An International Journal of Analytical Chemistry

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1963 VOLUME 10 AUGUST

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.

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6/2345

SUMMARIES FOR CARD INDEXES

Use of oxycellulose for collection of traces of metals—I: Qualitative investigations: E. Schulek, Zs. Remport-Horváth and A. Lásztity, *Talanta*, 1963, **10**, 821 (Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest VIII, Múzeum körút 4/b, Hungary).

Summary—As a substance containing carboxyl groups oxycellulose is used for the collection and detection of metal ions in very high dilutions (0·001 to 0·1 ppm). From 3 to 5 mg of oxycellulose is applied for 100 or 1000 ml of solution. Also, the method proves to be suitable for the collection and detection of mixtures of various ions. The dependence of the collection of the following ions on pH is investigated: Ag^+, Al^{3+}, Ba^{2+}, Bi^{3+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sr^{2+}, UO_2^{2+}, VO^{2+} and Zn^{2+}.

Determination of small amounts of zirconium—II: Analysis of refractory samples: M. Rafiq, C. L. Rulfs and P. J. Elving, *Talanta*, 1963, **10**, 827 (Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.).

Summary—In connection with the determination of small amounts of zirconium in complex samples, procedures have been developed for bringing various types of sample into solution and removing possible interferences, which procedures allow *p*-bromomandelic acid to be used as a precipitant for the final recovery of zirconium for gravimetric measurement. The applicability of these procedures, which are described in detail, has been investigated by the analysis for zirconium of a variety of refractory mineral and metallurgical samples.

Applications of controlled-potential coulometry to the determination of plutonium: A review: W. D. Shults, *Talanta*, 1963, 10, 833 (Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.).

Summary—The determination of plutonium by controlled-potential coulometric titration has been studied and used at Oak Ridge National Laboratory over a period of several years. Two methods—the primary (direct) and secondary (indirect) titrations—have been applied to the analysis of a wide variety of materials. They have been used for the determination of total plutonium, of ionic and polymeric plutonium contents, and of the oxidation state distribution of plutonium solutions. This report describes the techniques, procedures and separations that have been developed. The effects of some contaminants that are common to plutonium-containing samples are also presented.

The infrared spectra of chelate compounds—I: A study of some metal chelate compounds of 8-hydroxyquinoline in the region 625 to 5000 cm^{-1}: R. J. MAGEE and LOUIS GORDON, *Talanta*, 1963, **10,** 851 (Department of Chemistry, Case Institute of Technology, Cleveland 6, Ohio, U.S.A.).

Summary—The infrared spectra of 8-hydroxyquinoline and its copper, zinc, manganese, magnesium and calcium chelate compounds have been determined between 2 and 16 μ. As far as possible, assignments of peaks have been made and correlations between peak position and stability constants have been drawn up. On the basis of the correlations the structure of the different chelates is discussed. From a study of the variation of peak height with concentration, it has been shown that the technique has considerable analytical value. A procedure is presented for the determination of copper and zinc as oxinates.

A method for the conductometric determination of sodium: D. CEAUSESCU, I. PÎRVU and FILOFTEI PÎRVUA, *Talanta*, 1963, **10,** 861 (Institut für Hygiene, Timisoara, Rumania).

Summary—A method for the determination of sodium is described, based on its precipitation as sodium zinc uranyl acetate. The precipitate is dissolved in water, and a conductometric titration is carried out using hydrochloric acid as the titrant. The method has the advantage that the ratio acetate:sodium is 9:1. It may be applied to any substance if sodium is precipitated as the triple acetate under suitable conditions. Experimental results for sodium, within the range 0·046–2·3 mg, are reported.

Ion exchange in mixed solvents: Adsorption behaviour of the rare earths and some other elements on a strong-base anion-exchange resin from nitric acid-alcohol media: Methods for separation and spectrophotometric determination: J. KORKISCH, I. HAZAN and G. ARRHENIUS,* *Talanta* 1963, **10,** 865 (Analytical Institute of the University of Vienna, IX, Währingerstrasse 38, Austria).

Summary—The anion-exchange behaviour of the rare earths and some other elements in aliphatic alcohols containing nitric acid is described. Based on the determination of the distribution coefficients and separation factors of the individual elements separation techniques are proposed. For the final determination of these elements the use of the azo dye Solochrome Fast Red as a spectrophotometric reagent is investigated.

Determination of mucopolysaccharide sulphate in connective tissue: GERALDINE ZDYBEK, D. S. MCCANN and A. J. BOYLE, *Talanta*, 1963, **10,** 879 (Department of Chemistry, Wayne State University, Detroit, 2, Michigan, U.S.A.).

Summary—A relatively rapid method for the determination of mucopolysaccharide sulphate is presented. The procedure depends on a desulphation technique combined with a turbidimetric determination of the sulphate.

A new principle of activation-analysis separations-IV: Substoichiometric determinations of traces of silver: Jaromír Růžička, Jiří Starý and Adolf Zeman, *Talanta*, 1963, **10,** 905 (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Charles' University, Praha 1, Břehová 7, Czechoslovakia).

Summary—A substoichiometric determination of traces of silver in germanium dioxide and in metallic lead has been developed. It consists of simultaneous irradiation of a standard and test sample in a nuclear reactor followed by dissolution and addition of silver carrier. After adjusting the pH, the samples are extracted with the same substoichiometric amount of dithizone in carbon tetrachloride and the activities of the organic extracts measured. This single-step separation procedure is fully satisfactory because of its high selectivity. Moreover, substoichiometry avoids the necessity of determining the chemical yield. The procedure developed could be adapted without difficulty for the determination of traces of silver in other materials.

Analysis of mixtures of mono- and di-alkyl orthophosphates: R. B. Lew, H. Gard and F. Jakob, *Talanta*, 10, 1963, 911 (Sacramento State College, Sacramento, Calif., U.S.A.).

Summary—Quantitative separations of mixtures of mono- and di-alkyl orthophosphates by salting-out chromatography on special Dowex 50-X4 resins of low capacity are described. Dimers of some of the mono-alkyl esters have also been isolated.

International comparison of analytical methods for nuclear materials—I: Accuracy and precision of some techniques in routine trace analysis: G. B. Cook, M. B. A. Crespi and J. Minczewski, *Talanta*, 1963, **10,** 917 (International Atomic Energy Agency, Seibersdorf Laboratory, Seibersdorf, Niederöesterreich, Austria).

Summary—The results of an international comparison designed to show the accuracy and precision of some techniques of trace analysis used routinely are given. The techniques are emission spectrography, absorption spectrophotometry, polarography and neutron activation. A common sample, an aqueous solution containing approximately 5 ppm of copper and manganese and 15 ppm of chromium and mercury has been analysed by 9 different laboratories. The statistical analysis of the results (551 in all) shows, with the limitations as to generality imposed by the design of the experiment, that the expected precisions of a single determination in the routine application of each of the techniques are: spectrography, $\pm 40\%$; polarography, $\pm 25\%$; activation, $\pm 20\%$ and spectrophotometry, $\pm 10\%$ at the 0·05-probability level. The accuracy follows the same pattern though the spread of results within a technique is wider. When all results are considered together the precision is $\pm 25\%$.

Studies of titrimetric and spectrophotometric methods for the determination of gold: A. Chow and F. E. Beamish, *Talanta*, 1963, **10,** 883 (Department of Chemistry, University of Toronto, Toronto 5, Ontario, Canada).

Summary—The titrimetric determination of gold by the iodometric technique is examined under various conditions. Irrespective of these conditions the stoichiometry of the reaction is found to be 1 atomic weight of gold to 2 formula weights of sodium thiosulphate. A modified bromoaurate spectrophotometric method is described, and the procedure is recommended for the determination of gold in amounts of 15 μg or more. The spectrophotometric determination of gold with methyl violet and trichloroethylene is examined critically. The method is recommended for concentrations of gold over the range 0·5–2·0 ppm. The stability of dilute gold solutions in acid media is also discussed.

Investigation of some hydrazine derivatives as reductimetric titrants: J. Vulterin and J. Zýka, *Talanta*, **10,** 891 (Department of Analytical Chemistry, Charles' University, Prague, Czechoslovakia).

Summary—The possible application of benzoylhydrazine, phenylhydrazine, *p*-nitrophenylhydrazine, 2,4-dinitrophenylhydrazine, isonicotinic acid hydrazide and semicarbazide as reductimetric titrants has been studied. The stability of these substances in various media has been determined and causes of the stability and changes of titre of the solutions are discussed. Among the compounds investigated, isonicotinic acid hydrazide has been found to be the most suitable titrant, its solutions being stable and permitting the rapid and quantitative reduction of a number of inorganic systems.

Contributions to the basic problems of complexometry—XII: Successive determination of Thorium, rare earths and some other elements: Rudolf Přibil and Vladimir Veselý, *Talanta*, 1963, **10,** 899 (Analytical Laboratory, Polarographic Institute, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia).

Summary—The successive determination of thorium and rare earths with diethylenetriaminepenta-acetic acid (DTPA) and triethylenetriaminehexa-acetic acid (TTHA) is described. Such a determination cannot be carried out with the commonly used EDTA or diaminocyclohexanetetra-acetic acid (DCTA). By combined titrations with DTPA and TTHA it is possible to determine successively not only thorium and rare earths, but also some bivalent elements which might be present in the material to be analysed.

Polarographic behaviour of dinitrochlorohydrin and diglycerinetetranitrate: J. S. Hetman, *Talanta*, 1963, **10**, 931 (British Polarographic Research Institute, 55, Oriental Road, Woking, Surrey, England).

Summary—The polarographic behaviour of dinitrochlorohydrin and diglycerinetetranitrate has been investigated. Only the first compound behaves in a similar way to nitroglycerine.

Spectrophotometric determination of hexanitrodiphenylamine in microgram quantities: R. D. Tiwari and J. P. Sharma, *Talanta*, 1963, **10,** 933 (Department of Chemistry, University of Allahabad, Allahabad, India.)

Summary—A spectrophotometric method for the determination of microgram quantities of hexanitrodiphenylamine is described. Conditions for the colour development are stated and it is suggested that the colour arises from the anion formed by the ionisation of hexanitrodiphenylamine in solutions of pH above 4.

Coprecipitation of microgram amounts of beryllium and thorium with organic reagents: K. Sudhalatha, *Talanta*,1963, **10,** 934 (Analytical Division, Atomic Energy Establishment, Trombay, Bombay, India).

Summary—Methods for coprecipitating microgram amounts of beryllium and thorium using organic coprecipitants are reported. The former is coprecipitated with methylene blue and tannic acid at pH 8–10, while the latter is coprecipitated with methyl violet and SPADNS at pH 8.

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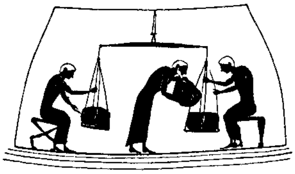

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1. General

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.

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

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

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

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

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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**

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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.

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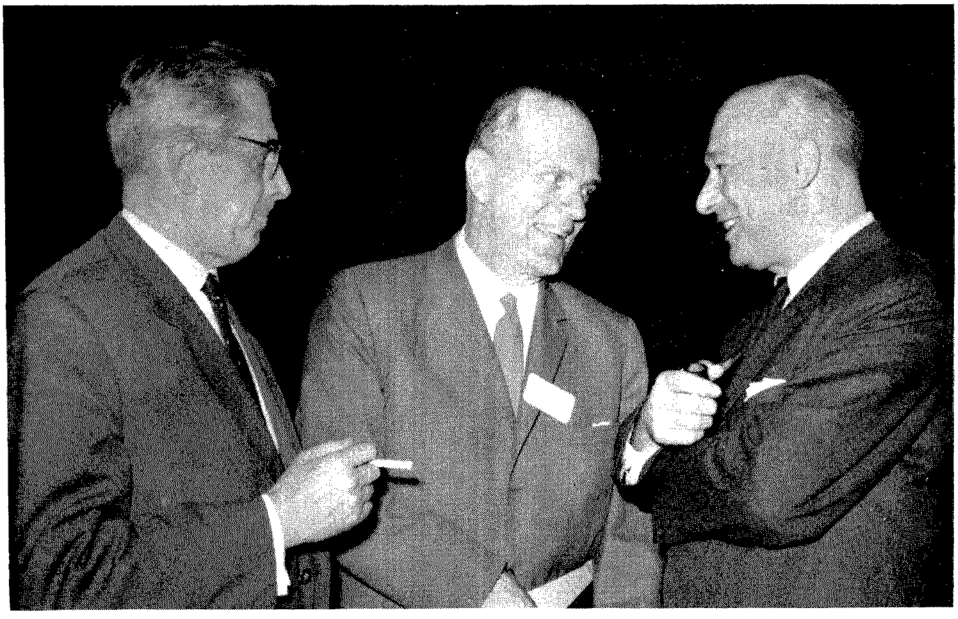
XIXth INTERNATIONAL CONGRESS OF PURE AND APPLIED CHEMISTRY

10–17 JULY 1963 LONDON

H.R.H. the **Duke of Edinburgh** (Patron) opens the Congress at the Royal Albert Hall. Seated next to the Duke (left to right) are **Lord Todd** (President of the Congress), **Sir Howard Florey** (President of the Royal Society) and Professor **W. A. Noyes, Jr.** (President of the IUPAC Conference which preceded the Congress).



The three Plenary Lecturers at the Analytical Chemistry Section of the Congress in conversation before the lecture by Professor **A. Ringbom**, Finland (in centre). Professor **I. P. Alimarin**, U.S.S.R. (on left) and Professor **P. J. Elving**, U.S.A., had previously delivered their lectures.

TALANTA MEDAL

Mr. I. R. Maxwell of Pergamon Press Ltd., Publisher of *Talanta*, presents the *Second Talanta Medal* to Professor G. Schwarzenbach, Switzerland (extreme left). The award recognised his pioneer work on complexometric titrimetry (see *Talanta*, 1963, **10**, 1). Mrs. Schwarzenbach and Professor C. L. Wilson (Editor-in-Chief of *Talanta*) are in the background. The presentation took place at a luncheon held in honour of Professor Schwarzenbach on Friday, 12th July, in London.

Professor Wilson and Professor R. Belcher, Chairman of the Advisory Board of *Talanta* (third person from the left) talk with some of the guests at the luncheon: Professor P. W. West and Dr. Alison Macdonald, Co-Editors of *Analytica Chimica Acta* (extreme left), Dr. D. C. Garratt, President of the Society for Analytical Chemistry (in centre) and Mr. L. J. F. Brimble, Editor of *Nature* (extreme right).

Professor L. Erdey, Hungary (on left), on behalf of the Hungarian Academy of Sciences, receives from Mr. Maxwell a special leather-bound copy of the *Hungarian Honour Issue of Talanta* (May, 1963). Advance copies of the Honour Issue were presented to the Academy by Professor Wilson at the *Winkler Symposium in Budapest* (see *Talanta*, 1963, **10**, *facing* 601).

Dr. D. F. C. Morris, U.K. (in centre) introduces a fellow member of the Advisory Board of *Talanta*, Mr. E. Bishop, U.K. (on right), to the U.S.S.R. Regional Editor of the journal, Professor I. P. Alimarin.

Some of the Editors and Members of the Advisory Board of *Talanta* at the luncheon: Dr. G. A. Rechnitz, U.S.A., Dr. R. Přibil, Czechoslovakia, Professor W. Kemula, Poland and Mr. A. F. Williams, U.K. (seated from left to right in upper photograph) with Dr. T. S. West, U.K. (standing); Dr. P. Zuman, Czechoslovakia, Mrs. J. C. White, Mrs. L. Erdey and Dr. J. C. White, U.S.A. (from left to right in lower photograph).

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USE OF OXYCELLULOSE FOR COLLECTION OF TRACES OF METALS—I

QUALITATIVE INVESTIGATIONS

E. SCHULEK, ZS. REMPORT-HORVÁTH and A. LÁSZTITY
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Budapest VIII, Múzeum körút 4/b, Hungary

(*Received* 15 *August* 1962, *Accepted* 18 *November* 1962)

Summary—As a substance containing carboxyl groups oxycellulose is used for the collection and detection of metal ions in very high dilutions (0·001 to 0·1 ppm). From 3 to 5 mg of oxycellulose is applied for 100 or 1000 ml of solution. Also, the method proves to be suitable for the collection and detection of mixtures of various ions. The dependence of the collection of the following ions on pH is investigated: Ag^+, Al^{3+}, Ba^{2+}, Bi^{3+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sr^{2+}, $UO_2{}^{2+}$, VO^{2+} and Zn^{2+}.

INTRODUCTION

RECENTLY a preliminary communication[1] was published on the use of oxycellulose for the collection of traces of metals. The present paper includes the details of technique and new results of this topic.

In highly dilute solutions, oxycellulose—prepared as described under Experimental—has proved a good collector of cations in acidic and also in basic pH ranges. The optimal conditions for collection of the following metal cations: Ag^+, Al^{3+}, Ba^{2+}, Bi^{3+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sr^{2+}, $UO_2{}^{2+}$, VO^{2+} and Zn^{2+} have been studied. The concentrations of metal ions most frequently used in the experiments were 0.001 to 0.1 ppm, and the amounts of oxycellulose were 3 to 5 mg. Most of the collections were carried out from 1000-ml volumes. In the qualitative investigations the sensitivity of the identification of the collected metal ions depended only on the spot test used.[2]

EXPERIMENTAL

Procedure

1. *Purification of distilled water.* The glass vessels for storage were thoroughly cleansed, rinsed with distilled water, then allowed to stand for 1 day in contact with distilled water and oxycellulose (500 mg/litre, prepared as described below). After filtering the distilled water through some cotton in a glass funnel, it was as suitable for trace work as was twice distilled water. The purified water was used in the experiments only when the ion to be tested was already not detectable in 1000 ml of water by the identification test on oxycellulose described below.

2. *Preparation of oxycellulose.* According to the literature, oxycellulose prepared by oxidation of cellulose with alkaline hypobromite has an acidic nature because of the presence of carboxylic acid groups.[3] For the oxidation of medical cotton the method described by Birtwell and coworkers[4] was used. By this method the oxycellulose could be readily prepared in a pure and almost constant quality.

Medical cotton of good quality was washed with 20% hydrochloric acid, then with distilled water until it was completely free of iron (distilled water purified by oxycellulose served as washing water). Cotton prepared in this way was treated by alkaline hypobromite.[4] During this treatment the cotton disintegrated to finer fibrils. The oxycellulose formed was washed with acid and with water, then dried at 90°. The fibrils were next shaken with water and fractionated by sedimentation. They had an average length of 0·5 to 1·0 mm and were 0·01 mm in diameter. The oxygen consumption of the cotton was studied by iodometry and found to be 0·306 atom per anhydroglucose unit (in agreement with the literature value of 0·305[5]).

3. *Suspension of oxycellulose, collection of ions and filtration of oxycellulose.* Relatively small amounts (generally 3 to 5 mg, but in isotope tests 10, 30 or 50 mg) of oxycellulose prepared as described above were suspended in the solutions containing 1 to 10 μg of ions. The volume of the solutions generally used in the experiments was 10, 100 or 1000 ml, but in certain cases it was 5000 or 10000 ml. The solution containing the oxycellulose was allowed to stand for 10 or 12 hr or shaken with a shaking device for 5 to 30 min, or in isotope experiments stirred with a magnetic stirrer. Boiling of the solution was also advantageous for shortening of the reaction period. Experiments dealing with this problem will be published in the near future among the isotope investigations. After the reaction period oxycellulose was collected by the help of a water pump on a 5-mm diameter sintered glass filter stick (type G_3) or eventually on a King-type filter stick using linen as the filtering medium, or in the case of isotope experiments on a Hirsch filter using paper as the filtering medium. Amounts of oxycellulose of a few mg could readily be separated in the form of minute discs from the sintered glass filter stick by using small glass rods with extruded ends.

4. *Detection of ions collected on oxycellulose.* Amounts of 1 to 10 μg of the same ions or of mixtures of various ions isolated in the described way were detected with different methods. In our previous paper[1] identifications by the spot tests of Feigl and the ring oven of Weisz were mentioned. The line oven method evolved by Biró[6] was also used with good results. In those cases where only one ion had to be identified, the best and quickest way was to put the oxycellulose disc on a spot plate and to use a sensitive spot test (pD 5–6) for the identification. This method also offered a semi-quantitative determination of the metal ion when the dependence of the oxycellulose-metal binding on the pH of the solution was investigated as follows:

The pH of each 100 ml of purified distilled water was adjusted with perchloric acid or ammonia. After the pH was measured by a pH meter, 10 μg of the examined metal ions were added to each of the solutions and 3 mg of oxycellulose were suspended in them. After standing overnight, the oxycelluose fibrils were collected on a G_3 filter stick as described above. The spot test reaction of the same ion collected from solutions of different pH was carried out at once and from the intensity of the coloured reaction the quantity of the bound metal ion was estimated. The most advantageous pH values are seen in Table V.

RESULTS

In Table I(a) the results are summarised of experiments by which it was proved that it is possible to detect 1 μg of Ni^{2+} in a solution of 5, 10, 100, 1000, 5000 and 10000 ml at pH 5·8–6·2 with the dimethylglyoxime test, provided the solution is allowed to stand at 20° for 1 hr in the case of the small volumes and 1 day at the most in the case of the larger volumes. Further, 1 μg of Ni^{2+} can be collected from 100 ml of water with only 0·15 mg of oxycellulose Table I(b). According to more recent experiments, the same amount of Ni^{2+} can be collected even from 10 litres of water after boiling and allowing the solution to stand for a few hr.

TABLE I.—COLLECTION OF Ni^{2+} IONS ON OXYCELLULOSE FROM DISTILLED WATER

(a) From different volumes of water on 3 mg of oxycellulose

Volume, *ml*	5	10	100	1000	5000	10000
Detection	+ +	+ +	+ +	+ +	+ +	+

(b) On different quantities of oxycellulose from 100 ml of distilled water

Oxycellulose, *mg*	5	3	1	0·75	0·25	0·15
Detection	+ +	+ +	+ +	+ +	+ +	+ +

+ = positive reaction by dimethylglyoxime spot test.

The quantities of some recently investigated ions which could be collected with oxycellulose from 1000 ml of distilled water of pH 5·8–6·2 are shown in Table II. Also the reactions applied for detection of the various ions are included. The solutions were allowed to stand 10–12 hr with the oxycellulose.

TABLE II.—QUALITATIVE INVESTIGATION OF OVERNIGHT COLLECTION OF METAL IONS ON OXYCELLULOSE (USING 3 mg OF OXYCELLULOSE).

Ion	Amount of ion collected, μg	Spot test used
Cr^{3+}	10	Diphenylcarbazide, after conversion into chromate[2]
Hg^{2+}	10	Diphenylcarbazide
VO^{2+}	10	Through reduction of iron$^{\mathrm{III}}$[2]
UO_2^{2+}	10	Potassium ferrocyanide[2]

Table III presents the results of experiments where 1 μg of each of 2 or 3 different ions was collected from the same 100 ml of water at pH 5·8–6·2 with 3 mg of oxycellulose. The collected ions were detected either immediately on the oxycellulose or after separation on the Weisz ring oven.

TABLE III.—COLLECTION OF MIXTURES OF IONS ON OXYCELLULOSE FROM DISTILLED WATER.

Ions	Detection
Al^{3+}, Bi^{3+}	+ + + +
Ni^{2+}, Pb^{2+}	+ + + +
Co^{2+}, Mn^{2+}, Ni^{2+}	+ + + + + +
Fe^{2+}, Mn^{2+}, Ni^{2+}	+ + + + + +
Al^{3+}, Cu^{2+}, Pb^{2+}	+ + + + + +
Al^{3+}, Mn^{2+}, Pb^{2+}	+ + + + + +

As was mentioned in our previous paper,[1] it was possible to detect the metal components of some metal cyanide complexes in diluted aqueous solutions after an adequate treatment with oxycellulose. Thus, cyanide complexes equivalent to 10 μg of copper, nickel and zinc were shaken with 3 mg of oxycellulose in various volumes of aqueous solution (pH 5·6–6·2). Without collecting these ions on oxycellulose, it was impossible to detect them by spot tests. In our experiments, the oxycellulose was filtered after standing for 10–12 hr, and it was attempted to detect the metal ions. As the data of Table IV show, copper, nickel and zinc cyanides could be detected in the order of their stability constants.

Table V shows the most advantageous pH values for collection of the listed metal ions from 100 ml of solution.

