectives of the Conference and meets with the approval of the Programme Committee.

Those who wish to make contributions are requested to submit an abstract of about 500 words not later than 10 July, giving the name of the intended speaker and the amount of time required for the presentation. Abstracts of papers and any enquires concerning the Conference should be directed to C. D. SUSANO, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee.

The American Society for Testing and Materials has announced that the following publications are now available:

ASTM Manual for Conducting an Interlaboratory Study of a Test Method, STP 335. The procedure described is intended for use in a programme to study the statistical aspects of a well-defined physical or chemical testing process or to compare the relative merits of two or more alternative methods It is designed to: (1) Extract from the data information that will help evaluate the precision of the method within a laboratory as well as on an interlaboratory scale, (2) Furnish the basis for specific recommendations concerning the number of specimens to be tested and the need for reference samples, and (3) Predict the improvement in precision that is likely to result from the use of reference samples. A secondary objective of the procedure is to obtain information on the most likely causes of aberrant results and thereby to lead to a better specification of the test method. (Price $2.00; $1.60 to ASTM members.)

ASTM Standards on Glass and Glass Products, C-14. Standards and tentatives contained in this compilation cover: Glass and Glass Containers, Glass Block and Insulation, Glass Insulators, Glass Fibre Materials, Glass Spheres for Use in Paints, Electrical Tests and Spectrochemical Analysis. The section on spectrochemical analysis gives the following methods of analysing glass and ceramics: (Analysing) Ceramics and Other Non-Metallic Materials by the Powder-D.C. Arc Technique, (Analysing) Glass for Alkali Elements by Flame Photometry and (Analysing) Glass for Alkaline Earth Elements by the Flame Photometer Technique. (Price $4.00; $3.20 to ASTM members.)

ASTM Standards on Coal and Coke, D-5. Particularly important is the preparation of coal samples for analysis (D 2013). Proposed methods for the mechanical sampling of coal are also included. The methods for measuring the gross calorific value of solid fuel by the adiabatic bomb calorimeter (D 2015) is especially pertinent because it is being presented to the International Standards Organisation for adoption as an international standard. (Price $3.50; $2.80 to ASTM members.)

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

ERRATA

Volume 9, *page* 715, *line* 18 *of Summary:* for *tungsten*^{IV} read *tungsten*^{VI}.

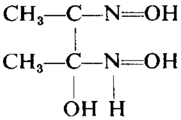
Volume 10, *page* 351, *line* 2 *of Stock uranium solution:* this should read *containing* 60 *ml of concentrated hydrochloric acid*. . . .

Volume 10, *page* 413, *line* 7 *from bottom of page:* the formula should be $Mg(ClO_4)_2 . 2H_2O$.

Volume 10, *page* 417, *Coulometric reduction of iridium*^{IV} *in perchloric acid emdia: Received* 24 *December* 1962. *Accepted* 24 *December* 1962.

Volume 10, *page* 419, *The reactions of biacetyl, hydroxylamine and metal ions to form chelates: Received* 28 *December* 1962. *Accepted* 30 *December* 1962.

Volume 10, *page* 419, *The reactions of biacetyl, hydroxylamine and metal ions to form chelates:* the second formula should be



$$\begin{array}{lll} CH_3- & C & -N=OH \\ & | & \\ CH_3- & C & -N=OH \\ & | & \;\;| \\ & OH & \;\;H \end{array}$$

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

PAPERS RECEIVED

Development and present state of complexometry: R. PŘIBIL. (30 *March* 1963).

Anion-exchange separation of rare earth elements and thorium from uranium with carbonate solutions: TOMITSUGU TAKETATSU. (30 *March* 1963).

Automatic recording analyser for determination of dissolved oxygen in boiler feed water: KAZUO TANNO. (1 *April* 1963).

A new reductimetric reagent: Iron^{II} in a strong phosphoric acid medium—Part IV: Simultaneous potentiometric determination of vanadium^{V} and uranium^{VI} (or molybdenum^{VI}) in mixtures: G. GOPALA RAO and L. S. A. DIKSHITULU. (3 *April* 1963).

Systematic titration errors in volumetric analysis: U. A. TH. BRINKMAN. (4 *April* 1963).

Semi-automatic determination of calcium and magnesium hardness in water: J. LACY. (8 *April* 1963).