In Fig. 1 the collector action of oxycellulose is plotted against pH. Generally it is possible to collect the 17 examined ions within a broad pH interval. Fig. 1 could be evaluated semi-quantitatively as was described under Experimental (4) and shown in Table V.

TABLE IV.—METAL IONS COLLECTED ON OXYCELLULOSE FROM THEIR GRADUALLY DILUTED CYANIDE COMPLEX SOLUTIONS.

Complex	Complex collected as	Volume, ml			
		0,3	10	100	1000
$Cu(CN)_4^{2-}$	Cu^{2+}	—	+ +	+ +	+ +
$Ni(CN)_4^{2-}$	Ni^{2+}	+	+ +	+ +	+ +
$Zn(CN)_4^{2-}$	Zn^{2+}	+ +	+ +	+ +	+ +

TABLE V.—THE MOST ADVANTAGEOUS pH VALUES FOR THE COLLECTION OF INDIVIDUAL METAL IONS ON OXYCELLULOSE.

pH	Ions
3	Bi^{3+}, Fe^{3+}
5	Al^{3+}, Ba^{2+}, Cd^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, UO_2^{2+}, VO^{2+}
6	Pb^{2+}
8	Co^{2+}, Ni^{2+}, Zn^{2+}
9	Ag^{+}, Bi^{3+}, Hg^{2+}

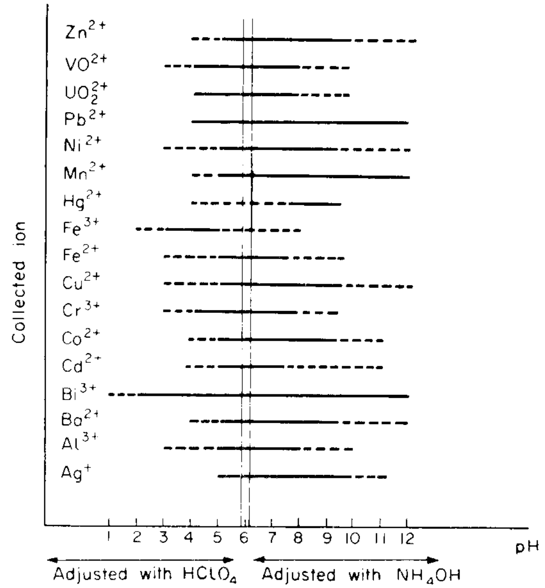

FIG. 1.—Variation of collector action of oxycellulose with pH (10-μg quantities of various ions collected from 100 ml of solution with 3 mg of oxycellulose):
— 10 μg of ion collected,
– – – less than 10 μg of ion collected.

As regards Fig. 2, this shows that it was possible to collect even 1 μg of Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+} and Pb^{2+} on 3 mg of oxycellulose at pH 4–6 when 100 ml of solution was allowed to stand 10–12 hr at room temperature. The minimum interference effect was shown by Na^+ and NH_4^+ ions, but generally even three-fold and four-fold order of quantities of other ions proved to have no interference at all. The collector action of oxycellulose was affected by other ions (Ag^+, Ba^{2+}, Hg^{2+}, Ca^{2+}, Cd^{2+}, Zn^{2+}, Bi^{3+}, Pb^{2+}, Mn^{2+}, Al^{3+} and Co^{2+}) in the given order of decreasing concentrations.

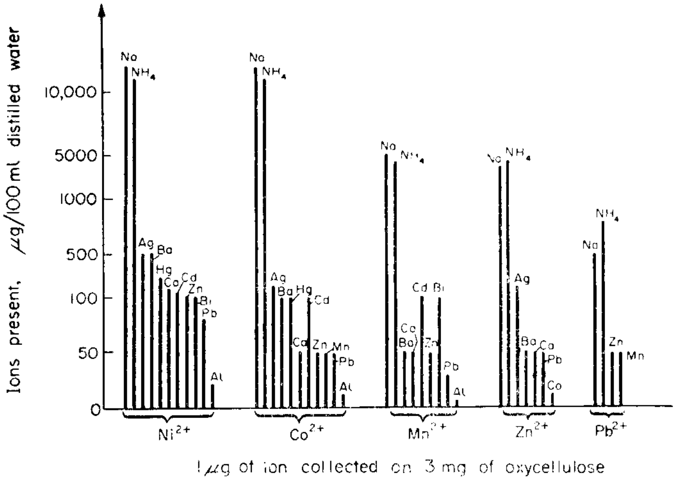

FIG. 2.—Separation and testing of various ions in the presence of each other using oxycellulose as collector.

CONCLUSION

From the results of qualitative and semi-quantitative experiments it has been established that oxycellulose is very suitable for the collection of traces of metals from highly dilute solutions. The metal contaminants of such solutions can be identified directly on the collector. Oxycellulose is especially suitable for the simple removal of the heavy metal contaminants of distilled water. The application of oxycellulose fibrils as an ion collector by the described technique is fairly quick and very simple.

Zusammenfassung—Oxyzellulose, als eine Verbindung mit Carboxylgruppen, wurde zum Anreichern und Bestimmen von Metallionen in sehr hohen Verdünnungen herangezogen. Die Metallionenkonzentrationen waren zwischen 0.001 und 0.1 p.p.m. und 3–5 mg Oxyzellulose wurden für 100–1000 ml Lösung eingesetzt. Die Methode ist auch für die Anreicherung und Bestimmung von Mischungen verschiedener Ionen geeignet. Die Anreicherung in Abhängigkeit vom pH der Lösung wurde für die Ionen der folgenden Metalle untersucht: Ag, Al, Ba, Bi, Cd, Co(II), Cr(III), Cu(II), Fe(II), Fe(III), Hg(II), Mn(II), Ni, Pb, Sr, UO_2^{2+}, VO^{2+} und Zn.

Résume—L'oxycellulose qui renferme des groupements carboxyliques a été utilisée pour concentrer des ions métalliques contenus dans des solutions très diluées. Les concentrations des ions métalliques étaient comprises entre 0,001 et 0,1 p.p.m. 3 à 5 mg d'oxycellulose ont été utilisé pour le traitement de 100 à 1000 ml de solution. La méthode convient également pour les concentrations et la détection de mélanges d'ions variés. L'influence du pH sur la récupération des ions suivants a été étudiée: Ag^+, Al^{3+}, Ba^{2+}, Bi^{3+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sr^{2+}, UO_2^{2+}, VO^{2+}, Zn^{2+}.

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DETERMINATION OF SMALL AMOUNTS OF ZIRCONIUM—II*

ANALYSIS OF REFRACTORY SAMPLES

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Summary—In connection with the determination of small amounts of zirconium in complex samples, procedures have been developed for bringing various types of sample into solution and removing possible interferences, which procedures allow *p*-bromomandelic acid to be used as a precipitant for the final recovery of zirconium for gravimetric measurement. The applicability of these procedures, which are described in detail, has been investigated by the analysis for zirconium of a variety of refractory mineral and metallurgical samples.

A PREVIOUS paper[1] described an investigation of the optimum and limiting conditions for the gravimetric determination of small amounts of zirconium using mandelic acid and its *p*-bromo and *m*-nitro derivatives as precipitants. The procedure employing *p*-bromomandelic acid has been applied with gratifying results to the determination of zirconium in a variety of refractory mineral and metallurgical samples, including several National Bureau of Standards analysed samples.

The procedures used in the dissolution of the various samples are given in the following sections. They were developed from the results of the previous paper[1] and other papers on the determination of zirconium.[2-6] The results obtained are given in Table I; as an indication of the selectivity of the zirconium precipitation, the compositions of the National Bureau of Standards samples analysed are given in Tables II and III.

EXPERIMENTAL

Minerals

Flint clay (National Bureau of Standards Sample No. 97)

A 0·500-g sample, dried for 2 hr at 140°, was mixed with 2 g of Na_2CO_3 and 2 g of $Na_2B_4O_7$ in a platinum crucible, which was covered and slowly heated with a Meker burner. After 5–6 min the heat was gradually increased, and the crucible was finally strongly heated for 35–40 min with occasional stirring. The cooled crucible and cover were then placed in a 400-ml beaker and the melt digested with 100 ml of hydrochloric acid (1 + 3). After removing crucible and cover with necessary washing, the solution was evaporated to dryness on a steam bath. The residue was dissolved with 50 ml of 10% HCl, filtered through a No. 40 Whatman paper (with suction) and washed with 10% HCl. The filtrate was saved.

The residue was ignited in a platinum crucible and fused with 2 g of Na_2CO_3. The cool melt was treated with 70–80 ml of HCl (1 + 3), and slowly evaporated on a sand bath; the residue was treated with 40–50 ml of 25% HCl, boiled to expel CO_2, filtered through a No. 40 Whatman paper (suction) and carefully washed with dilute HCl. The resulting filtrate, combined with the original filtrate, was evaporated on a steam bath in a 150-ml beaker. The residue obtained was taken up with 30 ml of

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15–20% HCl and filtered. The filtrate was heated to 50–60° and 30–35 ml of 1·5% *p*-bromomandelic acid added dropwise with constant stirring. The mixture was digested for 15 min at 80–85°, filtered after 3–4 hr through a No. 40 Whatman paper and washed with 20–25 ml of hot distilled water. The precipitate and paper were slowly charred in a platinum crucible, ignited at 900–1000° and weighed as ZrO_2.

Burnt refractory (National Bureau of Standards Samples No. 78)

A 0·500-g sample, dried for 1 hr at 110°, was mixed with 4 g of Na_2CO_3 in a platinum crucible, covered and heated very slowly with a Meker burner for a few min, then with gradually increasing heat and finally at full capacity of the burner for about 40 min; the melt was occasionally stirred. The cooled crucible and cover were placed in a 400-ml beaker, and treated with 100 ml of H_2SO_4 (1 + 4). The resulting solution was boiled to remove CO_2, evaporated nearly to dryness, diluted to about 50 ml with 10% HCl, boiled, filtered through a No. 40 Whatman paper and washed with 10 ml of dilute HCl. The filtrate was saved.

The filter paper and residue were ignited in a platinum crucible; 1 ml of H_2SO_4 (1 + 1) and 5 ml of HF were then added, and the contents thoroughly mixed with a piece of thick platinum wire (left in the crucible for further stirring). The crucible contents were evaporated on an electric hot plate in a hood with the aid of an infrared heating lamp; the heat was gradually increased until all free acids were driven off; the crucible was then ignited at dull redness, cooled and weighed. Treatment with HF–H_2SO_4, evaporation and ignition were repeated to constant weight.

The cold and weighed residue from HF–H_2SO_4 treatment was fused with 2 g of $K_2S_2O_7$, the melt leached with distilled water and added to the main filtrate. The latter was slowly concentrated on a sand bath to 20–30 ml and cooled; 5–8 ml of HCl (1 + 1) were added. If the solution was not clear, it was filtered after 4–5 hr, treated with about 25–30 ml of 1·5% *p*-bromomandelic acid reagent as described before but filtered after 24 hr.

The above procedure gave 0·114% of ZrO_2. Application of a decomposition procedure involving Na_2CO_3–$Na_2B_4O_7$ followed by Na_2CO_3, as described for Flint Clay, gave 0·10% of ZrO_2.

Bauxite (National Bureau of Standards Sample No. 69A)

A 0·500-g sample, dried at 140° for 2 hr was fused with 4 g of $K_2S_2O_7$ in a platinum crucible, gradually increasing the temperature to 600–700° and stirring the melt from time to time for 10–15 min. The cool crucible and cover were placed in a 400-ml beaker and digested with 50 ml of HCl (1 + 10). After removal and washing of crucible and cover, the mixture was evaporated on a sand bath, then digested with 50–55 ml of 10% HCl and filtered through a No. 40 Whatman paper. This filtrate was saved.

The residue was ignited, then mixed with 3 ml of H_2SO_4 (1 + 1) and 5 ml of HF. This mixture was evaporated on an electric hot plate with the aid of an infrared heating lamp. When all free acid was driven off, the crucible was ignited at dull redness and weighed. The silica removal procedure was repeated until constant weight was obtained.

The weighed residue was fused with 2 g of $K_2S_2O_7$, dissolved in hot water and added to the main filtrate. The latter was diluted to about 150 ml, treated with a slight excess of aqueous NH_3, boiled, filtered through a No. 40 Whatman paper with suction and washed with 2% aqueous NH_3. The precipitate was transferred to a beaker; the paper was washed with 40 ml of hot HCl (1 + 1), which was also added to the beaker; the resulting solution was digested for 10 min, diluted to 150 ml, evaporated to near dryness, and digested with 30–35 ml of 1·5% *p*-bromomandelic acid added dropwise with constant stirring, then digested for 15 min at 80–85°. After 4–5 hr, the precipitate was filtered, washed with hot water and ignited to ZrO_2.

Alloys

Electical-heating alloy (National Bureau of Standards Sample No. 169)

A 2-g sample was treated in a 150 ml beaker with 14 ml of HCl and 7 ml of HNO_3, then evaporated to about 5 ml on an electric hot plate; 15 ml of HCl were added and the solution evaporated to near dryness; on addition of 10 ml of HCl, the alloy was completely dissolved. The solution was evaporated to dryness; the residue was treated with 20 ml of HCl (1 + 2) and evaporated to dryness; the HCl addition and evaporation were repeated. The cooled residue was treated with 50–55 ml of HCl (1 + 4), filtered through a No. 40 Whatman paper using suction and washed with the same dilute acid.

The filtrate was evaporated to about 10 ml, diluted with distilled water to 120–150 ml, treated with a slight excess (few drops beyond neutrality) of aqueous NH_3, boiled for 1–2 min, filtered through a No. 40 Whatman paper (suction) and washed with 2–3% aqueous NH_3.

The precipitate was dissolved with about 50 ml of HCl (1 + 1), evaporated to dryness and taken up with 30–35 ml of 10% HCl, then heated to 50–60°; 30–35 ml of 1·5% *p*-bromomandelic acid were added dropwise with constant stirring; the mixture was digested for 15 min at 80–85°, filtered after 4–5 hr and washed with 20–25 ml of hot water. The precipitate was ignited and weighed as ZrO_2. Because the residue was green in colour, it was fused with a small amount of Na_2CO_3 in a platinum crucible; the cooled melt was dissolved in dilute HCl and heated to expel CO_2; the zirconium was then precipitated and ignited as before.

High-temperature alloy (National Bureau of Standards Sample Nos. 1203–4–5)

A 0·5-g sample (obtained by turning, washing with acetone and EtOH, and drying) was treated in a 150-ml beaker with 20 ml of HCl and evaporated to about 5 ml on an electric hot plate. After two or three repetitions of the HCl addition and evaporation, the sample was completely dissolved. The resulting solution was evaporated to dryness; the residue was dissolved with 20–25 ml of HCl (1 + 1) and the solution again evaporated to dryness. This residue was treated with 35–40 ml of HCl (1 + 5), filtered through a No. 40 Whatman paper and washed with the dilute acid. The filtrate was boiled to about 30–35 ml; 30–35 ml of 1·5% *p*-bromomandelic acid were added dropwise with constant stirring; the mixture was digested for 15 min at 80–85°, filtered after 4–5 hr and washed with 20–25 ml of hot water; the precipitate was ignited to ZrO_2. Because the ignited residue had a slight green colour, it was fused with a small amount of Na_2CO_3 in a platinum crucible; the cooled melt was treated with 30–35 ml of HCl (1 + 3) and the crucible washed with dilute HCl. The resulting solution was evaporated on a steam bath to 30 ml and zirconium precipitated as usual.

Magnesium alloys

The nature and zirconium content of the two high temperature magnesium alloys analysed have been discussed by Elving and Olson.[2] The following procedures were used to determine total zirconium content.

A 0·170-g sample of Alloy EK30 was dissolved with 7 ml of 10% H_2SO_4 in a platinum crucible, evaporated to dryness on an electric hot plate, ignited, treated with 2·5 ml of HF and 0·5 ml of H_2SO_4, and evaporated on the hot plate with the aid of an infrared heating lamp (stirring with a platinum rod); the HF–H_2SO_4 evaporation was repeated. To ensure removal of silica, the following procedure, which is probably unnecessary, was used: Na_2CO_3 was added; the crucible and its contents heated; the cooled crucible placed in a 150 ml beaker, treated with HCl (1 + 1), heated to expel CO_2, and filtered through a No. 40 Whatman paper; the residue was fused with *ca.* 1·5 g of Na_2CO_3, the cool melt dissolved with dilute HCl and warmed to expel CO_2; this solution was added to the main solution. The latter was evaporated to 20–25 ml; 20–25 ml of 1·5% *p*-bromomandelic acid were added dropwise with constant stirring, the mixture digested for 15 min at 80–85°, filtered after 3–4 hr and washed with 15–20 ml of hot water; the precipitate was ignited as usual.

A 0·5-g sample of Alloy ZK60 was treated in a covered 150-ml beaker at room temperature with 10 ml of 10% H_2SO_4. When dissolution was complete, 1·5 ml of H_2SO_4 (1 + 1) were added; the solution was evaporated to the appearance of fumes of H_2SO_4, cooled, diluted to 20 ml and heated to 50–60°. Then 20 ml of 1·5% *p*-bromomandelic acid were added dropwise, stirring constantly; the mixture was digested for 15 min at 80–85°, filtered after 3–4 hr and washed with 10–15 ml of hot water; the precipitate was ignited as usual.

A 0·5-g sample of EK30 treated by the procedure described for ZK60 gave 0·377% of zirconium.

DISCUSSION

The determination of zirconium, present as a relatively minor constituent, in mineral, metallurgical and other types of sample, is a difficult problem, especially when relatively accurate results are required. The high degree of selectivity and the sensitivity of *p*-bromomandelic acid as a precipitant for zirconium provide ample support for the use of this reagent as a pivotal means of isolating zirconium for gravimetric measurement, especially when combined with the classical methods of effecting solution and removing matrix constituents such as silica, *e.g.*, high temperature Lewis acid-base attack involving fusion with carbonate and borate, and lower temperature attack involving hydrofluoric and sulphuric acids.

The procedures developed, which are given in sufficient detail so that they can be used with a minimum of difficulty regarding conditions, amounts of reagents and operations, were applied to the determination of zirconium in nine standard mineral

TABLE I.—DETERMINATION OF ZIRCONIUM IN MINERAL AND METALLURGICAL SAMPLES

Sample nature and source	Zirconium content	
	Specified,[a] %	Found, %
Flint Clay, N.B.S. No. 97	0·25 ZrO_2	0·244 ZrO_2
Burnt Refractory, N.B.S. No. 78	0·12 ZrO_2	0·10 ZrO_2
	(0·09–0·13)	0·10 ZrO_2[b]
Bauxite, N.B.S. No. 69A	0·18 ZrO_2	0·174 ZrO_2
Electrical-Heating Alloy, N.B.S. No. 169	0·042 Zr	0·043 Zr
	(0·035–0·048)	
High-Temperature Alloys:		
N.B.S. No. 1203	0·05$_5$ Zr	0·043 Zr
N.B.S. No. 1204	0·12 Zr	0·114 Zr
N.B.S. No. 1205	0·46 Zr	0·469 Zr
Magnesium Alloys:		
EK30	0·346 Zr	0·377 Zr
		0·621 Zr[b]
ZK60	0·608 Zr	0·625 Zr

[a] Range of values on N.B.S. certificate is given in parentheses beneath average value.
[b] Use of an alternate procedure as indicated in the text.

TABLE II.—ANALYSES GIVEN FOR NATIONAL BUREAU OF STANDARDS SAMPLES IN WHICH ZIRCONIUM WAS DETERMINED (VALUES GIVEN AS PERCENTAGES)

Constituents	No. 97 Flint Clay	No. 78 Burnt Refractory	69A Bauxite
MoO_3	0·0002	—	—
CuO	0·003	—	—
MnO	0·003	—	<0·01
Total S as SO_3	0·04	—	0·04
BaO	0·015	—	0·01
MgO	0·26	0·5	0·02
CaO	0·10	0·36	0·29
Na_2O	0·32	0·53	<0·01
K_2O	0·55	2·83	<0·01
Cr_2O_3	0·085	—	0·05
Total V as V_2O_5	0·04	0·047	0·03
P_2O_5	0·07	0·62	0·08
Total Fe as Fe_2O_3	0·98	0·79	5·82
ZrO_2	0·25	0·12	0·18
TiO_2	2·35	3·37	2·78
Al_2O_3	38·80	69·97	55·0
SiO_2	42·85	20·69	6·01
Loss on ignition	13·34	0·26	29·55

TABLE III.—ANALYSIS GIVEN FOR NATIONAL BUREAU OF STANDARDS SAMPLES IN WHICH ZIRCONIUM WAS DETERMINED (VALUES GIVEN AS PERCENTAGES)

Constituent	No. 169 Electrical Heating Alloy (77Ni–20 Cr)	High-Temperature Alloy		
		No. 1203	No. 1204	No. 1205
N	0·031			
C	0·043	(0·01)	(0·03)	(0·19)
Co	0·19			
Cu	0·015	0·19	0·12	0·056
Mn	0·073	0·31	0·41	0·29
S	0·002			
Ca	0·015			
Cr	20·26	11·90	12·75	13·82
V	0·018			
Fe	0·54	(1·4)	(3·1)	(1·55)
Zr	0·042	$0{\cdot}05_5$	0·12	0·46
Ti	0·006	1·09	0·63	0·36
Al	0·095	4·34	5·60	6·68
Si	1·42	0·86	0·56	0·63
Ni	(77)	75·5	70·6	67·5
Mo		3·01	4·28	5·75
W		<0·01	0·028	0·019
Nb		1·00	1·31	1·95
Ta		0·34	0·46	0·67

and metallurgical samples, seven of which were analysed National Bureau of Standards standard samples. The results obtained were eminently satisfactory as indicated by the data of Table I.

Obviously the dissolution and fusion procedures described can be modified as the nature of the sample may indicate. Consequently, in some cases alternate procedures are indicated; other possible ways of shortening the procedures will be apparent.

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Zusammenfassung—Im Zusammenhang mit der Bestimmung kleiner Mengen von Zirkonium in Komplexverbindungen wurden Methoden entwickelt, um verschiedene Arten von Proben in Lösung zu bringen und Störungen auszuschalten, damit di Fällung mit p-Brommandelsäure zur gravimetrischen Bestimmung von Zirkonium möglich wird. Die Anwendbarkeit dieser im einzelnen beschriebenen Verfahren wurde bei der Bestimmung von Zirkonium in verschiedenen feuerfesten Mineralien und Metallproben geprüft.

Résumé—En relation avec la détermination de micro-quantités de zirconium dans les composés complexes, certains procédés ont été développés comme convenant à des types variés d'échantillons en solution, et éliminant les influences gênantes possibles; à ces procédés, se rattache l'emploi de l'acide p-bromomandélique comme agent précipitant du zirconium dans la récupération finale pour les mesures gravimétriques. L'application de ces procédés qui ont été décrits en détail a été essayé pour l'analyse du zirconium contenu dans une variété de minéral réfractaire et dans certains échantillons métallurgiques.

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APPLICATIONS OF CONTROLLED-POTENTIAL COULOMETRY TO THE DETERMINATION OF PLUTONIUM

A REVIEW

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Summary—The determination of plutonium by controlled-potential coulometric titration has been studied and used at Oak Ridge National Laboratory over a period of several years. Two methods—the primary (direct) and secondary (indirect) titrations—have been applied to the analysis of a wide variety of materials. They have been used for the determination of total plutonium, of ionic and polymeric plutonium contents, and of the oxidation state distribution of plutonium solutions. This report describes the techniques, procedures and separations that have been developed. The effects of some contaminants that are common to plutonium-containing samples are also presented.

INTRODUCTION

THE controlled-potential coulometric titration of plutonium has been used at ORNL during the past several years for determining the plutonium content of so-called "product" samples, that is, relatively pure solutions of $Pu(NO_3)_4$. During that time, the method has been used with increasing frequency for analysis of many other types of samples. Such samples often require chemical pretreatment and (or) alteration of titration conditions and of the procedure itself if satisfactory results are to be obtained. This report collects in one place information about the techniques that are required in preparing samples for titration and about the procedures that are used to perform the various determinations. Procedures are given for the determination of (1) total Pu, (2) Pu^{III}, (3) Pu^{IV}, (4) Pu^{VI}, (5) mixtures of these oxidation states, (6) ionic plutonium in the presence of polymeric plutonium, and (7) polymeric plutonium. Information is also included on the effects of some contaminants that are often present in plutonium solutions. Finally, several separation procedures have been studied with the aim of increasing the applicability of this method; these are also discussed.

APPARATUS AND REAGENTS

Reagents

Standard plutonium solutions were prepared from high purity (99·8 ± 0·2%) plutonium metal by dissolution in 6*M* HCl and dilution to volume. Other reagents were prepared from analytical reagent grade materials.

Instrumentation

Coulometric titrations of plutonium at ORNL are made with an ORNL Model Q-2005 controlled-potential coulometric titrator[3,5] that has been modified[6] to provide greater sensitivities (more read-out voltage per coulomb) and greater ease of adjustment of integrator drift. Recently, the prototype of a high-sensitivity controlled-potential coulometric titrator was built at ORNL specifically for determining elements of high equivalent weight such as plutonium.[4] It is being evaluated.

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

Cell design: The titration cell design preferred at ORNL for all coulometric titrimetry is shown schematically in Fig. 1. This type of cell can be so arranged that titrations can be made at either the mercury or the platinum electrode. Plutonium is titrated at a platinum gauze electrode (1·5 × 10 cm 45-mesh) that is fitted in a circle inside the bottom of the cell. Solution volume is 10–15 ml; the solution is stirred mechanically with a propeller-type stirrer pitched to give maximum mixing without splashing. The counter- and reference-electrodes are separated from the solution by means of two porous glass tubes (Vycor glass, type 7930) as salt bridges. These tubes contain 1M HNO_3 when primary titrations of plutonium are made and 0·5M H_2SO_4 when secondary titrations are made; these solutions are replaced daily. Porous Vycor tubes have proved to be very satisfactory low-resistance (100 ohms) salt bridges. They must be stored wet and must not be exposed to strongly basic solutions or acid solutions that contain free fluoride. When properly cared for, the tubes will perform satisfactorily for long periods of time (as long as one year). Total resistance through the reference electrode (Beckman 270, 4970–29) and the Vycor tube associated with it is generally 2·5 to 5 kilohms. When the electrical resistance in that circuit is greater than 10 kilohms. the titration is affected adversely, that is, titration times are lengthened and the accuracy and precision are poor.

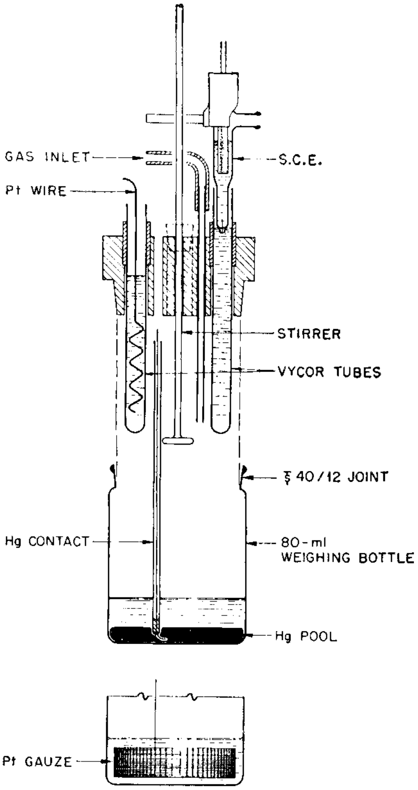

FIG. 1.—Coulometric titration vessel.

The cell is provided with an inlet for inert gas. Exclusion of oxygen from the titration vessel is unnecessary when primary titrations are made in $HClO_4$, HCl, or HNO_3, but is mandatory when H_2SO_4 is the supporting electrolyte or when secondary titrations are made. Helium is used as the inert gas blanket; it is used directly from the cylinder without further purification except that it is saturated with water vapour before it enters the cell.

Care of electrode: The platinum gauze electrode can be cleaned by heating to bright red in a flame or by soaking in 1:4 HNO_3, and then rinsing it thoroughly with distilled water. Experience has shown that the electrode seldom needs to be cleaned when it is used and stored routinely in 10% $HClO_4$ solutions. Routine use of the electrode in 1M HCl solutions requires that the electrode surface be cleaned daily in order to maintain optimum electrode behavior. When 1M HCl is used continually as the supporting electrolyte solution, "fouling" of the electrode surface gradually occurs and causes low initial currents, extended titration times, and low results. Substances that are adsorbed on the electrode surface, particularly small amounts of organic material, cause immediate "fouling" of the electrode. Thus, these materials must be destroyed or removed before a titration is made and the electrode should be cleaned immediately if it is exposed to such materials.

GENERAL DISCUSSION

Primary controlled-potential coulometric determination of total Pu

The determination of plutonium by primary controlled-potential coulometric titration was developed by Scott and Peekema.[11,12] That method was evaluated and has been used at ORNL with minor modifications for routine analysis of "product" samples from the Power Reactor Fuel Processing Plant[15] as well as for non-routine analysis of other types of samples.[13] The method has been studied or used at the Los Alamos Scientific Laboratory, Rocky Flats Plant, and Lawrence Radiation Laboratory of the United States Atomic Energy Commission, as well as the Harwell Laboratory of the United Kingdom AEA.[8]

The method is based on the fact that the Pu^{III}, Pu^{IV} couple behaves reversibly under suitable electrolytic conditions and that current efficiencies of very nearly 100% are attainable. Consequently, plutonium can be adjusted to either the ter- or quadrivalent state by electrolytic pretitration and then determined by coulometric conversion to the other oxidation state. Some workers prefer the reduction of Pu^{IV} to Pu^{III} as the quantitative electrolysis, whereas others prefer the oxidation of Pu^{III} to Pu^{IV}. In either case, the method is precise, accurate, rapid, and free of interference from a number of impurities common to plutonium-containing samples, that is, relatively large amounts of uranium, aluminium, and nitrate. The method has therefore proved to be extremely useful for the precise determination of total plutonium.

The supporting electrolyte solution preferred at ORNL for the primary titration is 10% ($\sim 1M$) $HClO_4$ because the platinum electrode requires less attention when this medium is used and because reagent blanks obtained in this medium are insignificant when 1 mg or more of plutonium is titrated. Titrations can be made satisfactorily in molar solutions of HCl and HNO_3 at slightly different potentials and can also be made in $0{\cdot}5M$ H_2SO_4 at considerably different potentials. The use of H_2SO_4 medium is preferred in certain instances. For example, when the titration follows a depolymerisation or an anion-exchange separation, the solution is fumed with H_2SO_4 to remove fluoride and (or) organic impurities, is diluted, and is then titrated in the H_2SO_4 solution. Samples that contain appreciable amounts of Pu^{VI} are also conveniently titrated in H_2SO_4 medium because Pu^{VI} can be electrolytically reduced to Pu^{III} quantitatively in that medium.

Serious interference in the primary titration can be caused by materials that are electrolytically active within the potential span of the plutonium couple (*e.g.*, iron) and by materials that prevent attainment of 100% current efficiency (*e.g.*, reductants, oxidants, and organic matter). Also, Pu^{VI} is only partially reduced to Pu^{III} in $HClO_4$, HCl, and HNO_3 supporting electrolyte solutions (it is completely reduced in H_2SO_4) and therefore can lead to inaccurate results when present as an appreciable fraction of the total plutonium present in the test portion. Analysis for total plutonium by primary titration will also be inaccurate when the polymerised species is present because the polymer is not electrolytically active. Means of circumventing these difficulties have been developed and are discussed in detail in later paragraphs.

Secondary controlled-potential coulometric titration of Pu^{VI}

A procedure alternative to the direct electrolytic titration of Pu^{III} or Pu^{IV} is the reduction of Pu^{VI} to Pu^{IV} by means of an internally generated intermediate such as Fe^{II}.[14] This procedure requires two coulometric electrolyses: the first accomplishes reduction of Pu^{VI} and Fe^{III} to a mixture of Pu^{III} and Fe^{II}, and the second accomplishes oxidation of Pu^{III} to Pu^{IV} and of Fe^{II} back to Fe^{III}. The net result is reduction of Pu^{VI} to Pu^{IV} and is measured as the difference in the current consumed during the reduction and oxidation electrolyses.

This procedure may be used under certain conditions for the analysis of samples for Pu^{VI}. It may also be used for the determination of total plutonium in samples that contain large quantities of iron if both the plutonium and iron are oxidised quantitatively to their higher oxidation states before the coulometric titrations are made.

These two procedures—the primary and secondary titrations—can be used together in order to perform an oxidation state analysis of mixtures of Pu^{III}, Pu^{IV}, and Pu^{VI}.

Either $1M$ $HClO_4$ or $0{\cdot}5M$ H_2SO_4 can be used as the supporting electrolyte for secondary controlled-potential coulometric titrations of Pu^{VI} with Fe as the intermediate. The use of H_2SO_4 is generally preferred because the electrolyses can be made within a narrower potential span in that medium than in $1M$ $HClO_4$. Perchloric acid is the preferred medium for oxidation state analysis because the various oxidation states do not interact in $HClO_4$ solution appreciably during the required analysis time.

Choice of electrolysis potentials

In Table I are listed the formal redox potentials of the $Pu^{III} \rightleftharpoons Pu^{IV}$ and $Fe^{II} \rightleftharpoons Fe^{III}$ couples in solutions of $HClO_4$, H_2SO_4, HCl, and HNO_3 of various concentrations. These potentials were obtained from titration curves (current consumed *vs.* electrode potential) obtained under the actual titration conditions. From such values and the Nernst equation,

$$E = E^\circ - \frac{0{\cdot}059}{n} \log \frac{[\mathrm{red}]}{[\mathrm{ox}]},$$

it is possible to select optimum potentials for essentially complete reduction or oxidation in a given medium. For a reversible one-electron reaction, such as the reduction or oxidation of Pu^{III} or Pu^{IV}, and for a degree of completion of 99·9%, a potential span of $E^\circ \pm 0{\cdot}18$ volt is generally selected. However, because small amounts of iron are commonly present as an impurity even in "pure" plutonium solutions, it is often desirable to use a somewhat narrower potential span and thereby to minimise the effect of iron in the plutonium electrolysis. Consequently, slightly different potentials are used for prereduction (primary titration) when Fe is present and when it is absent. The reduction and oxidation potentials used at ORNL for both primary and secondary titrations in different media are shown in Table II.

It would, of course, be possible to carry out the electrolyses by use of potentials at which the extent of reaction is less than complete, but is known, and then to correct mathematically for the amount of plutonium remaining unreacted. For example, electrolyses could be made at $E^\circ \pm 0{\cdot}12$ volt, the reactions proceeding to 99% completion, and the results corrected for the 1% error. This technique has been used by Scott and Peekema[11] at Hanford but has not been used at ORNL.

TABLE I.—FORMAL REDOX POTENTIALS OF $Pu^{III} \rightleftharpoons Pu^{IV}$ AND $Fe^{II} \rightleftharpoons Fe^{III}$ COUPLES IN VARIOUS MEDIA

Medium	Conc., *M*	*E°, volt vs. S.C.E.*	
		Pu	Fe
$HClO_4$	1·0	0·715	0·465
	2·5	·72	·47
	5·0	·73	·46
HCl	0·1	0·76	0·51
	0·25	·75	·49
	1·0	·72	·45
	3·0	·68	·39
	5·0	·64	·31
HNO_3	0·5	0·69	0·48
	1·0	·69	—
	1·5	·65	—
	2·0	·64	—
H_2SO_4	0·25	0·50	—
	0·5	·49	0·45
	1·0	·48	·45
	2·5	·46	—
	5·0	·43	—
$AlCl_3$ HCl	0·2	0·71	0·48

The selection of proper electrode potentials for the secondary titration of plutonium as Pu^{VI} with an internally generated intermediate such as Fe^{II} must be made in a different manner. Cognisance must be taken of the formal potentials of both couples that are present and of the initial and final oxidation states that are desired in the net reaction. Thus, in the reduction of Pu^{VI} and Fe^{III} in 0·5*M* H_2SO_4, a potential of +0·270 volt *vs.* the S.C.E. is used, that is, the potential at which Fe^{III} is reduced to Fe^{II}. The oxidation is then made at +0·670 volt *vs.* the S.C.E., at which potential Fe^{II} is not only oxidised to Fe^{III} but Pu^{III} is also oxidised to Pu^{IV}. The use of these potentials ensures that the overall reaction is $Pu^{VI} \rightarrow Pu^{IV}$, a two-electron change, since the oxidation state of the intermediate (iron) is unchanged by the reduction-oxidation cycle.

Reduction: $Fe^{III} \rightarrow Fe^{II}$
$Pu^{VI} \rightarrow Pu^{III}$
Oxidation: $Fe^{II} \rightarrow Fe^{III}$
$Pu^{III} \rightarrow Pu^{IV}$
Net Reaction: $Pu^{VI} \rightarrow Pu^{IV}$

Similarly, potentials for reduction and oxidation in $HClO_4$ medium are chosen to ensure that the net reaction is reduction of Pu^{VI} to Pu^{IV}. These potentials are also listed in Table II.

Precision attainable

The precision that can be obtained by these two procedures at various Pu concentration levels is presented in Table III. On the basis of these results, quantities of plutonium of about 5 mg are taken for titration when the utmost precision is desired.

Titration of smaller quantities is permissible, but the results will be correspondingly less precise. Titrations of 1 mg or less of plutonium should be corrected for contributions from the reagent blank, that is, reagent blanks should be titrated and these results deducted from the results obtained when plutonium is titrated. At times, it is desirable to concentrate plutonium by anion exchange before titration in order to obtain more precise analytical results.

TABLE II.—ELECTROLYSIS POTENTIALS USED AT ORNL

Primary Titration	Potential, *volt vs. S.C.E.* Reduction	Oxidation
$HClO_4$, $1M$ (Fe present)	+0·555	+0·895
(Fe absent)	+0·535	+0·895
HCl, $1M$ (Fe present)	+0·560	+0·900
(Fe absent)	+0·540	+0·900
H_2SO_4, $0{\cdot}5M$ (Fe absent)	+0·310	+0·670
Secondary Titration		
$HClO_4$, $1M$	+0·285	+0·895
H_2SO_4, $0{\cdot}5M$	+0·270	+0·670

TABLE III.—PRECISION ATTAINABLE BY PRIMARY AND SECONDARY PROCEDURES

Pu titrated, *mg*	σ, % Primary	Secondary
0·05	1·5	—
0·25	0·3	—
1	0·1	0·2
2·5	—	0·1
5	0·1	0·1
10	0·07	—

SPECIFIC DISCUSSION—PROCEDURES AND TECHNIQUES

Plutonium^{III}

Samples are sometimes encountered that contain Pu^{III} and no excess reducing agents or other impurities. Such samples can be analysed by direct coulometric oxidation. Much more prevalent, however, are sample solutions that contain an excess of reducing agent to "hold" plutonium in the lower oxidation state. It is then necessary to destroy the reductant before an analysis for total plutonium can be made. Several methods of pretreatment of this type of sample before electrolysis have been used successfully at ORNL.

Direct coulometric oxidation: In the rare case where the sample contains Pu^{III} and no impurities, direct coulometric oxidation at +0·895 volt *vs.* the S.C.E. in 10% $HClO_4$ can be used to determine the Pu^{III} content of the sample test portion. Samples that may contain Pu^{V} as well as Pu^{III} can be analysed for Pu^{III} and total Pu by performing a coulometric oxidation at +0·895 volt first (to determine Pu^{III}), then performing a reduction at +0·535 volt and reoxidation at +0·895 volt (to determine total Pu). Perchloric acid is preferred over H_2SO_4 as the medium for determining Pu^{III}

by direct oxidation because Pu^{III} in H_2SO_4 medium is oxidizable by oxygen which may lead to erroneous (low) results for Pu^{III} content. Results obtained by direct oxidation are comparable in precision and accuracy with those obtained when similar amounts of plutonium are titrated for total ionic plutonium content by the primary coulometric technique.

Chemical oxidation with Ce^{IV}*:* Samples that contain very small excesses (less than approximately 0·1 meq in the test solution) of reducing agents can be conveniently analysed if a solution of $Ce(NO_3)_4$ is used to destroy the reducing agent. To the sample test portion in 10% $HClO_4$ in the electrolysis cell, 0·1N $Ce(NO_3)_4$ is added dropwise until the faint yellow colour of excess Ce^{IV} persists for 30 sec or more. Upon reduction of this solution at +0·535 volt, the excess Ce^{IV} is reduced to Ce^{III}, and Pu^{IV} is reduced to Pu^{III}. The Pu^{III} can then be oxidised coulometrically at +0·895 volt; Ce^{III} is not oxidised at this potential. The solution that contains excess Ce^{IV} should not be allowed to stand for an unnecessarily long period of time before the reduction is made because Ce^{IV} will in time oxidise Pu^{IV} to Pu^{VI}. The precision of the results obtained by this procedure is comparable with that of the results obtained by the primary coulometric titration when similar amounts of plutonium are titrated.

This procedure is especially useful for determining total plutonium when the sample contains small amounts of Pu^{VI}. Plutonium^{VI} is first reduced by addition of a small amount of $NH_2OH{\cdot}HNO_3$ or N_2H_4 solution; then the excess reductant is destroyed with Ce^{IV} before the titrations are made.

Chemical oxidation with HNO_3*:* Samples that contain large or unknown amounts of reducing agents can be prepared for titration by destroying the reducing material with hot HNO_3. To the sample test portion in the electrolysis cell, 3–5 drops of concentrated HNO_3 are added, and the solution is evaporated to incipient dryness on a hot plate. To the cool residue is added 10–15 ml of 10% $HClO_4$ and 5 drops of a saturated solution of NH_2SO_3H. The sulphamic acid is added to destroy any nitrites that may be present as a result of the evaporation step. The solution can then be prereduced and coulometrically oxidised to determine total Pu. Oxidation with HNO_3 is used most often at ORNL for preparing samples for titration.

Plutonium^{IV}

By far the majority of samples analysed by coulometric titration at ORNL contain plutonium as Pu^{IV} or as a mixture of Pu^{III}-Pu^{IV}. Such samples are usually titrated in 10% $HClO_4$ by the primary coulometric titration method: prereduction at a suitable potential (Table II), followed by coulometric oxidation at +0·895 volt, each electrolysis being terminated when the current decreases to 30 μA. Other media are sometimes used when it is advantageous to do so. For example, 1M HCl is used as the supporting electrolyte when the sample contains mercury because mercury is not electrolytically active within the potential span of the plutonium titration in chloride medium. Another example is the use of 0·5M H_2SO_4 as supporting electrolyte when the sample contains appreciable amounts of Pu^{VI}. Sulphuric acid is a useful electrolyte for this type of sample because Pu^{VI} can be electrolytically reduced to Pu^{III} quantitatively in that medium, but is only partially reduced in solutions of the other mineral acids. However, H_2SO_4 can be used as supporting electrolyte in the primary titration procedure only when iron is absent because iron and plutonium are reduced and oxidised at essentially the same potentials in sulphate medium.

The primary controlled-potential coulometric titration of plutonium in $HClO_4$ medium has been used with excellent results for determining plutonium in a wide variety of materials. The effects on this procedure of some of the more common contaminants that are often present are discussed below.

Effect of HNO_3*:* Nitric acid when free of nitrite, does not interfere in the primary coulometric titration of plutonium over a reasonably wide concentration range, as shown by the results of Table IV. Indeed, $1M$ HNO_3 can itself be used as supporting electrolyte solution although it is inferior to perchloric or hydrochloric acids. Sulphamic acid is included in the supporting electrolyte when nitrates are present in order to destroy any nitrites that may be present. Sulphamic acid can be added dropwise as the saturated solution ($\sim 1M$), 5 drops being sufficient in almost all instances; or the stock 10% $HClO_4$ solution can be made $0{\cdot}02M$ in sulphamic acid.

Effect of $Al(NO_3)_3$*:* Some results obtained by titrating plutonium in the presence of various concentrations of $Al(NO_3)_3$ are also shown in Table IV. Again, sulphamic acid is included in the supporting electrolyte solution in order to destroy any nitrites that may be present. Titrations in the presence of very large amounts of $Al(NO_3)_3$ (that is, $1M$ or so) exhibit extended prereduction times and normal oxidation times. Thus, although correct results can be obtained when the $Al(NO_3)_3$ concentration in the electrolyte solution is greater than $1M$, it is better to limit the size of the test portion so as to keep the $Al(NO_3)_3$ concentration below $1M$ in the supporting medium.

Effect of U^{VI}*:* Plutonium can be determined by the primary titration procedure even when large amounts of U^{VI} are present. Some titration results obtained by titration of plutonium in the presence of various amounts of U^{VI} are presented in Table IV. Samples that contained as much as 1000:1 weight ratios of U^{VI} to Pu^{IV} have been analysed successfully for plutonium by this procedure.

Effect of Fe^{III}*:* The determination of plutonium without interference from small amounts of iron is based on the fact that Pu^{IV} can be prereduced electrolytically to Pu^{III} without reducing a significant amount of Fe^{III} to Fe^{II}. Subsequent coulometric oxidation of Pu^{III} to Pu^{IV} is then not subject to interference from Fe^{II}. However, since the E°_{Pu} and E°_{Fe} values differ by only 250 mv in $HClO_4$, Pu^{IV} can be reduced without significant reduction of Fe^{III} only when the Pu:Fe ratio is large (if most accurate results are to be obtained). As the ratio of iron to plutonium in the sample increases, the positive error in the results increases. The results in Table IV show this effect. When the Pu:Fe weight ratio is 50:1, no significant error is introduced, but when the ratio is 40:1, the error is $+0{\cdot}2\%$ and at a Pu:Fe ratio of 17:1, the error is 1%. Samples that contain interfering amounts of iron can be satisfactorily analysed by secondary controlled-potential coulometric titration, as discussed in a following section.

Effect of sulphate: Because of the strong complexing action of sulphate on Pu^{IV} and the resultant shift in redox potential of the $Pu^{III} \rightleftharpoons Pu^{IV}$ couple (Table I), only small amounts of sulphate can be tolerated in the primary titration of plutonium. Some titration results obtained when various amounts of H_2SO_4 were included in the supporting electrolyte are presented in Table IV.

If sulphate is present in the sample in other than trace amounts, it is best to titrate in $0{\cdot}5M$ H_2SO_4 medium and to use potentials appropriate to that medium (Table II). A $0{\cdot}5M$ H_2SO_4 medium can be used only when iron is absent, however, because iron and plutonium are titrated simultaneously in that medium. Samples that contain both iron and sulphate cannot be analysed by primary coulometric titration unless plutonium is separated by anion exchange before titration. Samples that contain iron and sulphate can be analysed for total plutonium by the secondary coulometric procedure after the plutonium is oxidised to Pu^{VI} with AgO.

Effects of other ions: Free fluoride cannot be tolerated, even in trace amounts, by the primary coulometric titration procedure. Consequently, samples that contain fluoride can be analysed only if the fluoride is complexed strongly or is removed from the test portion. Aluminium can be used to complex the fluoride when small amounts of fluoride are present. For example, samples that result from the dissolution of aluminium-plutonium alloys have been analysed for plutonium by performing the titrations in 0·2*M* $AlCl_3$-0·2*M* HCl solution. In this solution, aluminium complexes fluoride, and chloride complexes mercury (present as dissolution catalyst). Prereduction was made at +0·590 volt *vs.* the S.C.E., and coulometric oxidation was made at +0·890 volt. Boric acid and Ce^{III} are inferior to aluminium as complexing agents for fluoride in this procedure. Fluoride can also be removed from the test portion by evaporation with H_2SO_4, and the plutonium can then be titrated in H_2SO_4 medium at potentials appropriate to that medium. This technique is used in the analysis of samples that contain polymeric plutonium.

TABLE IV.—RESULTS OF THE TITRATION OF PLUTONIUM IN THE PRESENCE OF SOME COMMON REAGENTS

Reagent	Amount in supporting medium	Pu, mg Taken	Pu, mg Found	Error, %
HNO_3	0 *M*	5·16	5·17	+0·2
	0·5		5·17	+0·2
	1·0		5·15	−0·2
	1·5		5·12	−0·8
	2·0		5·08	−1·6
	3·0		5·00	−3·2
$Al(NO_3)_3$	0 *M*	5·16	5·16	—
	0·25		5·17	+0·2
	0·5		5·17	+0·2
	0·75		5·15	−0·2
	1·0		5·15	−0·2
	1·2		5·17	+0·2
H_2SO_4	0 *M*	5·16	5·16	—
	0·001		5·16	—
	0·004		5·17	+0·2
	0·007		5·14	−0·4
	0·02		4·97	−3·7
	0·04		4·57	−11·5
	0·12		3·00	~ −41·8
U^{VI}	0 mg	5·22	5·22	—
	30		5·22	—
	300		5·23	+0·2
Fe^{III}	0 mg	5·22	5·22	—
	0·125		5·23	+0·2
	0·250		5·24	+0·4
	0·275		5·29	+1·4
	0·500		5·42	+4·0

Samples that contain Hg^{II} can be titrated in chloride medium without interference from mercury, as mentioned above. A solution of HCl or a chloride salt can be used for this purpose. Mercury can also be separated from plutonium by anion exchange or by plating on an auxiliary electrode, but these techniques are more troublesome than titration in the presence of chloride. Titrations of plutonium in chloride medium have been made satisfactorily when the Hg:Pu weight ratio was as high as 10:1.