Potassium dichromate in high phosphoric acid medium as a new oxidimetric reagent: G. GOPALA RAO and P. KANTA RAO. (16 *April* 1963).

Studies on the mode of action of Fajans' adsorption indicators: E. PUNGOR and I. KONKOLY THEGE. (17 *April* 1963).

Amperometric determination of lanthanum as molybdate: R. S. SAXENA and M. L. MITTAL. (19 *April* 1963).

Spectrophotometric studies of lower oxidation states of technetium: G. B. S. SALARIA, CHARLES L. RULFS and PHILIP J. ELVING. (27 *April* 1963).

Qualitative applications of mercaptohydroquinone and 4-mercaptoresorcine in inorganic analysis: F. BUSCARONS and J. ALSINA. (27 *April* 1963).

SOLUBILITIES OF INORGANIC AND ORGANIC COMPOUNDS

Volume I, Part I.

Edited by H. STEPHEN and T. STEPHEN

This work, in two volumes, is a compilation of published data on the solubility of elements, inorganic compounds, metallo-organic and organic compounds in binary, ternary and multicomponent systems. The extremely comprehensive material comprising the contents was obtained from a detailed survey of periodical literature, published in all languages and carried out by a panel of scientists specially appointed for the purpose by the Academy of Sciences of the U.S.S.R., Moscow.

In Volume 1, dealing with solubility in Water and Anhydrous Solvents, information is presented in the form of tables arranged systematically for easy reference. Table 1 lists the solubility of about 2,000 compounds in water; each subsequent table is devoted to the solubilities of a single compound, or a number of closely related compounds. There are in all 6,540 tables covering a vast number of compounds.

964 pages **£10 net**

THE APPLICATION OF MATHEMATICAL STATISTICS TO CHEMICAL ANALYSIS

V. V. NALIMOV

Translation Editor: M. WILLIAMS, *Birmingham College of Advanced Technology*

This translation of an important Russian book gives an up-to-date account of mathematical statistics as applied to problems connected with the chemical and physical methods of analysis, the emphasis being mainly on practice. The principal theorems of mathematical statistics are explained with examples taken from researches connected with the analysis of substances. Theoretical problems are considered only insofar as they are necessary for an understanding of the metrological aspect of the matter. A detailed account of contemporary literature in this field is included which demands from the reader only a knowledge of the mathematics normally included in the courses of technical colleges and an acquaintance with the principles of the theory of probability.

Invaluable as a handbook to engineers, physicists and chemists working in research laboratories, it will also act as a useful guide to further development in statistical methods of investigation.

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; Dispersional analysis; Statistics of linear connections; Some methods of work connected with the statistical planning of an experiment.

Distributed in the U.S.A. by Addison-Wesley Publishing Co. Inc. 304 pages Numerous illustrations **84s. net**

THE APPLICATION OF ORGANIC BASES IN ANALYTICAL CHEMISTRY

E. A. OSTROUMOV, *Academy of Sciences, Moscow*

The chemical analysis of naturally-occurring inorganic compounds—various rocks, ores and minerals—is often rendered difficult by the complex composition of the substance being analysed. The present work is 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. Accurate and rapid methods for the separation and determination of a number of elements have been developed, involving the use of the organic bases pyridine, α-picoline and hexamethylenetetramine. These methods have found extensive application in the analytical chemistry involved in geochemical studies. Since the Russians have a large background knowledge to call upon in the methods of analysis involving precipitation by pyridine, this book should prove of the utmost interest to all specialists in the field.

The book is divided into six parts: (1) The precipitation of metals using pyridine (2) The precipitation of metals by pyridine in the presence of its salts (3) The precipitation of metals with hydrogen sulphide in the presence of pyridine (4) The precipitation of metals using α-picoline (5) The precipitation of metals with hydrogen sulphide in the presence of hexamethylenetetramine (6) Methods for the separation of metals using pyridine α-picoline and hexamethylenetetramine; Conclusion; References.

180 pages **50s. net**

PERGAMON PRESS

Headington Hill Hall, Oxford

Pergamon Press books are distributed in the Western Hemisphere and the Philippines by the Macmillan Company, 60 Fifth Avenue, New York 11, N.Y., and Collier-Macmillan (Canada) Ltd., 132 Water Street South, Galt, Ontario, Canada.

VOLUME 10, NO. 6 JUNE 1963

CONTENTS