Molybdenum as molybdate does not interfere in the primary coulometric titration of plutonium, at least when present in equal amounts (weights).

Zirconium interferes seriously, even when present in small amounts ($<100\ \mu g$). The nature of its interference is similar to that of organic material, namely, low initial currents, extended titration times, and low results are obtained. This behavior worsens when successive titrations are performed in the presence of zirconium. The interference apparently is due to hydrolysis, which causes "fouling" of the electrode. Samples that contain zirconium can be analysed after separating plutonium by anion exchange, provided that the resin column is thoroughly washed free of zirconium before plutonium is eluted.

Scott and Peekema[11] have reported on the tolerance of the primary titration toward other ions.

Plutonium^{VI}

Plutonium^{VI} is not completely reduced electrolytically in $1M$ $HClO_4$, HCl, or HNO_3 solutions. Accordingly, its presence may lead to low results when total plutonium is determined by primary coulometric titration in these media. The presence of an interfering amount (about 50 μg or more) of Pu^{VI} is apparent when, on prereduction, the electrolysis current becomes constant at a value exceeding 30 μA. Obviously, chemical treatment that is likely to oxidise plutonium to Pu^{VI} (*e.g.*, fuming with $HClO_4$) is to be avoided. Samples that contain interfering amounts of Pu^{VI} can be analysed in several different ways.

Titration in H_2SO_4 *medium:* Samples that contain interfering amounts of Pu^{VI} and no iron can be analysed by performing the electrolyses in H_2SO_4 medium at potentials appropriate to that medium (Table II). Reduction of Pu^{VI} proceeds to completion in sulphate medium because, as Pu^{III} is formed during electrolysis, it serves as an intermediate agent by reducing Pu^{VI} to Pu^{IV}. Ultimately, all the plutonium is converted electrolytically to Pu^{III}. The electrolysis proceeds somewhat more slowly than it would in the absence of Pu^{VI}. After prereduction, Pu^{III} can be coulometrically oxidised to Pu^{IV} as a measure of total plutonium. This procedure cannot be used for analysis of samples that contain iron, because iron is reduced and oxidised along with plutonium in sulphate medium.

Chemical reduction of Pu(VI)*:* Samples that contain small but interfering amounts of Pu^{VI} can be analysed for total plutonium content by chemically reducing the Pu^{VI} with a slight excess of NH_2OH or N_2H_4, destroying the excess reductant with Ce^{IV}, and then making an electrolytic prereduction and coulometric oxidation in 10% $HClO_4$ at appropriate potentials (Table II). This technique was discussed previously. It is useful primarily for samples that contain small amounts of Pu^{VI}. When large amounts of Pu^{VI} are present, the amounts of extraneous reagents that must be added become prohibitively large.

Secondary coulometric titration: Samples that contain plutonium in any oxidation state can be analysed for total plutonium by secondary coulometric titration with an internally generated intermediate such as Fe^{II}. The sample test portion plus an iron "spike" is first oxidised in order to convert plutonium and iron quantitatively to Pu^{VI} and Fe^{III}. Once oxidised, plutonium is determined as the sexavalent species by performing two successive coulometric titrations: first, a reduction at +0·270 volt *vs.* the S.C.E. until an excess of the intermediate, Fe^{II}, is generated and, second, a coulometric oxidation of the excess intermediate and of Pu^{III} at +0·670 volt. These titrations are made in 0·5*M* H_2SO_4. The difference in current consumed upon reduction and reoxidation is a measure of the total (sexavalent) plutonium present, as explained earlier.

TABLE V.—RESULTS OBTAINED BY SECONDARY COULOMETRIC TITRATION OF PLUTONIUM*

Present, *mg*			Pu found, *mg*	σ,%	Error, %
Fe	U	Pu			
0	0	1·280	1·281	0·2	<0·1
0	0	2·559	2·562	0·1	+0·1
0	0	5·119	5·120	0·1	<0·1
0·25	0·25	2·559	2·557	—	−0·1
2·5	2·5	2·559	2·556	—	−0·1
25·0	25·0	2·559	2·559	—	<0·1
2·5	250·0	2·559	2·559	—	<0·1
250·0	25·0	2·559	2·579	—	+0·8
250·0	250·0	2·559	2·588	—	+1·1

* Known amounts of Pu^{IV}, Fe^{III}, and U^{VI} were oxidised with $HClO_4$ and diluted to 10-ml volume. Results presented were obtained by titration of 1·000-ml aliquots of these dilutions.

$Plutonium^{VI}$ can be prepared for titration by this procedure by fuming the test portion with 2 ml of concentrated $HClO_4$ for 15 min. Alternatively, the sample test portion can be evaporated to fumes with H_2SO_4, diluted to ~0·5*M* H_2SO_4, and treated for 10 min with excess of solid AgO to convert Pu^{IV} to Pu^{VI}. The excess AgO is destroyed by warming the solution to 85° before the titrations are made. Oxidation with AgO must be used if the sample contains sulphate because hot concentrated $HClO_4$ will not oxidise Pu^{IV} to Pu^{VI} in the presence of sulphate.

This procedure, though more difficult and time-consuming than the direct coulometric titration, can be used for analysis of samples that otherwise could not be analysed coulometrically, namely, samples that contain large amounts of iron with or without sulphate present. The relative standard deviation of results obtained by this procedure is 0·2% or so, even when the Fe:Pu ratio weight is as high as 10:1. Some titration results obtained by this procedure are presented in Table V.

OXIDATION-STATE ANALYSIS OF Pu^{III}-Pu^{IV}-Pu^{VI} MIXTURES

The primary and secondary coulometric titration procedures can be used to perform an oxidation-state analysis on samples that contain Pu^{III}, Pu^{IV}, and Pu^{VI}. Such analyses are seldom required but have been requested occasionally at ORNL during the course of spectrophotometric and other studies of the various plutonium species.

The test portion is placed in a supporting electrolyte solution of 10% $\mathrm{HClO_4}$ that contains a known amount of $\mathrm{Fe^{III}}$. Three successive coulometric titrations of that solution are made:

(1) Oxidation at +0·895 volt to 30 μA background current. This oxidation quantitatively converts $\mathrm{Pu^{III}}$ to $\mathrm{Pu^{IV}}$.

$$\mathrm{Pu^{III}} \rightarrow \mathrm{Pu^{IV}}$$

(2) Reduction at +0·285 volt to 30-μA background current. This reduction completely converts all the plutonium, now $\mathrm{Pu^{VI}}$ and $\mathrm{Pu^{IV}}$, to $\mathrm{Pu^{III}}$ and also converts $\mathrm{Fe^{III}}$ to $\mathrm{Fe^{II}}$.

$$\mathrm{Pu^{VI}} \rightarrow \mathrm{Pu^{III}}$$
$$\mathrm{Pu^{IV}} \rightarrow \mathrm{Pu^{III}}$$
$$\mathrm{Fe^{III}} \rightarrow \mathrm{Fe^{II}}$$

(3) Oxidation at +0·895 volt to 30 μA background current. During this electrolysis, $\mathrm{Pu^{III}}$ is converted quantitatively to $\mathrm{Pu^{IV}}$, and $\mathrm{Fe^{II}}$ is converted to $\mathrm{Fe^{III}}$.

$$\mathrm{Pu^{III}} \rightarrow \mathrm{Pu^{IV}}$$
$$\mathrm{Fe^{II}} \rightarrow \mathrm{Fe^{III}}$$

From the amount of current consumed during each of these electrolyses, the amount of plutonium present in each oxidation state can be calculated as follows:

(*a*) $\mathrm{Pu^{III}}$ is measured by the current consumed in the first oxidation with $n = 1$.

(*b*) $\mathrm{Pu^{VI}}$ is measured by the difference between the currents consumed during the second (reduction) and third (reoxidation) electrolyses with $n = 2$.

(*c*) Total Pu is measured from the third (oxidation) electrolysis with $n = 1$. The amount of current consumed by iron during this electrolysis must be considered in this calculation.

(*d*) $\mathrm{Pu^{IV}}$ is calculated by difference since $\mathrm{Pu^{III}}$, $\mathrm{Pu^{VI}}$, and total Pu are now known.

Exact evaluation of the accuracy of this method is impossible because of the difficulty of preparing and maintaining standard plutonium solution in which plutonium is present in a known oxidation state and which are free of "holding" agents. The method was checked by use of three stock solutions prepared to contain known amounts of plutonium, mostly in one of the three oxidation states. These three stock solutions were analysed separately for their oxidation-state distribution. Portions of the solutions were then mixed and the mixtures analysed for oxidation-state distribution. The results of these analyses are given in Table VI.

Table VI.—Results of the oxidation-state analysis of stock solutions of $\mathrm{Pu^{III}}$ -$\mathrm{Pu^{IV}}$ -$\mathrm{Pu^{VI}}$

Stock Solution Taken			Total Pu, *mg*	Pu found, *mg*			
$\mathrm{Pu^{III}}$	$\mathrm{Pu^{IV}}$	$\mathrm{Pu^{VI}}$		$\mathrm{Pu^{III}}$	$\mathrm{Pu^{IV}}$	$\mathrm{Pu^{VI}}$	Total
×			4·13	3·71	0·39	*	4·10
	×		5·16	*	5·14	0·02	5·16
		×	4·43	*	*	4·47	4·47
×	×		9·29	3·70	5·54	0·02	9·26
×		×	8·56	3·71	0·41	4·43	8·54
	×	×	9·59	0·01	5·22	4·46	9·69
×	×	×	13·72	3·68	5·53	4·48	13·69

* None detected.

Perchloric acid is used as the supporting electrolyte for these titrations rather than H_2SO_4 in order to prevent interaction among the various plutonium species before titration. Iron must be present to drive the reduction of Pu^{VI} to completion, and the current consumed by it in each electrolysis must be accurately corrected for in the calculations. In practice, it is most convenient to run a portion (~1 mg of Fe) of standard $FeCl_3$ solution through the electrolyses as a blank and to include that same amount of iron in the titrations of plutonium. Correction for iron is then made simply as a "reagent blank."

Determination of polymeric plutonium

Samples that contain both ionic and polymeric plutonium in various proportions can be analysed coulometrically for the ionic or unpolymerised species by primary coulometric titration. Polymeric plutonium is not electrolytically active and thus does not contribute to the analysis so long as the polymer is not disturbed by the supporting electrolyte itself. For this reason, 2·5% (~0·3*M*) $HClO_4$ is used as supporting electrolyte for this titration. The amount of polymer present can be determined by difference if an analysis for total plutonium is made in addition to the analysis for ionic plutonium. Total plutonium is determined after depolymerisation (treating the test portion with 1–2 drops of concentrated HF, then fuming off the fluoride with H_2SO_4) by primary coulometric titration in H_2SO_4 medium at appropriate potentials (Table II).

TABLE VII.—TYPICAL RESULTS: ANALYSIS OF PU POLYMER

Solution analysed	Pu found, *mg*			σ, %	
	Ionic	Total	Polymeric	Ionic	Total
Standard ionic "spike" (5·16 mg of Pu)	5·17	5·18	0·01	0·2	0·3
Polymer solution	0·22	4·92	4·70	1·0	0·3
Polymer + "spike"	5·35	10·10	4·75	0·2	0·2

This procedure has been used successfully to determine ionic and polymeric plutonium in many samples in which the relative amounts of the two species, as well as the acidity, varied considerably. Some typical results are presented in Table VII. They were obtained by analysis of a typical polymer sample alone and when a known amount of ionic plutonium was added.

Separations

A considerable effort has been devoted at ORNL to the study of methods for separating plutonium before its determination by controlled-potential coulometric titrimetry. The following separations have been studied: the carrying of plutonium on $BiPO_4$ and on LaF_3, extraction with thenoyltrifluoroacetone (TTA), with tri-n-octylphosphine oxide (TOPO), and anion-exchange adsorption of Pu^{IV} from HNO_3 medium. Of these, carrying on $BiPO_4$ and extraction with TTA were found to be unsatisfactory for this type of application because impurities (PO_4^{-3} and organic material) are introduced into the supporting electrolyte and subsequently prevent satisfactory titration. The other separations are discussed below.

Separation with LaF_3*:* The procedure used for separating plutonium by carrying on a LaF_3 precipitate was as follows. The sample that contained Pu^{IV} or Pu^{III} plus 3 drops of La carrier (5 mg/ml) was placed in a centrifuge cone and was adjusted to have a volume of 3 ml and to be approximately $3M$ in HCl. To this solution, 10 drops of concentrated HF was added; the solution was stirred; the mixture was digested for 5 min and then centrifuged; and the supernatant liquid was discarded. The precipitate was then washed with 2 ml of $1M$ HNO_3-$1M$ HF, the mixture was centrifuged, and the wash liquid was discarded. The precipitate was dissolved with 2 drops of $1M$ HNO_3 and 10 drops of $2{\cdot}5M$ $Al(NO_3)_3$ and was quantitatively transferred to the titration cell with 10% $HClO_4$ solution and 5 drops of a saturated solution of NH_2SO_3H. The plutonium was then prereduced at +0·535 volt and coulometrically oxidised at +0·895 volt.

The relative standard deviation of this method is 0·5% at the 250-μg level; the recovery is 99·8%. Plutonium was carried as Pu^{IV}, rather than as Pu^{III} as is usually done, in order to avoid the introduction of reducing agents into the supporting electrolyte.

Because this separation is difficult to perform, and indeed would be almost impossible to perform by remotely controlled operations, it has not been studied extensively.

Separation by anion exchange: Separation of Pu^{IV} by anion exchange from nitrate systems is a well known process,[1,9,10] and Hanshuh[2] has used this technique for separating plutonium before its determination by controlled-potential coulometric titration. A great deal of effort has been devoted to this procedure at ORNL with the aim of developing a precise and reliable method for determining plutonium in solutions of nuclear reactor fuels.

$Plutonium^{IV}$ is separated by adsorption from $8M$ HNO_3 on 3 ml of Dowex 1-X4 (50 to 100-mesh) contained in a resin column tube of i.d. 8–10 mm. The resin is then washed with $8M$ HNO_3. Two problems are involved at this point in the determination. First, suitable elution conditions are required, that give fast and quantitative recovery of plutonium from the resin column. Second, organic material introduced into the solution by the resin interferes seriously in the coulometric titration procedure, and must be destroyed before satisfactory titration can be made.

A number of different reagents have been used as eluents for plutonium by different workers. For process work, $0{\cdot}35M$ HNO_3 is used. For analytical work, Pu^{IV} is often reduced to Pu^{III} with NH_2OH in order to hasten quantitative elution. Neither of these agents is satisfactory for the present application because the plutonium "tails" badly, even at elevated temperature, and requires an unduly large solution volume for quantitative recovery. Reducing agents (NH_2OH, I^-, SO_3^{2-}, N_2H_4) cause gas formation within the column and also must be destroyed before a titration can be made. Elution with $0{\cdot}5M$ HCl was found to be quantitative and rapid when the elution is carried out at 60–70°, but is considered to be inferior to dilute HNO_3 that contains a trace of HF.

The use of dilute HNO_3-HF solutions as eluting agents for plutonium in this separation was suggested by Waterbury.[17] $Plutonium^{IV}$ is rapidly (3–4 column volumes) and quantitatively desorbed from the resin by $0{\cdot}1M$ HNO_3-$0{\cdot}01M$ HF at room temperature. Enough HF must be present to prevent polymerisation of plutonium on the column, thereby ensuring rapid and quantitative elution, but the HF concentration must not be great enough to cause loss of plutonium by precipitation as PuF_4. When the HF concentration is 0·005–$0{\cdot}025M$, however, the elution proceeds very satisfactorily. Plutonium is recovered quantitatively from a 3-ml resin column by approximately 10–15 ml of eluent but the elution is continued until 20 ml has been collected.

The second problem, that of organic impurities from the resin, cannot be prevented, but its effects can be eliminated by evaporating and fuming the solution before titration. Different resins (Dowex 1 and 21K, Permutit SK, Biorad A.G.-1), different cross linkages (X1, X2, X4, X8), and many different washing techniques were studied with the aim of finding a way of preventing the introduction of organic material into the eluate but without success. The resin is apparently degraded by exposure to strong HNO_3 during the adsorption and washing steps.

The eluate is evaporated and fumed with H_2SO_4 before titration. Fuming with $HClO_4$ would, of course, destroy the organic matter, but it also would result in oxidation of all or part of the plutonium to Pu^{VI}. Fuming with H_2SO_4 also removes HF from the solution so that the sample can be diluted and titrated in H_2SO_4 medium at appropriate potentials (Table II).

This procedure has been used primarily for analysis of solutions that contain small amounts of plutonium, in which case it is convenient to collect about 1 mg of plutonium on the column before washing, eluting, and titrating. The relative standard deviation of the complete procedure is 0·5% at the 1-mg level; the recovery is 99·8%.

Separation with TOPO: The extraction of Pu^{III}, Pu^{IV}, and Pu^{VI} with $0{\cdot}1M$ tri-n-octylphosphine oxide in cyclohexane has been reported[7] and the results have been duplicated at ORNL. Extraction of Pu^{IV} from 4–$10M$ HNO_3 by this reagent is quantitative in one equilibration of 10 min (phase ratio, 1:1). In view of the fact that uranium has been determined by TOPO extraction, stripping, and coulometric titration in the stripping agent without further chemical treatment,[16] this procedure offers considerable promise as a means of separating plutonium before its determination by coulometric titration. Studies of this procedure are currently in progress at ORNL.

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TABULAR SUMMARY OF PROCEDURES

Sample Composition	Analysis	Pretreatment	Medium	Potential, Volt vs. S.C.E.
(1) Pu^{III}	Pu^{III}	None	$1M$ $HClO_4$	+0·895
(2) Pu^{III} or Pu^{IV} + excess reductant	Total Pu	Ce^{IV}, or hot HNO_3	$1M$ $HClO_4$	Prereduce at +0·535 Oxidise at +0·895
(3) Pu^{III} or Pu^{IV} + Fe(<2% Pu)	Total Pu	Hot HNO_3	$1M$ $HClO_4$	Prereduce at +0·555 Oxidise at +0·895
(4) Pu^{III} or Pu^{IV} + Pu^{VI} (<50 μg)	Total Pu	None	$1M$ $HClO_4$	Prereduce at +0·555 Oxidise at +0·895
(5) Pu^{III} or Pu^{IV} + Pu^{VI} (>50 μg)	Total Pu	None	$0{\cdot}5M$ H_2SO_4	Prereduce at +0·310 Oxidise at +0·670

TABULAR SUMMARY OF PROCEDURES (*cont.*)

Sample composition	Analysis	Pretreatment	Medium	Potential, Volt vs. S.C.E.
Same		Slight excess N_2H_4, then Ce^{IV}	1M $HClO_4$	Prereduce at +0·535 Oxidise at +0·895
(6) Pu^{III} or Pu^{IV} + Pu polymer	Ionic Pu	None	0·25M $HC10_4$	Prereduce at +0·535 Oxidise at +0·895
(7) Pu^{III}, Pu^{IV}, Pu^{VI}, Pu polymer	Total Pu	2 drops HF, 0·5 ml H_2SO_4; fume, dilute to 15 ml	0·5M H_2SO_4	Prereduce at +0·310 Oxidise at +0·670
(8) Pu^{VI}	Pu^{VI}	None	0·5M H_2SO_4	Prereduce at +0·310 Oxidise at +0·670 difference = Pu^{VI}
(9) Pu^{III}, Pu^{IV}, Pu^{VI} + Fe(>2% of Pu)	Total Pu	Hot conc. $HClO_4$	0·5 $M$$H_2SO_4$	Prereduce at +0·310 Oxidise at +0·670 difference = Pu^{VI} = Total Pu
(10) Pu^{III}, Pu^{IV}, Pu^{VI} + Fe(>2% of Pu) + H_2SO_4	Total Pu	Fume with H_2SO_4, oxidise with AgO	0·5M H_2SO_4	Prereduce at +0·270 Oxidise at +0·670; difference = Pu^{VI} = Total Pu
(11) Pu^{III}, Pu^{IV}, Pu^{VI}	Oxidation-state analysis	None	1M $HClO_4$ + known amount of Fe^{III}(~1mg)	Oxidise at +0·895 Reduce at +0·285 Oxidise at +0·895
(12) Pu^{III}, Pu^{IV}, Pu^{VI} + H_2SO_4	Total Pu	None	0·5M H_2SO_4	Prereduce at +0·310 Oxidise at +0·670
(13) Pu in dissolver solutions	Total Pu	Adsorb on Dowex 1-×4, elute with HNO_3-HF, fume with H_2SO_4	0·5M H_2SO_4	Prereduce at +0·310 Oxidise at +0·670

Zusammenfassung—Die Bestimmung von Plutonium mittels coulometrischer Titration bei kontrolliertem Potential wurde über lange Zeit in Oak Ridge studiert und angewendet. Eine direkte und eine indirekte Methode wurde auf ein Vielfalt von Probenmaterial angewendet. Gesamtmenge, ionisiertes und polymerisertes Plutonium wurden bestimmt und die Oxydationsstufen ermittelt. Die Arbeit gibt Vorschriften für Bestimmungs und Trennungsmethoden. Einflüsse von Verunreinigungen werden beschrieben.

Résumé—Le dosage du plutonium par coulométrie à potentiel contrôlé a été étudié et utilisé au Laboratoire National d'Oak Ridger durant plusieurs années. Deux méthodes de dosage (direct et indirect) ont été appliquées à l'analyse d'un grand nombre de composes. On peut ainsi doser le plutonium total, les composés contenant du plutonium sous forme ionique ou polymérique, ainsi que les solutions correspondant à divers degrés d'oxydation. On a décrit des méthodes et des procédes de séparation utilisé et les effets des impuretés habituellement présentes dans les échantillons contenant du plutonium.

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THE INFRARED SPECTRA OF CHELATE COMPOUNDS—I

A STUDY OF SOME METAL CHELATE COMPOUNDS OF 8-HYDROXYQUINOLINE IN THE REGION 625 to 5000 cm $^{-1}$

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Summary—The infrared spectra of 8-hydroxyquinoline and its copper, zinc, manganese, magnesium and calcium chelate compounds have been determined between 2 and 16 μ. As far as possible, assignments of peaks have been made and correlations between peak position and stability constants have been drawn up. On the basis of the correlations the structure of the different chelates is discussed. From a study of the variation of peak height with concentration, it has been shown that the technique has considerable analytical value. A procedure is presented for the determination of copper and zinc as oxinates.

ALTHOUGH the number of publications dealing with the infrared spectra of metal chelate compounds is still not large,[1–7] interest in the field has increased during the last few years. This has, however, been centred almost completely on the metal complexes of acetylacetone.[1,4–6] Further, much of the attention has been directed to the structure of the reagent with little reference to the use of infrared measurements in relation to stability of chelate bonds, or in possible analytical applications.

In the case of 8-hydroxyquinoline and its metal chelates, only two reports of infrared studies have appeared in the literature. Charles *et al.*[7] studied the infrared spectra of 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline, 4-methyl-8-hydroxyquinoline, and a number of metal chelates derived from these reagents. No attempt was made to use the information analytically. In an earlier communication, Stone[3] examined magnesium and bismuth oxinates in the infrared region in an attempt to find an explanation for the insolubility of magnesium oxinate dihydrate in chloroform, a fact which is in marked contrast to the behaviour of the other metal oxinates.

As far as analytical chemistry is concerned, the use of the infrared spectra of the metal chelates has been negligible.[8,9] Because 8-hydroxyquinoline and its metal chelates appeared to offer an interesting study in the use of the infrared technique, the present work was carried out to investigate the infrared absorption characteristics of the oxinates of copper, zinc, manganese, magnesium and calcium, with attention, in particular, given to the possible analytical use of the technique. The results of this study are presented below.

EXPERIMENTAL

The oxinates of zinc[10] and copper[11] used in this investigation were prepared by the method of precipitation from homogeneous solution;[12] this resulted in uniform particle size and more regular

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crystalline shape. The oxinates of manganese, magnesium and calcium were prepared by conventional precipitation.[13] For each metal oxinate the conditions outlined in the appropriate publication were adhered to.

Infrared spectra were recorded on two Perkin-Elmer Spectrophotometers, the "Infracord", Model 237 and Model 21.

Potassium bromide discs were prepared using a Perkin-Elmer die in conjunction with an "Elmes" hydraulic press capable of delivering 23,000 pounds total load on a ram 3 inches in diameter. Before use the KBr, which was of spectroscopic grade (supplied by Harshaw Co.), was dried at 150° for 24 hr and ground to pass 100 mesh.

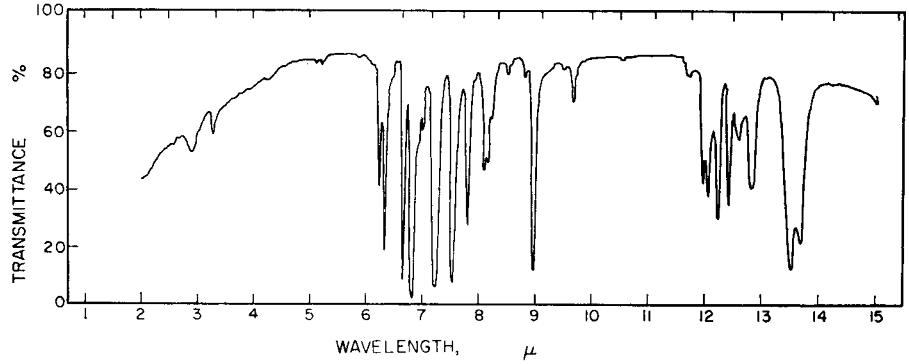

FIG. 1.—The infrared spectrum of copper oxinate between 2 and 15 μ. (1 mg of complex in 400 mg of KBr.)

The spectra of copper oxinate and zinc oxinate are shown in Figs. 1 and 2. These spectra were obtained on the Perkin-Elmer Model 21 instrument with a sodium chloride prism. Those obtained on the "Infracord" agree exactly with them but peaks cannot be assigned as accurately as with the larger instrument. All spectra on the "Infracord" were obtained at the slowest speed of the instrument.

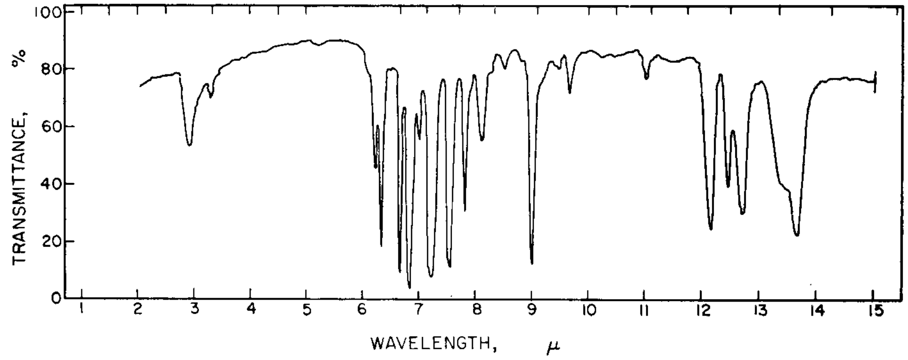

FIG. 2.—The infrared spectrum of zinc oxinate between 2 and 15 μ. (1 mg of complex in 400 mg of KBr.)

RESULTS AND DISCUSSION

The principal absorption peaks in cm^{-1} for 8-hydroxyquinoline and the metal chelates, as obtained from the spectra, are shown below:

8-Hydroxyquinoline

711, 741, 781, 808, 818, 866, 894, 975, 1060, 1094, 1140, 1167, 1204, 1215, 1273, 1286, 1385, 1416, 1439, 1473, 1508, 1588, 1635, 3050 (a broad peak).

Copper oxinate

732, 740, 777, 794, 805, 816, 828, 836, 852, 854, 949, 1035, 1052, 1113, 1135, 1178, 1224, 1233, 1280, 1324, 1381, 1425, 1465, 1500, 1580, 1604, 1894, 1941, 3050.

Zinc oxinate

732, 787, 803, 824, 869, 908, 955, 978, 1034, 1058, 1112, 1135, 1175, 1209, 1232, 1280, 1325, 1385, 1429, 1465, 1499, 1579, 1610, 1920, 3050, 3430.

Manganese oxinate

742, 783, 792, 803, 820, 862, 905, 954, 978, 1034, 1069, 1108, 1139, 1176, 1203, 1239, 1280, 1323, 1370, 1385, 1427, 1465, 1500, 1580, 1608, 1650, 1695, 1915, 1953, 2340, 3060.

Magnesium oxinate

742, 791, 805, 822, 856, 908, 954, 978, 1039, 1075, 1112, 1140, 1178, 1208, 1242, 1285, 1327, 1375, 1388, 1430, 1471, 1509, 1585, 1611, 1660, 1710, 1914, 1958, 2350, 3200.

Calcium oxinate

724, 745, 788, 803, 823, 868, 902, 1034, 1060, 1068, 1082, 1106, 1135, 1178, 1201, 1233, 1255, 1284, 1325, 1371, 1386, 1425, 1468, 1495, 1575, 1594, 1610, 1700, 1740, 1826, 1920, 3060, 3430.

In all cases spectra were first obtained using 2 mg of the metal oxinate in 400 mg of KBr. The amount of chelate was then progressively reduced until the best spectrum with the maximum resolution was obtained. The values for the prominent peaks shown above appear in all the spectra obtained for that metal chelate. In the region below 1500 cm^{-1} values could be read to an accuracy of about ± 2 cm^{-1}. Above 1500 cm^{-1} the accuracy is poorer.

Spectra of the metal chelates

Generally, the spectra of the metal chelates are similar to one another,[7] but detailed examination reveals many differences. There are also considerable differences between the spectra of the metal oxinates and that of 8-hydroxyquinoline itself.

The spectra agree closely with those reported by Charles *et al.*[7] and by Stone.[3] The latter examined only the bismuth and magnesium chelates, but the former carried out investigations on a number of the metal chelates. However, from the list of principal peaks given and the spectra shown by Charles *et al.*, it is clear that a number of important peaks revealed in the present work were missed.

The spectrum of 8-hydroxyquinoline is complicated but shows similarities to that of quinoline.[16] It is suggested that the peaks at 1580 cm^{-1}, 1504 cm^{-1}, 1515 cm^{-1} and 1545 cm^{-1} in this reagent are due to C=C and C=N vibrations.[14] The peaks around 782 cm^{-1} as well as those in the region 1000–1200 cm^{-1} are attributed to ring vibrations and C—H deformations. Following this reasoning it would be expected that on chelation with a metal, the peaks around 780 cm^{-1} should alter materially. It can be seen from the spectra of the metal chelates that this is indeed the case. In fact, alteration in this region appears to be characteristic of the metal present and has considerable analytical significance in a qualitative sense.

Charles *et al.*,[7] in their examination of metal oxinates in the infrared came to the conclusion that the 9-μ peak which occurs in the spectra of all the metal oxinates, but not in 8-hydroxyquinoline itself, is associated with C—O vibrations in the molecule. These workers found that the 9-μ peak varied by a small amount from one metal oxinate to another, being displaced to lower frequencies as the atomic weight of the metal was increased. In the present work, however, the position of this peak did not vary markedly from metal to metal. With the maximum accuracy available, the following values were found: copper (1113 cm^{-1}), zinc (1112 cm^{-1}), manganese (1108 cm^{-1}), magnesium (1112 cm^{-1}), and calcium (1106 cm^{-1}). When these values for the position of the peak were plotted against the atomic weight of the metal, no simple relationship was obtained.

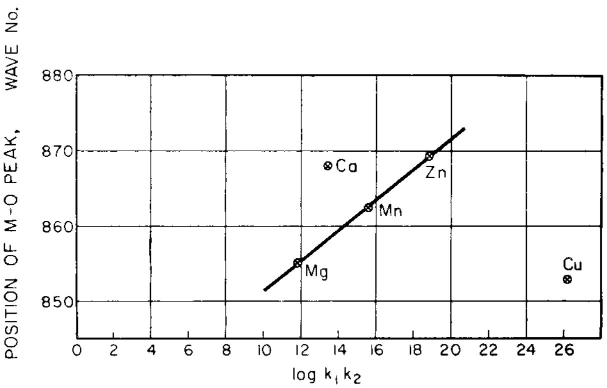

FIG. 3.—The position of the M—O peak in wave numbers plotted against log k_1k_2.

In the results from the present work, it will be observed that a significant peak occurs in the metal oxinates in the region 850–870 cm^{-1}. The appearance of this peak in all the metal chelates suggests that it is due to a diatomic vibration, possibly the C—O bond, or a metal-oxygen stretching frequency. The position of this peak varies markedly with the metal. It might be expected that the position of the peak would be influenced by the stability of the complex. To test this supposition the peak position for each metal oxinate was plotted directly against log k_1k_2.[15] The result is shown in Fig. 3. It will be seen from the figure that zinc, manganese and magnesium lie on a straight line, while calcium and copper lie at considerable distances from this line. If a plot is made of the position of the peak against atomic weight, as carried out by Charles *et al.*,[7] a similar result is obtained.

Merritt[16] determined the structure of zinc oxinate dihydrate by X-ray diffraction and showed that it has octahedral co-ordination around the zinc atom. The same author, however, concludes that in a rigid co-ordinating molecule such as 8-hydroxyquinoline, where the reacting groups are firmly fixed, the final structure may involve a great distortion of the usual valence bond angles to the metal ion. This would depend on the size of the metal ion. The bivalent ionic radii of the metals used in the present work are: Cu, 0·69 Å; Zn, 0·74 Å; Mn, 0·80 Å; Mg, 0·65 Å; Ca, 0·99 Å.

This importance of the metal ion size in determining the structure of the metal oxinates may be seen more clearly by considering "limiting radius ratios." In this concept the radius of the metal ion (r_m) to the radius of the other ion (r_x) in a complex structure must lie within certain limits for each type of co-ordination. Dunitz and Orgel[17] have shown for various co-ordination polyhedra, for example, that for an octahedron (co-ordination number 6) the minimum radius ratio must be 0·414; for a tetrahedron 0·225; for a cube 0·732; and for a square antiprism 0·645.

When the values of the radii for the oxygen ion (r_x) and each metal ion (r_m) are used in this manner, the results shown in Table I are obtained:

TABLE I

	Cu	Zn	Mn	Mg	Ca
r_m/r_x	$\frac{0{\cdot}69}{1{\cdot}40}$	$\frac{0{\cdot}74}{1{\cdot}40}$	$\frac{0{\cdot}80}{1{\cdot}40}$	$\frac{0{\cdot}65}{1{\cdot}40}$	$\frac{0{\cdot}99}{1{\cdot}40}$
	0·493	0·529	0·571	0·464	0·707
	Octahedron	Octahedron	Octahedron	Octahedron	Square antiprism
Co-ordination no.	6	6	6	6	8

Using the limits set by Dunitz and Orgel, it can be seen that calcium produces a different structure from the other metals. Now, if the lower limit for a feasible metal oxinate structure is set at tetrahedron (minimum radius ratio = 0·225), then ions of radius less than 0·32 Å would not be expected to form an oxinate, *e.g.*, Be^{2+} (0·31 Å). On the other hand, if the upper limit for a feasible structure is set at square antiprism (minimum radius ratio = 0·645), then ions of radius greater than about 1·1 Å would not be expected to form an oxinate, *e.g.*, Ag^+, 1·26; Au^+, 1·37.

Analytical applications

It was mentioned earlier that differences in the spectra of the different metal oxinates are significant enough to permit their use in the detection of the element. These differences occur principally in the region 10–14 μ. Close examination of the spectra in this region confirms the analytical value of these differences. As a quantitative technique in inorganic analytical chemistry, infrared spectrophotometry has up to the present time found little application; only a few cases have been reported.[8,9] In the present work, however, it was the intention to investigate possible qualitative aspects of the technique and preliminary investigations revealed hopes of success in this direction. Attention was focused on zinc and copper only, and an attempt was made to use certain peaks quantitatively.

Examination of the spectra of these elements reveals (Figs. 1 and 2) that for copper oxinate a characteristic peak occurs at 852 cm^{-1} (11·73 μ). This peak does not occur in the spectrum of zinc oxinate nor is there any peak in the vicinity which could lead to confusion in identification. At the same time, a characteristic peak occurs in the spectrum of zinc oxinate at 908 cm^{-1} (11·02 μ) which suffers no interference from any copper peaks. Although other peaks exist which serve to distinguish copper from zinc, in the present work, only these two peaks were used quantitatively.

Variation of peak height with concentration

In order to test the quantitative use of the copper and zinc peaks, the variation of the peak height with concentration was examined. The results are shown in Figs. 4 and 5 where it will be seen that the peaks under consideration behave linearly with concentration. Although in the investigation as little as 0·1 mg of the copper oxinate precipitate was taken, it was nevertheless found that the 11·73-μ peak is not sensitive below 1 mg of precipitate and results using less than this amount are likely to be subject to error. With zinc, on the other hand, the method may be extended to at least 0·1 mg of zinc oxinate precipitate.

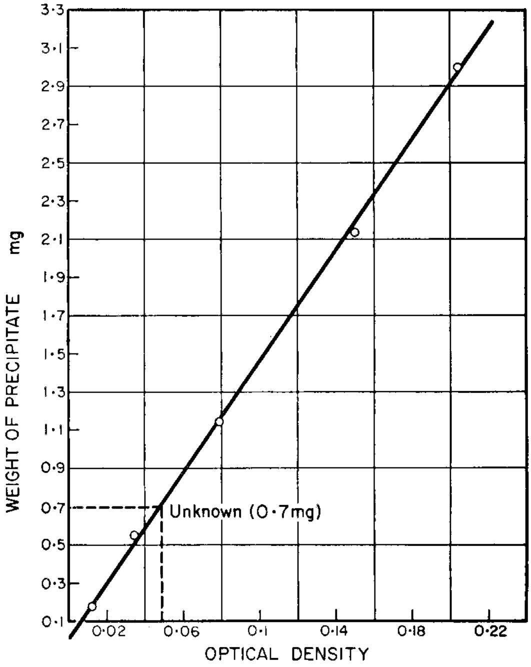

FIG. 4.—The zinc calibration curve for the peak at 11·02 μ.

Procedure

Weigh out a portion of the metal oxinate which has been dried for several hr at 130°. For copper, the optimum amount is in the range 1–3 mg; for zinc, 0·1–3 mg.

Mix this weighed amount of precipitate with about 300 mg of potassium bromide.* Place the mixture in an agate mortar and mix to a homogeneous powder.†

Transfer the homogeneous mixture to the die and form it into an even layer with the plunger. It is

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* The potassium bromide disc method for the preparation of solid samples was discovered independently by Stimson and O'Donnell[18] and by Scheidt[19] in 1952 and in recent years has come in for some criticism. The principal criticism appears to be that difficulties arise which may be attributed to anion exchange between the compound and the alkali halide, and to pressure or orientation effects on the sample as a result of compression.[20] In the present work these effects were looked for, but in no case were observed, perhaps because of the high stability of these chelates. Samples were left for 1 week or more in a desiccator and on re-examination produced exactly the same spectra as before. The great advantage of the method over mull techniques is, of thecourse, fact that it can be used quantitatively and that very small samples may be employed.

† Precipitates obtained by the method of precipitation from homogenous solution (PFHS) are ideally suited for this technique and a satisfactory mixture can be obtained in from 30 secs to 1 min.

not necessary to transfer the mixture quantitatively, because the optical density of the finished disc is corrected to the 300-mg disc. After replacing the plunger, evacuate the die for 2 min. A disc will be produced by this procedure which should be clear.

Fix the disc in a suitable holder and place in the sample beam of the infrared spectrophotometer. A potassium bromide disc of similar weight should be used in the reference beam.

The spectrum may be recorded over the range 2–15 μ, but it is satisfactory for quantitative work to record only the range 10–12 μ.

To calculate the optical density of the peak, use a base-line technique.[8] In this technique a line is drawn at the base of the band and the optical density calculated from the incident (I_0) and transmitted (I_t) intensities. This value is then corrected to a 300-mg basis by multiplying by the factor $300/W$, where W is the weight of the disc in mg. From a calibration curve the concentration of copper or zinc may be determined.

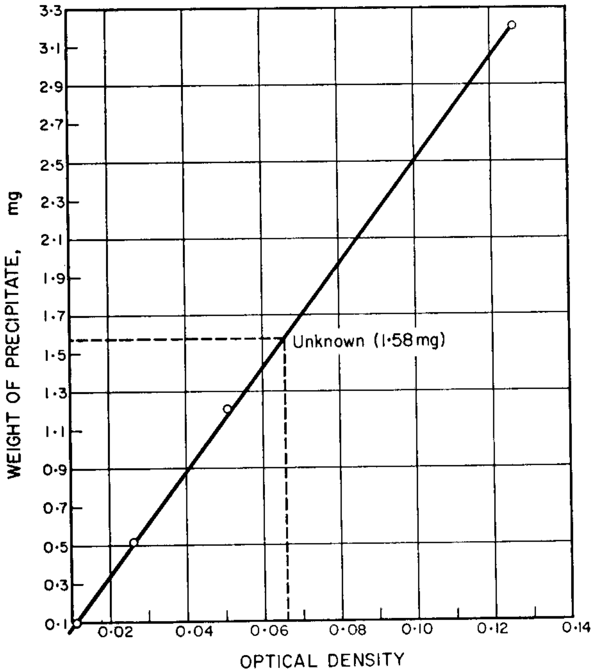

FIG. 5.—The copper calibration curve for the peak at 11·73 μ.

As a test on the technique a mixture of the oxinates of copper and zinc was examined. Fig. 6 shows the spectrum of the mixture of these two oxinates. By comparison of this with the spectra of the two metals alone, it is quite easy to decide that these two particular metals are present. The two characteristic peaks at 11·02 μ for zinc and 11·73 μ for copper can be clearly seen. Further, the mixture supplied consisted of 0·70 mg of zinc oxinate and 1·54 mg of copper oxinate and, after determining the optical densities at the appropriate peaks and using the calibration curves, the amount of each oxinate in the mixture was found to be 0·70 mg of zinc and 1·58 mg of copper.

It should be pointed out that while in this work the quantitative behaviour of only zinc and copper was investigated, the method may be extended readily to calcium, manganese and magnesium, as characteristic peaks for these metals are present in their spectra. Furthermore, it will be noted that in the discussion of the spectra of these chelates that no mention was made of the metal-nitrogen bond. Absorption peaks characteristic of this stretching frequency should occur at frequencies below 625 cm^{-1}. Investigations of this region are reported in Part II of this series.[21]

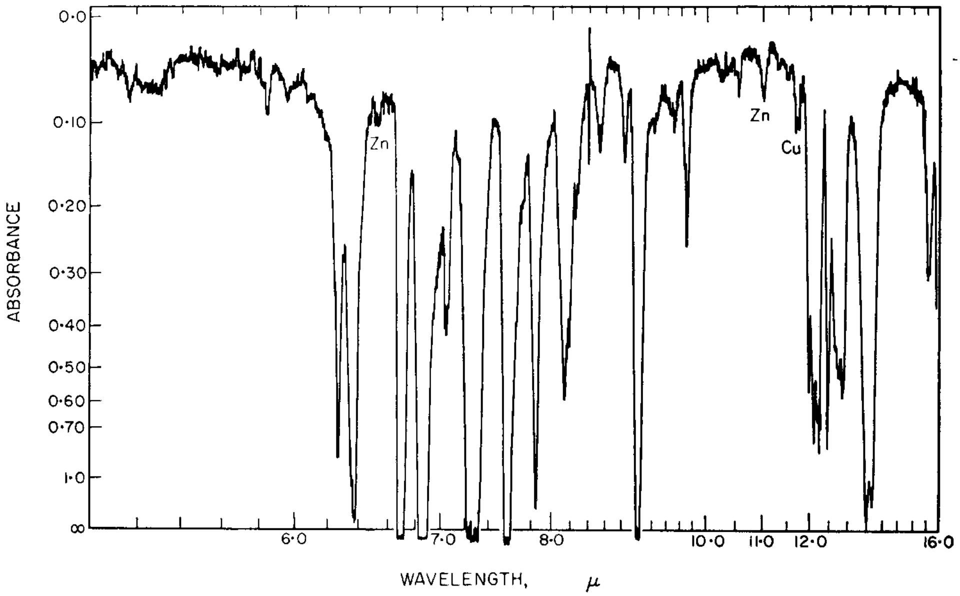

FIG. 6.—The infrared spectrum of mixed oxinates of copper and zinc. (0·70 mg of zinc oxinate and 1·54 mg of copper oxinate.)

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Zusammenfassung—Die Infrarotspektren von Oxin und seinen Chelaten mit Cu, Zn, Mn, Mg und Ca wurden im Bereich 2–16 Mikron untersucht. Soweit es möglich war, wurden die Absorptionspitzen zugeordnet und Beziehungen zwischen der Lage der Absorptionspitzen und den Stabilitästkonstanten aufgezeigt. Auf Grund dieser Beziehungen wird die Struktur der verschiedenen Chelaten diskutiert. Eine Untersuchung über die Änderung der Spitzenhöhe mit der Konzentration lässt erwarten, dass die Methode analytische Bedeutung erlangen kann. Eine Methode zur Bestimmung von Cu und Zn als Oxinate wurde ausgearbeitet.

Résumé—On a étudié des spectres infra-rouges dans la région 2 à 16 microns, de l'hydroxy-8-quinoléine et de ses composés chélatés avec le cuivre, le zinc, le manganèse, le magnésium et le calcium. L'attribution des pics a été faite d'une manière aussi poussée que possible, et des corrélations ont pu être déduites entre la position de ces pics et les constantes de stabilité. A partir de ces corrélations, les auteurs proposent la structure de différents chélates. L'étude de la variation de la hauteur des pics en fonction de la concentration, montre que cette technique a une valeur réelle au point de vue analytique. Un procédé de dosage du cuivre et du zinc sous forme d'oxinates est donné.

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EINE METHODE ZUR KONDUKTOMETRISCHEN BESTIMMUNG DES NATRIUMS

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Zusammenfassung—Man fällt das Natrium als Zink-Uranyl-Natriumazetat. Man lösst den Niederschlag in Wasser auf. Man titriert konduktometrisch mit einer Salzsäurelösung bekannter Konzentration. Es findet eine Verdrängungsreaktion statt. Die Methode ist vorteilhaft wegen des sehr günstigen Verhältnisses zwischen dem Azetat und dem Natriumion und zwar ist dieses 9:1. Indem man die Fällung als dreifaches Azetat unter den vorgesehenen Bedingungen für den Stoff, in dem man die Bestimmung macht, ausführt, kann man behaupten dass das Verfahren allgemeine Anwendung findet. Es wurden Versuche in dem Bereich 0,046–2,3 mg Na gemacht.

DIE Bestimmung des Natriums kann gewöhnlich gravimetrisch als Natrium-Sulfat oder -Chlorid nach vorhergangener Abtrenung der übrigen Ione vor sich gehen, oder in Form von Natrium-Zink-Uranylazetet auf volumetrischem, gravimetrischem oder kolorometrischem Wege geschehen.[1]

Die gravimetrische Methode, welche die Bestimmung in der Form des dreifachen Azetats ausführt, leidet unter wechselnder Zusammensetzung der Verbindung, welche von 6 bis 9 Moleküle Wasser enthalten kann (Ref. 1, Seite 27). Die Grundlage volumetrischer oder kolorimetrischer Bestimmungsmethoden ist die Bestimmung der UO_2^{+2} oder Zn^{+2}-Ionen des dreifachen Azetats.[1] Eine sehr günstige Methode vom stoechiometrischen Standpunkt ist die Titration mit Natriumhydroxid. Theoretisch, das Verhältnis NaOH:Na ist 8:1, aber die Reaktion ist von den Arbeitsbedingungen abhängig, drückt nicht genau das Verhältnis 8:1 aus, und der Titer wird empirisch festgestellt.[2–4] Wenn man das dreifache Zink-Uranyl-Natriumazetat über einen in H-Form gebrachten Ionenaustauscher in Essigsäure überführt, kann man die Bestimmung bequem auf acidimetrischem Weg durchführen.[5] Das Verhältnis CH_3COOH:Na ist 9:1, die Genauigkeit der Methode ist vollauf befriedigend.

Da die Konduktometrie eine Methode darstellt, mit der sich besonders die Verdrängungsreaktionen verfolgen lassen,[6] haben wir an die Möglichkeit gedacht die Bestimmung des Natriums auf Grund der Reaktion:

$$NaZn(UO_2)_3(CH_3COO)_9 + 9HCl \rightarrow NaCl + ZnCl_2 + 3UO_2Cl_2 + 9CH_3COOH$$

zu studieren.

Auf diesem Wege werden ebenfalls die CH_3COO^--Gruppen, so wie in der vorhererwähnten Methode bestimmt, aber die Bestimmung geschieht direkt, ohne dass noch eine Uberführung in CH_3COOH über Ionenaustauscher notwendig wäre.

Die Versuche zeigten sehr gute Ergebnisse in einem weiten Konzentrationsbereich: 0,046–2,3 mg. Na^+.

EXPERIMENTELLER TEIL

Apparatur

Es wurde ein Konduktibilitätsmesser mit Elektronenröhre und Lautsprecher verwendet, welcher von Stromnetz gespeist wurde. Immersionselektroden von platiniertem Platin.

Reagenzien

Natriumchloridlösung: 0,1 n: 0,02 n und 0,002 n.

Zink-Uranylazetatlösung, welche in folgender Weise hergestellt wurde:[8]

(*a*) Zu 10 g. kryst. Uranylazetat gibt man 6 g. 30%-ige Essigsäure und 50 ml dest. Wasser hinzu.

(*b*) Zu 30 g. kryst. Zinkazetat gibt man 3 g. 30%-ige Essigsäure und 30 ml. dest. Wasser hinzu.

Die beiden Lösungen werden vermischt.

Äthylalkohol: 96%-iger gesättigt mit Zink-Uranyl-Natriumazetat.

Äthyläther.

Salzsäurelösung: 0,5 n:0,1 n und 0,01 n.

Analysengang

In einer Zentrifugierröhre werden zu 1 ml Probelösung 3 ml Zink-Uranylazetatlösung hinzugegeben. Man lässt 2–3 Stunden stehen-bei kleinen Konzentrationen 4–6 Stunden. Manzentrifugiert ca. 1/4 Stunde, dann entfernt man vorsichtig die obere Flüssigkeit. Man wäscht den Niederschlag 4–5 mal mit je 3 ml gesättigter alkoholischer Lösung des dreifachen Azetats und 2–3 mal mit je 3 ml Äther. Man löst den Niederschlag in 50 ml. destilliertem Wasser auf, und titriert dann konduktometrisch mit einer Salzsäurelösung passender Konzentration.

VERSUCHERGEBNISSE

Die Titrationskurven sind in Abb. 1 dargestellt. Anfangs haben wir das Natrium als dreifaches Azetat in 3 Proben von je 1 ml 0,1 n Natriumchloridlösung gefällt. Zwei dieser Proben wurden konduktometrisch mit 0,5 n Salzsäurelösung titriert. Die Titrationskurve zeigte eine deutlichen Knick, die Äquivalenz richtig anzeigend.

Um ein Bild der Titrationskurven bei höheren Verdünnungen zu erhalten, wurden aus der dritten Probe zweimal je 10 ml entnommen, zu 50 ml verdünnt-also erhielt man fünffach verdünnte Lösungen-und mit 0,1 n Salzsäurelösung titriert. Dan wurde zweimal je 1 ml auf 50 ml verdünnt-also 50 fach verdünnte Lösungen erhalten-und mit 0,01 n Salzsäurelösung titriert. Die Titrationskurven erwiesen sich vollauf befriedigend. Die Versuchsergebnisse sind in der Tabelle I wiedergegeben:

TABELLE I

Gegeben Na, *mg*	Gefunden Na, *mg*
2,30	2,27;2,30
0,460	0,455;0,465
0,0460	0,0465;0,0465

Es wurde dann die Fällung des Natriums in 2 Proben von je 1 ml, 0,02 n Natriumchloridlösung und in 2 Proben von je 1 ml 0,002 n Natriumchloridlösung durchgeführt. Nach Trennung und Waschen des Niederschlags, wurde mit 50 ml destilliertem Wasser gelösst und konduktometrisch mit 0,1 n bzw. 0,01 n Salzsäurelösung titriert. Die Ergebnisse dieser Versuchsreihe, velche in Tabelle II ersichtlich sind, stimmen sehr gut überein mit denen der ersten Versuchsreihe.

TABELLE II

Gegeben Na, *mg*	Gefunden Na, *mg*
2,30	2,29;2,34
0,460	0,458;0,460
0,0460	0,0455;0,0475

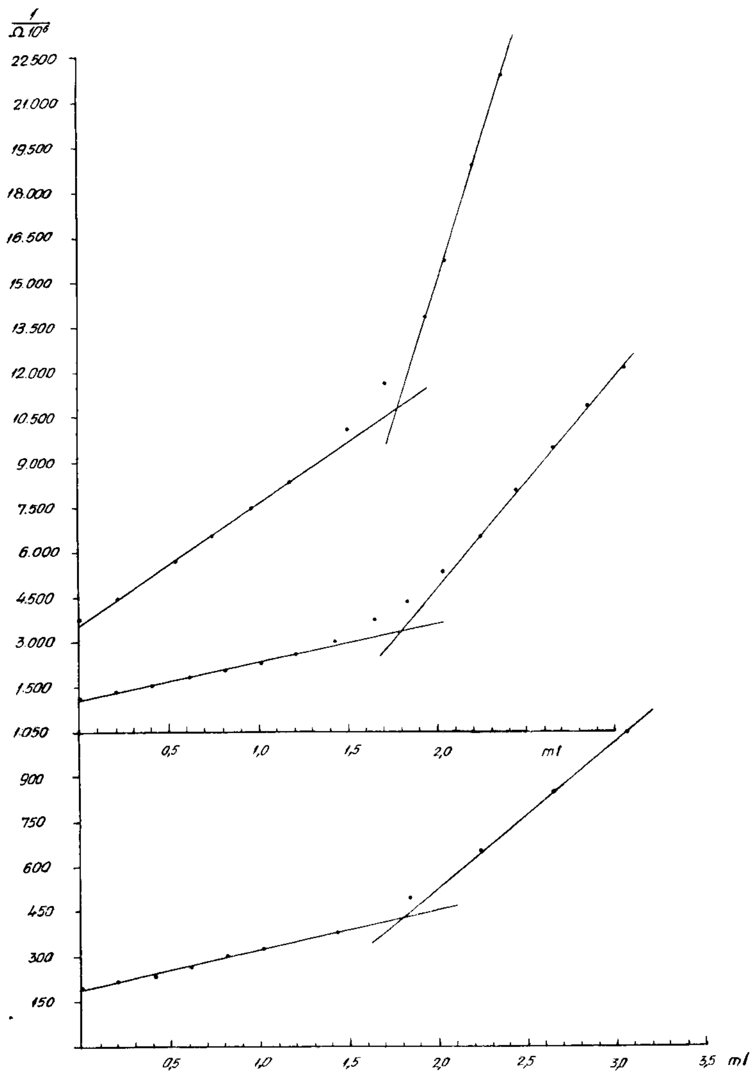

Abb. 1.

Summary—A method for the determination of sodium is described, based on its precipitation as sodium zinc uranyl acetate. The precipitate is dissolved in water, and a conductometric titration is carried out, using hydrochloric acid as the titrant. The method has the advantage that the ratio acetate:sodium is 9:1. It may be applied to any substance if sodium is precipitated as the triple acetate under suitable conditions. Experimental results for sodium, within the range 0·046–2·3 mg, are reported.

Résumé—On décrit une méthode de dosage du sodium par précipitation au moyen d'uranyl acétate de zinc. Le précipité est dissous dans l'eau, et dosé par conductimétrie en utilisant l'acide chlorhydrique comme réactif. Cette méthode présente l'avantage d'un rapport acétate/sodium égal à 9/1. Elle peut être appliquée à d'autres substances susceptibles de fournir un précipité d'acétate triple. On decrit des résultats expérimentaux concernant le sodium dans un domaine allant de 0,046 à 2,3 mg.

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ION EXCHANGE IN MIXED SOLVENTS

ADSORPTION BEHAVIOUR OF THE RARE EARTHS AND SOME OTHER ELEMENTS ON A STRONG-BASE ANION-EXCHANGE RESIN FROM NITRIC ACID-ALCOHOL MEDIA

METHODS FOR SEPARATION AND SPECTROPHOTOMETRIC DETERMINATION

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Summary—The anion-exchange behaviour of the rare earths and some other elements in aliphatic alcohols containing nitric acid is described. Based on the determination of the distribution coefficients and separation factors of the individual elements separation techniques are proposed. For the final determination of these elements the use of the azo dye Solochrome Fast Red as a spectrophotometric reagent is investigated.

INTRODUCTION

Ion exchange in pure aqueous media as a means for the quantitative separation of the rare earths and various other elements has now been extensively employed for many years. Numerous complexing agents were successfully applied for the chromatographic elution of the rare earths from cation-resin columns. Because the literature on the cation-exchange behaviour of these elements is very extensive we restrict ourselves here to a mention of the important recent review by Powell.[1]

In contrast, information as to the anion-exchange behaviour of the rare earths in aqueous mineral acid media is scarce because adsorption from such solutions is rather poor, as has been verified by a number of investigators.[2–8] Adsorption from inorganic nitrate solutions of low acidity, however, has been reported to be better.[9–11] Furthermore, adsorption of the rare earths from aqueous solutions containing lithium chloride,[12] thiocyanate,[13] citrate[14] and EDTA[15,16] on strong-base anion exchangers has been reported.

The fact that the adsorption of many elements increases on decreasing the aqueous component by adding miscible organic solvents, as for instance the aliphatic alcohols,[17] is also true for the rare earths. Consequently, a number of pertinent investigations have been carried out using hydrochloric acid-alcohol solutions[18–20] and mixtures of organic solvents with nitric[10,21] and sulphuric acid.[22] Based on the work by Korkisch and Tera[23] who found that the rare earths and thorium were strongly adsorbed on Dowex 1 from nitric acid-methanol mixtures, Faris and Warton[24] developed a successful separation technique for the rare earths, yttrium and scandium in such media. Their results can be regarded as the starting point for the development of further useful separation methods in mixed solvents as was, and still is, the case with uranium and thorium.[17]

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In the present paper the research work presented by Faris and Warton[24] is extended; in addition to methanol, some other aliphatic alcohols have been investigated as to their applicability for the separation of the rare earths from other elements, mainly uranium and thorium. Based on the results obtained from the determination of the distribution coefficients in various media the separation factors were calculated and separation possibilities indicated or outlined. For the final determination of the rare earths a new spectrophotometric technique employing the azo dye, Solochrome Fast Red was used.

EXPERIMENTAL

Reagents

Ion exchange resin: The strongly basic anion exchanger Dowex 1, X8 (100–200 mesh; chloride form) was transformed to the nitrate form,[17] which was then air dried and used for the batch experiments and column operations

Standard solutions: Exactly weighed amounts of the rare earths, scandium, yttrium, aluminium, gallium, indium, iron, vanadium and molybdenum, either as metals, oxides or nitrates were dissolved in excess 5*M* nitric acid and the solutions were evaporated to dryness. In each case the residue was taken up in 5*M* nitric acid so as to give solutions containing 5 mg/ml. From these solutions which were employed for the equilibrium experiments, diluted standard solutions (1*M* in nitric acid) were prepared for the spectrophotometric investigations. The preparation of the uranium and thorium standard solutions has been described previously.[17]

Solvents: For determination of the distribution coefficients, *etc.*, the reagent-grade aliphatic alcohols methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol and a mixture of the amyl alcohols were used.

Dyestuff solution: A 0·1 % methanolic solution of the azo dye Solochrome Fast Red, which can also be successfully applied for the quantitative determination of uranium and thorium,[25] was employed.

2·5M sodium acetate solution

Apparatus

The photometric measurements were performed in 1-cm cells using the Beckman models DU and B spectrophotometers. The column operations were carried out in columns of the same type and dimensions as described earlier.[17]

Quantitative determination of the elements

Solochrome Fast Red was used for the spectrophotometric determination of uranium, thorium[25] and all other elements (see below), with the exception of molybdenum which was determined by employing the Solochrome Dark Blue B method.[26]

Spectrophotometric Studies

These investigations were carried out in order to develop photometric methods not only suitable for the precise determination of the rare earths but also for all other elements the adsorption behaviour of which was studied here. As the most suitable reagent Solochrome Fast Red was selected from a series of dyestuffs investigated for this purpose. Because all the elements tested react with this dyestuff under the same experimental conditions, however, the quantitative photometric determination of a certain element can only be carried out in absence of all other elements.

Selection of a suitable wavelength

To solutions containing μg-amounts of the elements dissolved in 1 ml of 1*M* nitric acid, 1 ml of the 0·1 % dyestuff solution and 1 ml of sodium acetate solution were added. These solutions were then diluted to 10 ml with methanol and measured against a reagent blank solution over the wavelength region from 450 to 540 mμ.

Some typical spectra are shown in Fig. 1. The wavelength of maximum absorbance for the various elements was found to be:—Al: 480 mμ; G: 492 mμ; In: 490 mμ; Sc: 484 mμ; Y: 484 mμ; La: 480 mμ; Ce: 476 mμ; Pr: 478 mμ; Nd: 478 mμ; Sm: 478 mμ; Eu: 478 mμ; Gd: 480 mμ; Tb: 484 mμ; Dy: 484 mμ; Ho: 484 mμ; Er: 484 mμ; Tm: 484 mμ; Yb: 484 mμ; Lu: 484 mμ; Fe^{III}: 476 mμ; V: 494 mμ. All of these elements have orange-coloured complexes with the exception of gallium and $iron^{III}$ which form red and brown complexes, respectively.

Effect of acidity and concentration of organic solvent

In studying the effect of acidity at the wavelength of maximum absorbance it was found that it was the same as that earlier observed with uranium^{VI}.[25] Thus, the addition of 1 ml of the sodium acetate solution proved to be most suitable. By lowering the pH of the solutions the absorption was decreased and it became zero in 0·1*M* nitric acid (over-all acidity), *i.e.*, if no sodium acetate solution was added, whereas the addition of more than 1 ml of this solution did not increase the absorbance. On the contrary, the presence of more than 2 ml of the sodium acetate solution caused a drop of the maxima to lower absorbances because of the decrease of the methanol content of the measuring solutions, which was found to be optimal when applying 8 ml of methanol/10 ml of measuring solution. If water, other aliphatic alcohols or acetone are used in place of methanol a sharp decrease of the absorbance was noticed, so that methanol proved to be the most suitable solvent.

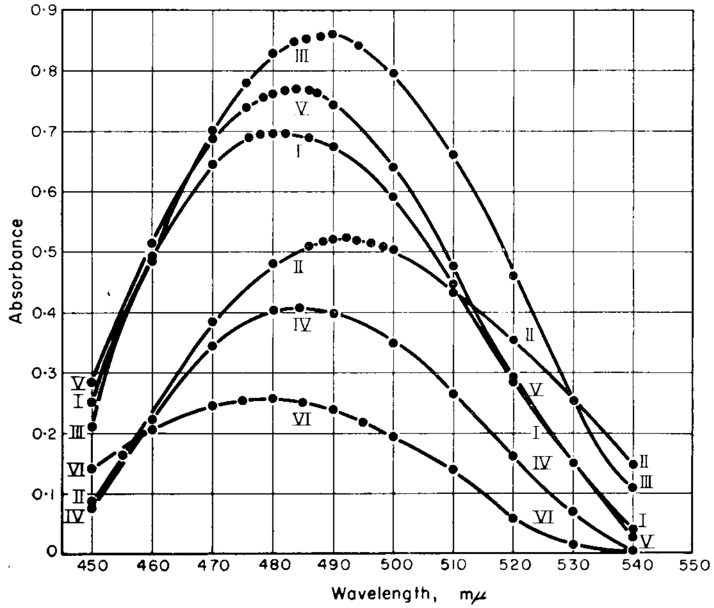

FIG. 1.—Typical absorption spectra with Solochrome Fast Red:

I—aluminium (10 μg),	IV—scandium (7·5 μg),
II—gallium (10 μg),	V—yttrium (50 μg),
III—indium (40 μg),	VI—lanthanum (51·3 μg).

Effect of dyestuff concentration and time

By using 0·1–8·0 ml of the dyestuff solution and 50 μg of the element (dissolved in 1 ml of 1*M* nitric acid), 1 ml of sodium acetate solution and methanol up to 10 ml it was found that 1 ml of the dye solution was sufficient for full development of the coloured complex. This was always the case for all elements investigated. Within the range of a few min to 2 days after preparation of the test solutions, no effect of time on the measurements could be observed.

Working procedure and calibration curves

Transfer the solution containing the element to be determined to a platinum dish and evaporate to dryness on a water bath. Briefly ignite the residue to remove organic matter and dissolve the oxide thus formed in 5 ml of 6*M* hydrochloric acid, then evaporate this solution to dryness. Take up the residue in 1 ml of 1*M* nitric acid and transfer the solution to a 10-ml calibrated flask by washing the dish with 5–6 ml of methanol. To this solution add 1 ml of the dyestuff solution and 1 ml of the sodium acetate solution, then dilute to the 10-ml mark with methanol. Measure the absorbance of this solution against a reagent blank solution at the wavelength of maximum absorbance. The amount of the element in the test solution is obtained by comparison with the corresponding calibration curve (see Fig. 2).

This working procedure can be employed for the determination of Ga, In, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Fe and V. In the case of Ce a few crystals of hydroxylamine hydrochloride have to be added to the 5 ml of 6*M* hydrochloric acid in order to ensure complete dissolution of the cerium oxides, and quantitative formation of cerium^{III} ions. In the determination of iron 1 ml of 1*M* hydrochloric acid is used in place of 1*M* nitric acid. For the determination of aluminium the procedure described above had to be modified in as far as the insoluble aluminium oxide obtained after the ignition of the residue must be evaporated to dryness with hydrofluoric acid. Thereafter the residue is successively evaporated three times with 1 ml of concentrated nitric acid in order to remove all fluoride ion. The residue thus obtained is taken up in 1 ml of 1*M* nitric acid, *etc.*

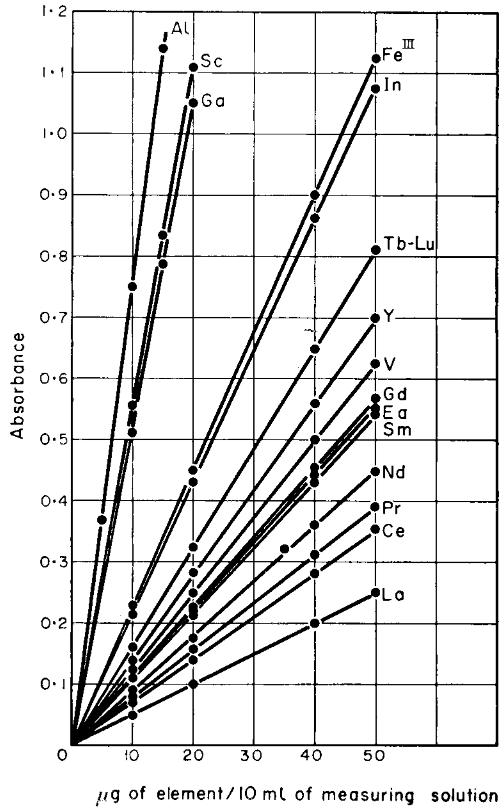

FIG. 2.—Calibration curves

By comparing the individual absorption values (at maximum absorbances and identical concentrations) of the different elements (see Fig. 2) with their K_d values in methanol-nitric acid media (see Fig. 3), it can easily be seen that in many cases the spectrophotometric sensitivities are roughly inversely proportional to the K_d values. This can be explained on the basis that the degree of neutral salt formation is high in the cases where K_d is high because the dissociation is suppressed and the equilibrium shifted to the left-hand side of the following general equation:

$$Me(NO_3)_3 \rightleftharpoons Me^{3+} + 3NO_3^-.$$

This means that in such solutions only a small amount of free metal ion exists and can react with the dyestuff to form coloured complexes.

Ion Exchange Studies

Determination of distribution coefficients

Weighed amounts of the air-dried resin (mostly 1 g) were added to the alcohol-nitric acid mixtures containing the element (usually 5 mg in 20 ml of the mixture) and agitated mechanically for 24 hr.

Thereafter the resin was filtered off and the element determined in an aliquot portion of the filtrate using the working procedure described above. From the data thus obtained the distribution coefficient of the element in question was calculated using the following equation:

$$\text{Distribution coefficient} = K_d = \frac{\mu\text{g of element/g of resin}}{\mu\text{g of element/ml of mixture}}.$$

In Figs. 3–7 the results obtained by using this procedure are shown.

Column operations

The column operations pertaining to the separation methods (see Table III) were performed in the manner described earlier.[17]

RESULTS AND DISCUSSION

In Figs. 3 and 4 the influence of alcohol concentration on the distribution coefficients is shown by taking methanol and n-propanol as examples. With the other aliphatic alcohols similar curves were obtained. By comparing Fig. 3 with Fig. 4 it is seen that the linear increase of K_d with increasing percentage of alcohol is interrupted in the case of n-propanol at the alcohol concentrations of 20% and 80%. From Fig. 4 it is also evident that in 90% n-propanol solutions all elements with the exception of scandium, aluminium, gallium, indium, iron and molybdenum are strongly adsorbed, whereas in 90% methanol mixtures (Fig. 3) only thorium and lanthanum–europium are retained to an extent suitable for quantitative isolation. In 90% butanol media the adsorption was found to be somewhat lower than in n-propanol, but still high enough to guarantee the quantitative retention of all of these elements. In some cases the adsorption increases first with increasing chain length of the alcohol (methanol to propanol), then usually decreases in butanol and amyl alcohol mixtures. This effect is not, however, shown by all elements because occasionally the reverse is true, as can clearly be seen from the variation of the separation factors in the different alcohols (see Tables I and II). Because the rare earths terbium–lutetium showed distribution coefficients which were practically identical, their arithmetic mean values were represented in these and all other figures and tables.

In Fig. 5 the relationship between distribution coefficient and ionic radius is shown. The points corresponding to the elements of similar chemical properties were connected by lines, thus the curves in this figure were obtained, which show that the adsorption increases with increasing ionic radius. A striking anomaly can now be seen, namely that lanthanum has a lower K_d than cerium although its ionic radius is greater (this was not, however, the case in 90% ethanol, isopropanol, isobutanol and 95% amyl alcohol–5*M* nitric acid mixtures). Furthermore, it can be seen that the increase of adsorption with growing ionic radius is much more pronounced in the case of the transition elements.

Distribution coefficients of other tervalent ions of rather great ionic radius like antimony, thallium and gold could not be measured because of hydrolysis (antimony), and reduction to lower valencies ($Tl^{3+} \rightarrow Tl^{+}$; $Au^{3+} \rightarrow Au^{0}$) in the alcohol–nitric acid media. The K_d-value of cerium^{IV} could also not be determined because of reduction to cerium^{III}, although cerium was primarily adsorbed as cerium^{IV} which was, however, reduced on the resin within a short time. In the case of the iso-alcohols and amyl

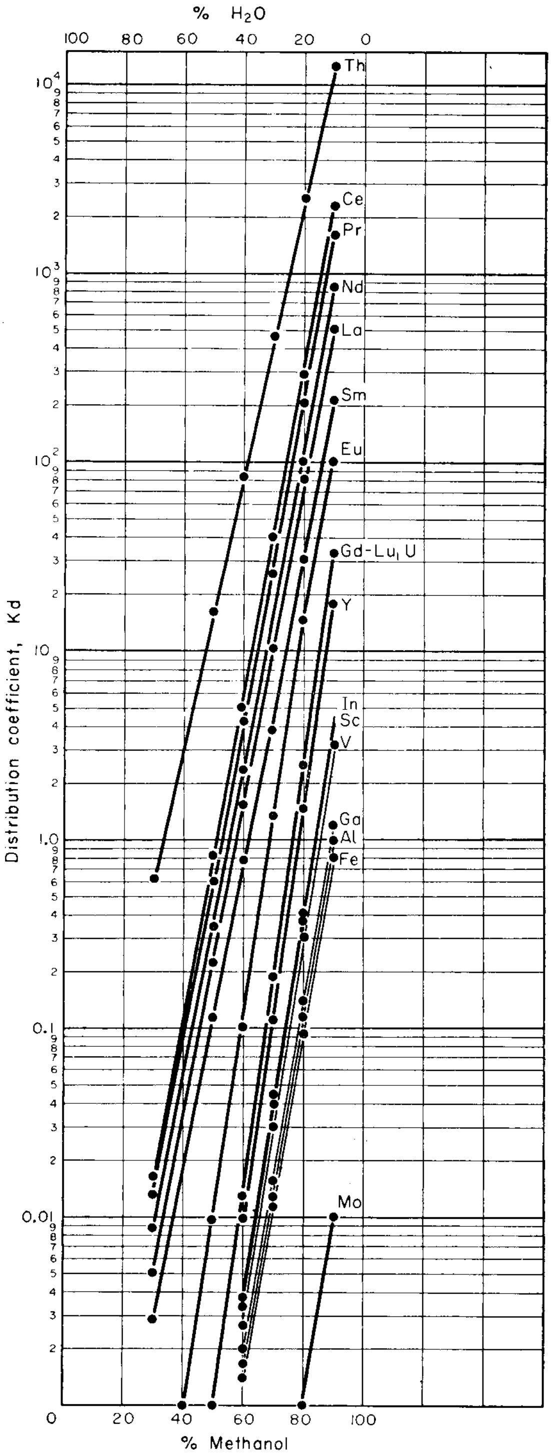

FIG. 3.—Effect of alcohol concentration (methanol) on distribution coefficient (over-all acidity: 0·5M HNO_3)

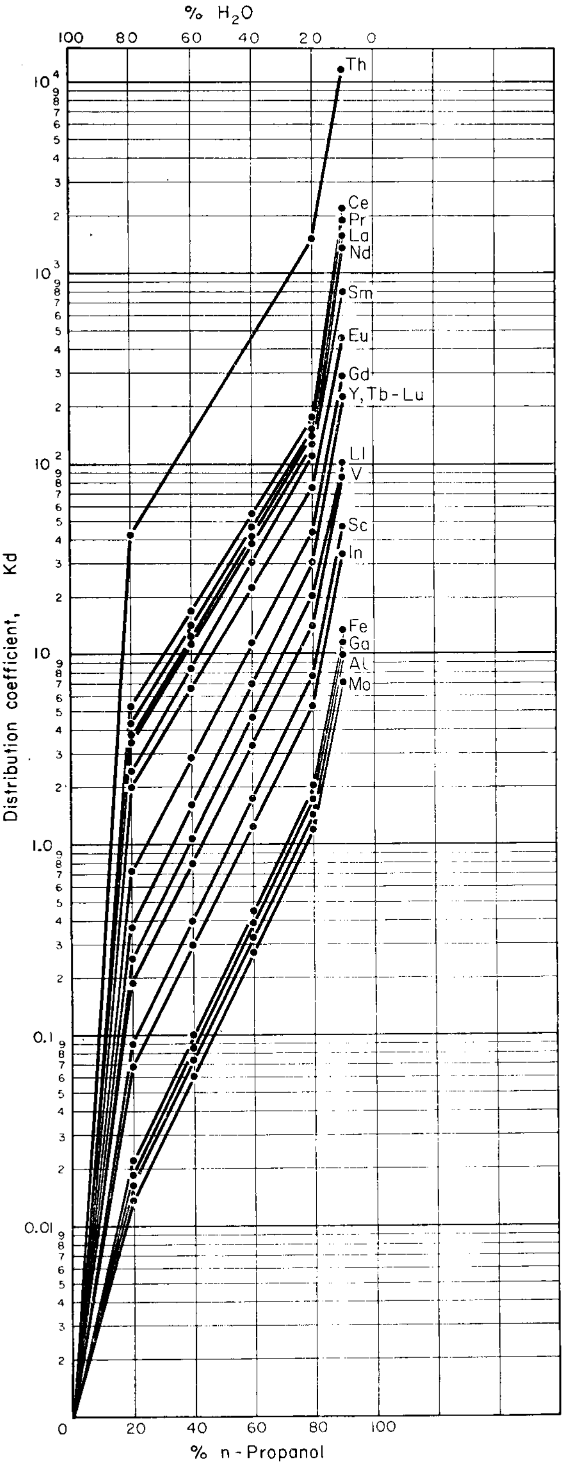

FIG. 4—Effect of alcohol concentration (n-propanol) on distribution coefficient (over-all acidity: 0·5*M* HNO_3)

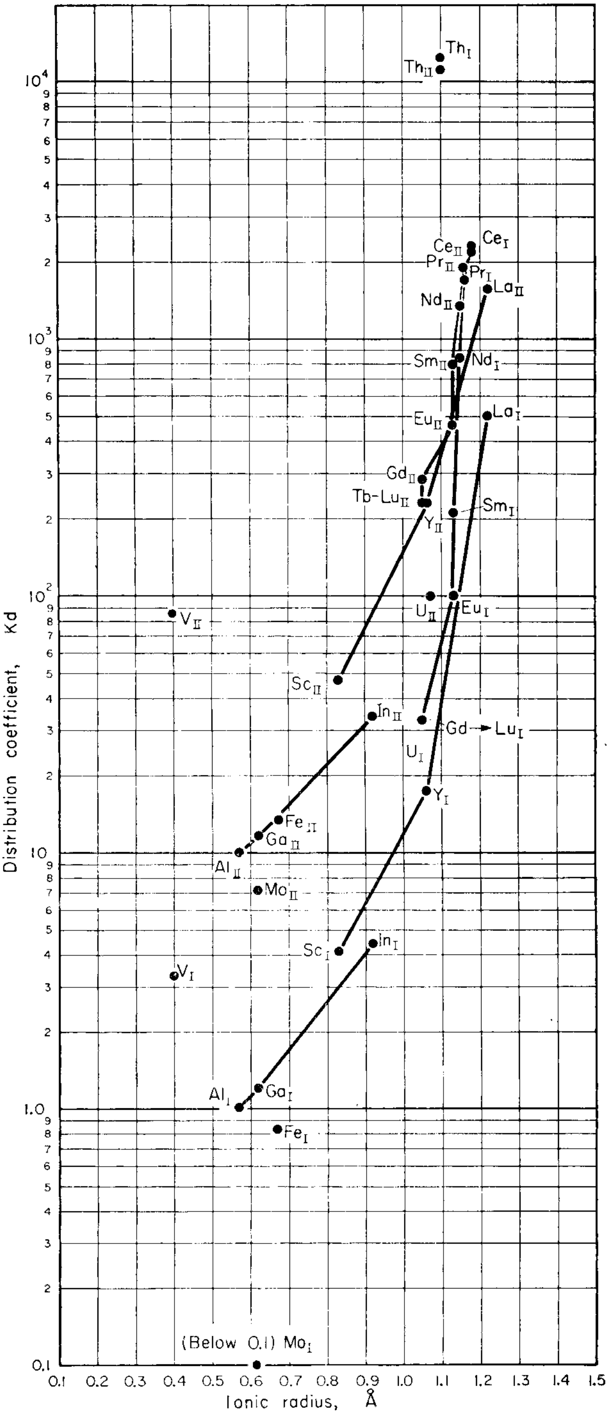

FIG. 5.—Relationship between ionic radius and distribution coefficient:
I—90% of methanol + 10% of $5M$ HNO_3,
II—90% of n-propanol + 10% of $5M$ HNO_3.

alcohol (mixture of isomers), an instantaneous reduction can be observed on adding the alcohol.

In Fig. 6 the effect of acidity on the distribution coefficients of praseodymium and erbium (as examples of the tervalent transition elements investigated) is shown. It can be seen that in the region betweeen 0·25 and 0·5M nitric acid the adsorption increases by 10% (erbium) and 16% (praseodymium) for each increase in over-all acidity by 0·1M. For these elements the effect on Kd of decreasing the acidity from 0·5 to 0·1M is similar to that produced by decreasing the alcohol concentration from 90 to 85% at a fixed acidity of 0·5M.

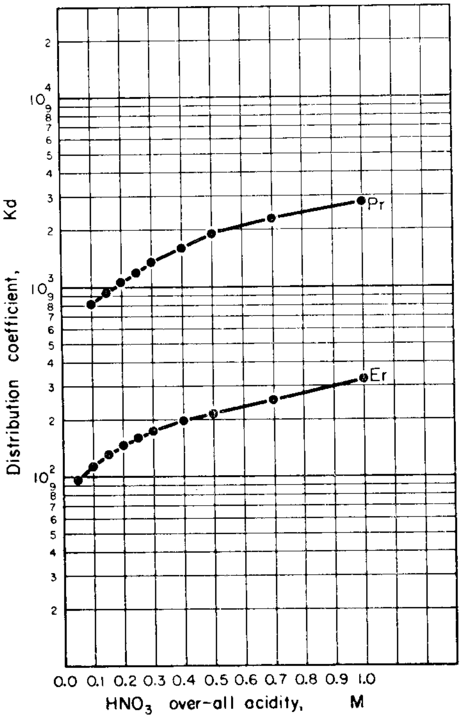

FIG. 6.—Effect of acidity on distribution coefficient (90% n-propanol)

From Fig. 7, which shows the effect of concentration on the distribution coefficients of cerium and terbium (as examples of the tervalent transition elements), it is seen that the resin has a much higher capacity (region where Kd does not vary with the concentration) for cerium (high Kd) than for terbium (low Kd) under identical experimental conditions.

In Tables I and II the separation factors in several nitric acid-alcohol mixtures are shown. These factors were calculated relative to uranium employing the simple relationship:

$$\text{Separation factor} = \frac{\text{Kd of element}}{\text{Kd of uranium}}.$$

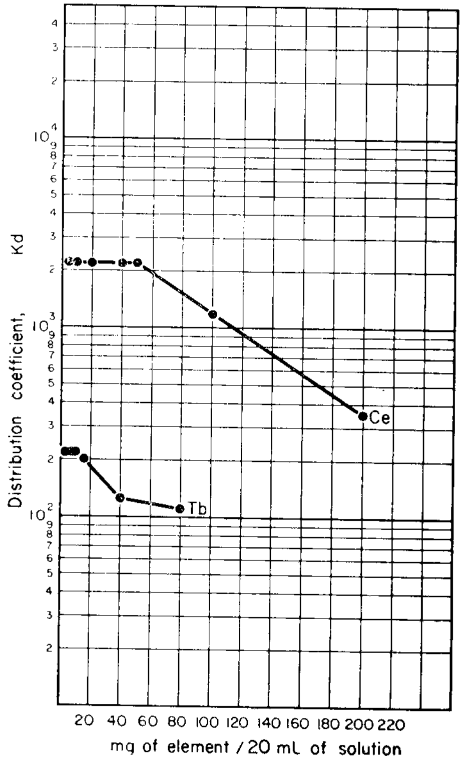

FIG. 7.—Effect of concentration on distribution coefficient (90% of n-propanol + 10% of $5M$ HNO_3/1g of resin)

TABLE I.—SEPARATION FACTORS* IN SEVERAL NITRIC ACID–ALCOHOL MIXTURES (90% of alcohol + 10% of $5M$ nitric acid)

Element	Methanol	Ethanol	n-Prop-anol	Isoprop-anol	n-Butanol	Isobuta-nol	Amyl-alcohol
UO_2^{2+}	1·0	1·0	1·0	1·0	1·0	1·0	1·0
Th^{4+}	382	125	110	108	20·0	20·0	15·4
Sc^{3+}	0·12	0·25	0·47	0·40	0·44	0·32	0·35
Y^{3+}	0·53	1·0	2·3	2·2	1·4	1·5	1·7
La^{3+}	15·1	41·0	16·0	22·0	10·3	11·7	13·3
Ce^{3+}	70	30·5	22·0	9·1	12·7	10·0	14·3
Pr^{3+}	48	18·2	19	9·1	11·1	7·1	4·6
Nd^{3+}	25·7	15·5	13·5	8·4	6·1	5·7	5·5
Sm^{3+}	6·3	7·1	8·0	6·8	4·4	5·0	4·8
Eu^{3+}	3·0	4·1	4·6	7·6	5·6	6·7	9·6
Gd^{3+}	1·0	1·8	2·8	1·0	1·6	1·7	1·6
Tb^{3+} — Lu^{3+}	1·0	1·7	2·3	0·83	1·6	0·47	1·13
Al^{3+}	0·03	0·06	0·1	0·09	0·083	0·09	0·08
Ga^{3+}	0·04	0·07	0·15	0·18	0·15	0·16	0·15
In^{3+}	0·13	0·22	0·34	0·38	0·27	0·28	0·15
Fe^{3+}	0·025	0·132	0·135	0·170	0·115	0·284	0·25
V^{5+}	0·10	0·52	0·85	0·61	0·25	0·32	0·558
Mo^{6+}	0·0003	0·001	0·07	0·05	0·023	0·032	0·028

* Expressed relative to uranium. The distribution coefficients for uranium in these mixtures were found to be 33 (methanol), 40 (ethanol), 100 (n-propanol and isopropanol) and 130 (n-butanol, isobutanol and amyl alcohol).

The reason why the Kd of uranium was selected as the basis for these calculations is that one of the most important separation problems encountered in reactor chemistry is the removal of the fission products (rare earths, *etc.*) from the nuclear fuel uranium. Thus, it is easily possible to estimate from the results presented in these tables which experimental conditions have to be selected in order to achieve successful separations. Besides, these factors also point out a possible means for the separation of uranium from thorium which is of great importance in respect of the process

$$^{232}\text{Th} \xrightarrow{n,\gamma} {}^{233}\text{Th} \xrightarrow[23\cdot5\ \text{min}]{\beta} {}^{233}\text{Pa} \xrightarrow[27\cdot4\ \text{day}]{\beta} {}^{233}\text{U}$$

occurring in the breeder reactor.

TABLE II.—SEPARATION FACTORS* IN SEVERAL NITRIC ACID–ALCOHOL MIXTURES
(95% of alcohol + 5% of 5*M* nitric acid)

Element	Methanol	Ethanol	n-Propanol	Isopropanol	n-Butanol	Isobutanol	Amyl alcohol
UO_2^{2+}	1·1	1·0	1·0	1·0	1·0	1·0	1·0
Th^{4+}	714	461	27·7	27·0	4·7	4·6	3·3
Sc^{3+}	0·25	0·42	0·81	0·85	0·87	0·72	0·63
Y^{3+}	1·23	1·30	1·70	1·65	1·32	1·25	1·10
La^{3+}	34·2	24·5	6·0	5·9	5·0	5·7	6·2
Ce^{3+}	143	34·1	10·0	9·9	6·3	6·3	4·0
Pr^{3+}	54·1	21·3	20·0	20·5	18·4	18·2	18·0
Nd^{3+}	42·3	19·2	18·8	17·3	16·5	16·6	15·9
Sm^{3+}	40·0	17·5	17·2	16·7	15·7	15·6	14·8
Eu^{3+}	21·4	15·3	15·6	15·4	15·0	14·5	14·2
Gd^{3+}	1·4	1·5	1·8	1·7	1·4	1·3	1·2
$Tb^{3+} - Lu^{3+}$	1·5	1·3	1·6	1·6	1·1	1·0	1·0
Al^{3+}	0·06	0·12	0·21	0·23	0·25	0·18	0·15
Ga^{3+}	0·07	0·15	0·30	0·31	0·29	0·25	0·22
In^{3+}	0·22	0·25	0·46	0·50	0·48	0·36	0·30
Fe^{3+}	0·07	0·115	0·13	0·31	0·31	0·33	0·372
V^{5+}	0·21	1·12	1·25	1·3	1·26	1·28	1·3
Mo^{6+}	0·001	0·02	0·09	0·15	0·09	0·08	0·10

* Expressed relative to uranium. The distribution coefficients of uranium in these mixtures were found to be 35 (methanol), 65 (ethanol), 180 (n-propanol and isopropanol) and 300 (n-butanol, isobutanol and amyl alcohol).

The following discussion of the separation possibilities on resin columns will therefore be centred around these two most important problems.

From Tables I and II it is seen that uranium can easily be separated from thorium, lanthanum, cerium, praseodymium, neodymium, samarium and europium, but not from the other rare earth elements, by using either a 90 or 95% methanol medium as the sorption solution. Similar but somewhat less favourable conditions are met in the ethanol-nitric acid media. In 90 and 95% n-propanol, isopropanol, n-butanol, isobutanol and amyl alcohol media, however, the separation of uranium from all of the rare earth elements and thorium in a single operation (*i.e.*, by just passing the mixtures through the resin columns) is impossible because all of the elements (uranium, thorium yttrium, lanthanum-lutetium) are strongly retained by the resin due to their rather high distribution coefficients in these media (compare with Fig. 4). In order to effect a separation of uranium from thorium all that has to be done is to wash the resin bed containing the adsorbed elements with 90 or 95% methanol-nitric acid mixture, whereby uranium together with yttrium, gadolinium-lutetium will be removed from the resin. A special feature of this separation process is that a simultaneous separation of the "light" (remaining adsorbed) from the "heavy" (passing into the effluent) rare earth elements takes place. A separation scheme based on this technique of separating one or more adsorbed elements from each other merely by changing the solvent is shown in Table III.

Table III.—Separation of uranium, thorium, the rare earths, *etc.*, on Dowex 1*

Medium (composition of sorption solution)	Elements adsorbed	Elements separated (effluent)
90 or 95% n-propanol or isopropanol, *etc.* 10 or 5% 5*M* nitric acid	U, Th, La Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, and V†	Sc, Al, Ga, In, Fe‡, V and Mo
↓		
90 or 95% methanol 10 or 5% 5*M* nitric acid	Th, La, Ce, Pr, Nd, Sm and Eu	U, Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu
↓		
90 or 95% water 10 or 5% 5*M* nitric acid	None	Th, La, Ce, Pr, Nd, Sm and Eu

* Several ion-exchange operations carried out in this manner have shown that quantitative separations can actually be achieved by applying this separation scheme.

† Vanadium is only appreciably adsorbed from 95% of alcohol- 5% of 5*M* nitric acid mixtures.

‡ Only 90% of the iron passes into the effluent.

In this connection the chromatographic fractionation of the rare earths in methanol-nitric acid media as described by Faris and Warton[24] requires special attention because a combination of their method, if employed for the separation of uranium and thorium from the rare earths with the separation scheme outlined in Table III, would constitute a valuable tool in reactor chemistry.

Besides, it should be noted here that this separation scheme will also be applicable for the isolation of the adsorbed elements prior to their determination in minerals, rocks and other materials. At present pertinent experiments for their assay in marine sediments are being carried out.

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Zusammenfassung—In der vorliegenden Arbeit wird das Anionaustauschverhalten der seltenen Erden und anderer Elemente in salpetersäurehaltigen aliphatischen Alkoholen beschrieben. Basierend auf Bestimmungen der Verteilungskoeffizienten und Trennfaktoren der einzelnen Elemente werden Trennungsmethoden vorgeschlagen. Zur spektrophotometrischen Endbestimmung dieser Elemente wurde die Anwendung des Azofarbstoffes Solochrome Fast Red untersucht.

Résumé—On décrit le comportement d'échange anionique des terres rares et d'autres éléments dans les alcools saturés contenant de l'acide nitrique. On propose une technique de séparation basée sur la détermination des coefficients de distribution et des facteurs de séparation des divers éléments. En vue du dosage final de ces éléments, on a étudié l'emploi du colorant azöique Solochrome Fast Red comme réactif spectrophotométrique.

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DETERMINATION OF MUCOPOLYSACCHARIDE SULPHATE IN CONNECTIVE TISSUE

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Summary—A relatively rapid method for the determination of mucopolysaccharide sulphate is presented. The procedure depends on a desulphation technique combined with a turbidimetric determination of the sulphate.

THIS communication describes a method for the determination of sulphated mucopolysaccharides in tissue based on sulphate content. Briefly the procedure consists of defatting an homogenised tissue specimen followed by water washing to remove inorganic sulphate. The tissue is then placed in anhydrous methyl alcohol through which dry hydrogen chloride gas is passed for 15 min. This effectively liberates sulphate from the mucopolysaccharide and it may then be determined turbidimetrically. Two features of the procedure are noteworthy: (1) It is not necessary to resort to enzymatic digestion of tissue protein followed by dialysis which is the classical approach. (2) The desulphation is accomplished quantitatively in minutes rather than days.[1]

EXPERIMENTAL

Procedure

Defat no more than 1 g of tissue with 50 ml of acetone in a suitable homogeniser and remove the fat-acetone phase by centrifugation or filtration. Briefly dry the defatted tissue in a vacuum desiccator. Weigh 0·1 g of dried tissue into a 12-ml Spinco ultracentrifuge tube, add approximately 10 ml of water and thoroughly agitate the mixture. Allow the tubes to stand for 15 min, then centrifuge for 15 min at 30,000 rpm. Remove the supernate and place in a 40-ml centrifuge tube, the top of which has been ground to fit into a gas inlet and outlet tube. Again agitate the residue with 10 ml of water and immediately centrifuge. Add this supernate to the first; supernate and residue are subsequently handled separately.

Evaporate the supernate in a boiling water bath to approximately 5 ml. Add four times this volume of ethyl alcohol containing 7 mg of potassium acetate. Stir the mixture and allow the flocculent precipitate to settle in the refrigerator, centrifuge and wash with the ethyl alcohol-potassium acetate solution. Discard the supernate. Dry the residue in a vacuum desiccator. Add approximately 10 ml of anhydrous methanol to the tube and free the residue from the walls of the tube with a spatula. Bubble in anhydrous hydrogen chloride for 10 min. Add 25 ml of anhydrous ethyl ether. Stir the mixture, cover and allow the precipitate to settle in the refrigerator after which it is centrifuged and the supernate placed in a 25 × 150-mm test tube, or an electrolytic beaker. Wash the residue with ether and add the supernate to the above discarding the residue. Evaporate the combined solution to dryness in the presence of Hengar stones, then carry through a sulphate analysis by a method previously developed in this laboratory.[2] This sulphate represents the water soluble sulphated mucopolysaccharides.

Transfer the residue from the ultracentrifugation to a 50-ml beaker where it is solubilised with agitation using 5 ml of 2% sodium hydroxide solution. Neutralise the solubilised material with dilute hydrochloric acid, transfer quantitatively to a desulphating tube and evaporate to near dryness in a 100° water bath. Complete the drying in a vacuum desiccator.

Add approximately 10 ml of anhydrous methanol and bubble in anhydrous hydrogen chloride for 30 min at 5°. Centrifuge the mixture and wash the residue twice with methanol-potassium acetate. Add 25 ml of anhydrous ethyl ether to the methanol phase and stir the mixture. Allow the precipitate to settle in the refrigerator, then centrifuge. Wash the residue well with ether and discard. Evaporate the combined solutions to dryness in a 25 × 150-mm test tube in the presence of Hengar stones, then carry through the sulphate analysis. This sulphate represents the water non-extractable sulphated mucopolysaccharides.

RESULTS AND DISCUSSION

Inorganic sulphate is removed from the homogenised tissue simply by two washings with water. This process was shown to be complete (1) by radiochemical techniques, (2) by a third washing and, (3) by taking portions of the same tissue homogenates through dialysis procedures rather than washings. Table I shows the distribution of radiocounts above background obtained by adding $Na_2{}^{35}SO_4$ to defatted homogenised trachea. To ensure ^{35}S exchange the water suspension was agitated for 24 hr at room temperature, filtered and dried. The dried material was then treated as outlined in the procedure. Radiocounts were performed on the combined water washings as well as the residues. Ninety-eight per cent of the total count was found in the water fractions. A third washing of tissue shows no further removal of sulphur. Finally, data using dialysis procedures showed that identical results can be obtained by the two methods, provided soluble mucopolysaccharides are precipitated and removed from the wash water. The presence of water-soluble mucopolysaccharides in connective tissue has previously been demonstrated by Malawista and Schubert.[3] That water-soluble sulphated mucopolysaccharides are indeed precipitated from the water washings with alcohol-potassium acetate was demonstrated using paper chromatographic techniques[4] on the precipitate.

TABLE I. REMOVAL OF $Na_2{}^{35}SO_4$ ADDED TO TRACHEA

Sample	Supernate, *cpm*/0·11 *g*	Residue, *cpm*/0·11 *g*	Total, *cpm*/0·11 *g*
1	259	8	267
2	245	6	251
3	265	9	274
4	266	7	273
5	273	11	284
6	239	0	239
7	219	4	223
8	219	0	219
		Av. 6	Av. 254
		Std. dev. 2	Std. dev. 27

Optimum conditions for the desulphation step were studied using commercially available purified chondroitin sulphate. In this case solubilisation in 2% sodium hydroxide solution is not necessary; however, it speeds the procedure so that complete desulphation can be obtained at 5° within 10 min (Table II).* In tissues in which the mucopolysaccharides are associated with protein, considerable solubilisation is desirable to obtain a fine state of subdivision so that the sulphate moiety will be susceptible to hydrolysis.

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* Keratosulphate is only 87% desulphated by this procedure. A sample obtained from Dr. Sara Schiller of LaRabida, University of Chicago consistently showed 13% sulphate left in the residue after desulphation. Animals injected with $^{35}SO_4{}^{2-}$ showed an equally consistent 13% of the sulphate radiocount left in the residue of the corneal keratosulphate after desulphation. This may imply a more complicated structure for keratosulphate than that currently postulated.

TABLE II. DESULPHATION OF CHONDROITIN SULPHATE AFTER BASE SOLUBILISATION AT 5°

Sample No.	Time for HCl-MeOH treatment, *min*	Total S, *μg*	S in supernate, *μg*	S in residue, *μg*	Recovery, %
1	30	204	189	0	93
2	30	204	205	0	100
3	30	204	212	0	104
4	30	204	199	0	98
5	30	264	254	0	96
6	30	264	254	0	96
7	30	264	248	0	94
8	30	264	246	0	93
9	30	264	242	0	94
10	30	264	258	0	100
11	20	264	274	0	104
12	20	264	268	0	102
13	10	264	288	0	109
14	10	264	270	0	102
					Av. 99
					Std. dev. 5

From Table II it will be seen that desulphation is virtually complete because in no instance was any sulphate recovered from the residue. The average in some 14 trials was 99% recovery with a standard deviation of 5%. The action of hydrogen chloride on the sulphated mucopolysaccharides appears to consist of the removal of the sulphate ester. Light scattering studies on chondroitin sulphate before and after desulphation showed little change in molecular weight so that there appears to be little or no depolymerisation of the polysaccharide chain under the conditions of the procedure.

Fraenkel-Conrat and Olcott[5] showed that the carboxyl groups of various proteins treated with acid-methanol mixture were esterified with consequent solubilisation of the proteins. The latter could be recovered by addition of several volumes of ether. A series of studies was carried out to ensure the removal of all sulphur-containing amino acids from the methanol supernate after desulphation. Pure albumin was utilised in these studies. Table III shows that after treatment of the albumin in methanol with hydrogen chloride gas all of the sulphur from the protein is found in the supernate. Precipitation with several volumes of ether eliminates all of this sulphur. Ether additions were continued until no more precipitate formed. This did not exceed three times the methanol volume in any of the experiments performed in this laboratory and generally twice the methanol volume is enough. That this ether precipitation does not affect the sulphate moiety split off from the polysaccharides

TABLE III. PROTEIN SULPHUR DISTRIBUTION AFTER METHANOL-HYDROGEN CHLORIDE TREATMENT WITH AND WITHOUT ADDITION OF ETHER

Albumin samples	Treatment	S in supernate, *μg*	S in residue, *μg*
1	No ether	135	0
2	No ether	139	0
3	Ether precipitated	0	130
4	Ether precipitated	0	140
5	Ether precipitated	0	132

by the methanol-hydrogen chloride treatment was shown by treating chondroitin sulphate and subsequently adding ether. The sulphate was recovered quantitatively from the supernate.

Reports from the laboratories of Bostrom[6] and Dziewiatkowski[7] have shown that ^{35}S administered to animals as inorganic sulphate appears in the tissue only as inorganic sulphate or is incorporated into the sulphated mucopolysaccharides. Some idea of the reproducibility of the analysis can be gained from Table IV which represents radiochemical data. These were obtained by analysing tracheas from rabbits which had been given $Na_2{}^{35}SO_4$ by injection. All counts were corrected for background.

TABLE IV. ^{35}S STUDY OF RADIOACTIVE TRACHEA

Sample	Water-soluble fraction		Water-insoluble fraction			Supernate totals, *cpm*/0·2 *g*
	Supernate*, *cpm*/0·2 *g*	Residue*, *cpm*/0·2 *g*	Residue†, *cpm*/0·2 *g*	Residue*, *cpm*/0·2 *g*	Supernate*, *cpm*/0·2 *g*	
1	296	6	0	0	190	486
2	259	0	0	0	163	422
3	257	0	5	0	208	465
4	296	8	0	0	185	481
5	305	0	3	0	146	451
6	276	0	9	0	198	474
	av. 282				av. 182	av. 463
	Std. dev. 21				Std. dev. 25	Std. dev. 24

* HCl-MeOH-Et_2O
† HCl-MeOH

The tracheas were cleaned, defatted in acetone, dried and lyophilised. Six homogeneous samples of approximately 0·2 g were weighed into Spinco ultracentrifuge tubes and carried through the desulphation procedure. Each supernate with the exception of that containing inorganic sulphate, as well as each residue obtained during the procedure, was analysed for sulphate. Supernates were evaporated to dryness and residues dried. The resulting solids were digested to incipient crystallisation at 120° with 3 ml of chloric acid. Any remaining acid was neutralised with 1 ml of saturated ammonium carbonate solution. The samples were transferred quantitatively to 150-ml beakers. After addition of 1 ml of 0·05*M* ammonium sulphate solution as a carrier, the sulphate was precipitated with 0·1*M* barium chloride solution. Radiocounts were made on the precipitates with a mica end window Geiger tube and scaler. Table IV demonstrates that ^{35}S is found in the hydrogen chloride methanol-ether supernates of the water soluble and water-insoluble fractions of trachea.

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Zusammenfassung—Es wird eine relativ schnelle Methode zur quantitativen Bestimmung von Mucopolysaccharidsulfat gezeigt. Man spaltet den Sulfatrest ab und bestimmt das Sulfat nephelometrisch.

Résumé—Une description d'une méthode relativement rapide de dosage des sulfates de mucopolysaccharides est presentée. Le procédé utilise la déconversion de l'ester sulfurique combinée à un dosage opacimétrique du sulfate.

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STUDIES OF TITRIMETRIC AND SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF GOLD

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Summary—The titrimetric determination of gold by the iodometric technique is examined under various conditions. Irrespective of these conditions the stoichiometry of the reaction is found to be 1 atomic weight of gold to 2 formula weights of sodium thiosulphate. A modified bromoaurate spectrophotometric method is described, and the procedure is recommended for the determination of gold in amounts of 15 μg or more. The spectrophotometric determination of gold with methyl violet and trichloroethylene is examined critically. The method is recommended for concentrations of gold over the range 0·5–2·0 ppm. The stability of dilute gold solutions in acid media is also discussed.

A wide variety of methods has been proposed for the determination of milligram to gram amounts of gold. For microgram samples, there exist relatively few spectrophotometric or titrimetric procedures. Despite the industrial importance of gold, and the resulting need for methods, the recorded spectrophotometric methods are acceptable only under restricted conditions. In the case of certain of the more generally applicable methods, contradictory claims have been made concerning the character of the reaction and, inexplicably, in some instances, acceptable results have been obtained by almost identical procedures based on different stoichiometric reactions. The present report deals with an experimental comparison of various proposed methods, and includes modified procedures for the titrimetric and spectrophotometric determination of gold.

APPARATUS AND REAGENTS

Beckman Model A-2 glass electrode pH meter.

Beckman Model B spectrophotometer: Used with Beckman Corex cells of 5-cm path length and silica cells of 1-cm path length.

Hydrobromic acid: Purified by accepting only the colourless, constant-boiling fraction from a distillation.

Isopropyl ether, trichloroethylene and ethyl acetate: Reagent-grade materials.

Sodium thiosulphate solution: A stock solution was prepared by dissolving 25 g of reagent in a litre of freshly boiled and cooled, distilled water, containing 1 ml of chloroform and 0·1 g of sodium carbonate. After standing for 1 week, the solution was standardised by titration with potassium iodate solution. From this solution 0·01N and 0·001N sodium thiosulphate solutions were prepared by dilution when required.

Standard gold solution: A standard solution of gold was prepared by dissolving a weighed quantity of gold in *aqua regia*, and removing the nitric acid by several evaporations just to dryness in the presence of 50 mg of NaCl and a few drops of HCl. The gold content was determined gravimetrically by hydroquinone.[1] Less concentrated gold solutions were prepared by appropriate dilutions with 0·12N HCl.

Unless specified, all other chemicals were reagent-grade.

TITRIMETRIC DETERMINATION OF GOLD

Although the iodometric determination of gold by titration with sodium thiosulphate is one of the few classical procedures, some controversy remains concerning the stoichiometry of the method, as well as the most favourable techniques.

The original procedure recorded by Peterson[2] in 1899 claimed the ratio between gold and sodium thiosulphate as 1:3 in accordance with the following reactions:

$$AuCl_3 + 3KI \rightarrow AuI + I_2 + 3KCl \tag{1}$$

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6 \tag{2}$$

$$AuI + Na_2S_2O_3 \rightarrow NaAuS_2O_3 + NaI \tag{3}$$

Later investigation by Gooch and Morley[3] gave no indication of reaction (3), and the gold to sodium thiosulphate ratio was taken as being 1:2; this was supported by acceptably precise experimental results. Scott and Furman[4] accepted this stoichiometry in a standard procedure for the determination of gold.

More recently, Brüll and Griffi[5] reported results supporting the following reactions:

$$AuCl_3 + 3KI \rightarrow 3KCl + AuI + I_2 \tag{4}$$

$$AuI + I_2 \rightarrow (AuI_3) \tag{5}$$

$$AuI_3 + AuI \rightarrow Au(AuI_4) \tag{6}$$

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6 \tag{7}$$

The overall reaction provides a ratio of 1:1 for sodium thiosulphate to gold.

Despite the fact that totally different stoichiometric reactions were accepted, the results obtained in each of these cases appeared to be accurate and precise. Because the proposed methods were based on identical iodine-thiosulphate reactions, it was obvious that the method required re-examination.

EXPERIMENTAL

Aliquots of standard 0·01*N* and 0·001*N* gold chloride solutions in 0·1*N* HCl were transferred to small Erlenmeyer flasks. An excess of a 1% aqueous solution of KI was added so that the precipitated gold$^{\mathrm{I}}$ iodide was redissolved. The liberated iodine was immediately titrated with 0·01*N* or 0·001*N* sodium thiosulphate solution added from a pipette and a micro-burette. The use of a pipette for the rapid delivery of the larger part of the titrant minimised vaporisation losses of iodine. The solution was titrated to a pale yellow before the addition of 1 ml of a 1% starch solution, and was then titrated until completely colourless as compared with an over-titrated sample, both viewed against a white background. Titrations made without starch and with varying amounts of starch showed that no significant indicator error was introduced for 0·01*N* or 0·001*N* solutions.

The results obtained by this method were calculated using a stoichiometric ratio of gold to sodium thiosulphate of 1:2 as indicated in equations (1) and (2). The amount of gold taken, the concentration of the gold solution, the pH, and the amount of KI used were each varied for different determinations. The precision and accuracy of the results are given in Table I, in which each result is the average of several determinations.

The results show that gold quantities of the order of 0·2–25 mg as the chloride may be determined iodometrically at a pH less than 5·0 by titration with sodium thiosulphate. The amount of KI added does not affect the titration, provided that sufficient to dissolve the precipitated gold$^{\mathrm{I}}$ iodide is used. The volume of 1% KI solution added and the dilution of the gold solution do not affect the determination except to make the end-point somewhat indistinct if either change in condition is

TABLE I. IODOMETRIC DETERMINATION OF GOLD

Conditions	Gold taken *mg*	Average gold found, *mg*	Range of % difference	Average % mean deviation
Various quantities of gold	0·873 −24·45	0·876 −24·49	±0·2%	<0·2%
pH 0 to 5·8	5·006	5·007	±0·3%	0·2%
Dilution with 0 to 40 ml of H_2O	5·006	5·010	±0·3%	0·2%
Different volumes of 1% KI used, 2–25 ml.	0·873	0·875	±1%	0·6%
Small quantities^A of gold	0·196	0·192	−4%–1%	1%
Gold and copper^C	4·931	4·890^B	0·8%	0·4%
	0·873	0·874	±4%	4%

A—The titration was made with 0·001*N* sodium thiosulphate.

B—The gold content was calculated by assuming the complete reaction of copper according to reaction (8), and by subtracting the appropriate amount of sodium thiosulphate from the volume used for the overall reaction.

C—The amount of copper titrated was approximately 1·2 times the weight of gold taken.

excessive. There was no evidence to support the ratios 1:1 or 1:3 of gold to sodium thiosulphate.

Contrary to the report of Brüll and Griffi,[6] copper interfered, reacting simultaneously as follows:

$$2CuCl_2 + 4KI \rightarrow 4KCl + 2CuI + I_2 \qquad (8)$$

It was concluded that the iodometric determination of gold can provide accurate and precise results. The method is simple and insensitive to variations in the reacting conditions.

SPECTROPHOTOMETRIC DETERMINATION OF GOLD

Bromoaurate determination of gold

A bromoaurate method for the determination of gold was reported by McBryde and Yoe[7] as a simple technique which was not affected by salt content or by trace quantities of many ions.

The colour is developed by making the gold chloride solution 5% in HBr and extracting the bromoaurate with two 15-ml aliquots of isopropyl ether. The organic phase is washed with 5 ml of 4*M* HBr and then extracted with one 20-ml and two10-ml portions of water. The proposed operations are supposed to separate gold from more than 99·5% of all platinum metals except osmium. The combined aqueous phase is heated briefly with 1 ml of HBr to remove ether and to restore maximum colour. The absorbance is measured at 380 mμ, where Beer's law is obeyed over the range of 0–40 ppm.

This method, applied as directed, failed to provide consistent results. It was found that the double extraction with isopropyl ether reduced the intensity of the coloured constituent, and the required extraction into water further reduced the colour intensity. Furthermore, heating the final aqueous phase with HBr did not restore the original intensity. It seemed probable that the errors were the result of an impure sample of isopropyl ether.

The reagent-grade isopropyl ether was purified by several techniques, including refluxing with sodium and washing with a potassium permanganate solution. None of the purified reagents provided satisfactory results. All attempts to duplicate the absorption curve obtained by McBryde and Yoe failed.

An analysis of the aqueous and organic phases after the isopropyl ether extraction showed that 50% of the gold remained in the acidic solution, and that the gold complex was completely extracted from the organic phase by the subsequent water extraction.

Ethyl acetate has also been recommended as an extractant for gold.[7] By this method, the absorbance is measured directly from the acetate phase after a preliminary wash with 5 ml of 4*M* HBr.

A gold chloride standard solution was extracted with two 15-ml aliquots of ethyl acetate. It was found that only 50% of the required intensity was developed in the final solution, as compared with a similar sample measured directly without extraction.

Preliminary experiments, to determine the distribution of gold in the various phases of the ethyl acetate extraction, were made by evaporating each phase to dryness, dissolving the gold, filtering, and determining gold directly. All filtrations failed to indicate the presence of metallic gold. The results showed that only traces of gold remained in the original phase and in the acid wash. It seemed probable, then, that the gold in the ethyl acetate phase was only partially present as the coloured bromoaurate.

Obviously, because only about 50% of the gold was indicated by a direct spectrophotometric measurement, and because the acetate phase contained the gold quantitatively, some treatment of the acetate phase would be required to restore the maximum colour intensity of the bromoaurate. This procedural complication could be justified because the method, in general, is simpler than the alternative isopropyl ether extraction, which in any case has proved unsatisfactory.

Procedure: Concentrated hydrobromic acid was added to the gold chloride sample to make it 5% in HBr. The bromoaurate was extracted twice with 15 ml of ethyl acetate, and the organic phase was washed with 5 ml of 4*M* HBr. The organic extract was evaporated to dryness, and the residue was dissolved in *aqua regia*. After the removal of any nitric acid by careful evaporation three times in the presence of 50 mg of NaCl and a few drops of HCl, one ml of HCl was added, and the solution was transferred to a 50-ml flask containing 5 ml of HBr. The absorbance was measured at 380 mμ in either 1- or 5-cm cells, as determined by the concentration.

A series of results was obtained for various standard gold solutions, using both the direct measurement and the ethyl acetate extraction as proposed. These are recorded in Table II, each being the average of three samples, each of which is measured twice. The results show that when extractions are required the above procedure will provide satisfactory results. In the absence of platinum metals, the extraction procedure is not required, in which case, the gold is determined directly by the addition of HBr followed by spectrophotometric measurement.

The direct bromoaurate procedure, as described above, is the simplest colorimetric method available for the determination of gold. When good accuracy and extraction are required, it is not recommended for amounts of gold less than 25 μg. The direct method can be used for quantities of 15 μg or more. It is insensitive to variations in technique, to salt, hydrochloric acid and hydrobromic acid concentrations, and to many trace ions. In the authors' opinion, the bromoaurate method is the most efficient recorded procedure for the determination of gold when extractions are not required.

Methyl violet determination of gold

Ducret and Maurel[8] have reported the use of methyl violet for the determination of microgram quantities of gold. The gold solution was adjusted to pH 1 in a suitably chosen volume, to this were added 3 ml of an aqueous methyl violet solution (0·4 g per litre) and 3 ml of 0·2*N* hydrochloric acid and the violet coloured complex was extracted into 15 ml of purified trichloroethylene by shaking for 3 min in a separatory funnel. The absorbance was measured at 600 mμ.

TABLE II. BROMOAURATE DETERMINATION OF GOLD

Concentrations of gold, *ppm*	Absorbance	
	Without extraction	With ethyl acetate extraction
0·50	0·060^{A}	—
0·75	0·090^{A}	—
1·10	0·134^{A}	—
$1{\cdot}04_3$	0·030	—
2·09	0·053	0·052
5·35	0·131	0·116
10·48	0·259	0·257
26·15	0·625	0·620

A—Absorbance measured in 5-cm cells.

Because the proposed procedure is one of the most sensitive methods available for gold, the problem of the stability of the gold solution becomes of significance. Some studies of the stability of gold solutions have been published. Sonstadt[9] reported that gold solutions were unstable in bright sunlight. A 0·04% gold solution showed preceptible reduction in 2 days and a 0·007% solution after a few hours. Svedberg[10] recorded that alkaline gold solutions produced smaller and more numerous particles when exposed to ultraviolet light. Leutwein[11] reported that 0·001% gold solutions in either an acid or basic medium showed only 0·1–0·3% of their original concentration after 230 days storage in Jena glass. Base-exchange reactions and adsorption by the glass were suggested as the reasons for the loss of concentration.

It was thus necessary to study the stability of dilute gold solutions under the storage conditions to be used for the application of the methyl violet method.

Standard gold solutions containing 0–25 ppm in 0·12*N* hydrochloric acid were stored in carefully cleaned, glass-stoppered bottles, and kept out of contact with light. At various intervals, samples were withdrawn, and the gold content was determined by the bromoaurate method already described.

The results of this study showed that the gold solutions used were quite stable for long periods of time, under the particular conditions of storage used. The concentration of gold remained from 90% to 99% of the original value after 300 days storage for the range of concentrations from 2·5–25 ppm.

All efforts to apply the methyl violet procedure as described by Ducret and Maurel[8] failed to produce acceptable precision or accuracy. The incorporation of precise techniques such as exact time intervals and special equipment, such as filtration through glass wool before introducing the solution into the absorption cell, were without noticeable effect.

It was found that the intensity of the colour of the organic phase was continuously reduced when it is retained in a Pyrex-glass container. When the trichloroethylene extract was transferred to a Teflon beaker and covered, the colour was stable. Because glass had an adverse effect on the colour, unbleached cotton wool was used to remove any water particles. Reasonably consistent results were then obtained.

The coloured complex adhered tenaciously to the glass wall of the various equipment used. Nitric acid or acetone were the most effective cleaning agents. Acetone was preferred because it could be removed completely by trichloroethylene, and the glassware could then be dried quickly as required. Because the silica absorption cells also retain some colour, it was necessary to clean the cells even between readings of the same extract. This cleaning procedure in conjunction with the above changes in technique gave consistent results.

It was found that reagent-grade trichloroethylene produced consistent results without resorting to the time consuming fractionation required in the method reported by Ducret and Maurel.[8]

Procedure: A series of standard solutions was prepared containing 0–10·0 μg of gold in 5 ml of 0·12*N* HCl solution. All equipment was cleaned with *aqua regia* to remove any contamination. Each gold determination was made individually. Five ml of the standard gold solution were added to a separatory funnel made with a Teflon stopcock to prevent any reaction with stopcock lubricants. Three ml of a methyl violet solution (0·4 g per litre) were added by pipette and then 3 ml of 0·24*N* HCl. After each addition, the funnel was swirled to mix the solutions, then 15·0 ml of trichloroethylene were added, and the separatory funnel was shaken vigorously for 3 min. The organic phase was drawn off through unbleached cotton wool into a Teflon beaker, and the absorbance was measured at 600 mμ in a 1-cm silica cuvette against pure trichloroethylene. Between determinations, the separatory funnel, Teflon beakers and cuvettes were washed with acetone and then rinsed thoroughly with trichloroethylene. The cuvettes were cleaned between readings by the same procedure.

TABLE III. METHYL VIOLET DETERMINATION OF GOLD

Concentration of gold		Average absorbance	Mean Deviation, %
ppm	*µg/5 ml*		
0	0	0·040	5
0·50	2·50	0·105	0·5
0·75	3·75	0·140	1·5
1·00	5·00	0·179	0·5
1·00	5·00	0·177	0·5
1·25	6·25	0·211	0·5
1·50	7·50	0·246	1·5
1·75	8·75	0·271	0·3
2·00	10·00	0·300	—

The results of a series of standard gold samples determined by this technique are recorded in Table III, in which each absorbance reported is the average of three separate samples, each of which is measured at least twice. The rather large blank of 0·040 absorbance, obtained with the methyl violet procedure, is at least partially the result of some extraction of the colour reagent. The need for a careful addition of reagent is therefore emphasised.

The results in Table III show that the coloured constituent obeys Beer's law over the range 0–1·50 ppm, *i.e.*, 0–7·5 μg contained in 5 ml of solution. The molar extinction coefficient is $2{\cdot}79 \times 10^4$ litre. mole^{-1}.cm^{-1}.

The problem of the destruction of the coloured complex adhering to Pyrex glass is an unusual one. Because Pyrex glass introduces an error from adsorption of the coloured constituent, silica absorption cells were used for the spectrophotometric determinations. Throughout the extraction procedure, the organic phase was interspersed throughout an acidic medium, and no evidence of adsorption on the walls of the separatory funnel was obtained.

The methyl violet method reported by Ducret and Maurel did not produce acceptable results. The changes in technique described in this paper modify the method to provide an unusually sensitive colorimetric method, which allows the determination of a few μg of gold with accuracy and precision.

CONCLUSIONS

The iodometric method for the determination of gold involves the reactions of 1 atomic weight of gold to 2 formula weights of sodium thiosulphate over a variety of conditions. The concentration and the absolute amount of gold do not affect the reaction. The volume of potassium iodide must always be in sufficient excess to dissolve the precipitated gold^{I} iodide, and the pH must be less than 5·0. This method can determine quantities of 0·2 mg or more.

A bromoaurate spectrophotometric method is described which is applicable to quantities of gold greater than 15 μg. The direct measurement of the bromoaurate is recommended for general use, although an ethyl acetate extraction and subsequent treatment to remove the acetate can extend the use of the procedure to samples which contain platinum metals or other trace constituents.

The methyl violet determination of gold as described by Ducret and Maurel[8] was found inapplicable. For gold samples of concentrations from 0 to 2.0 ppm, the modified methyl violet spectrophotometric method provides accurate and precise results. This method is useful because of its high sensitivity, though reasonable care must be taken to adhere to a definite technique.

Dilute gold solutions in acid media were found to maintain at least 90% of their gold strength over a period of 300 days when stored in glass out of contact with light.

Zusammenfassung—Die jodometrische Goldbestimmung wird unter verschiedenen Bedingungen geprüft. Unabhängig von den Bedingungen verbraucht ein Grammatom Gold zwei Formelgewichte Thiosulfat. Eine modifizierte spektral photometrische Methode über das Bromoaurat wird beschrieben und für die Goldbestimmung in Mengen über 15 μg empfohlen. Die spektralphotometrische Goldbestimmung mit Methylviolett und Trichloräthylen wird kritisch untersucht und für Goldkonzentrationen von 0,5 bis 2,0 ppm empfohlen. Ferner wird die Stabilität verdünnter Goldlösungen in sauren Medien diskutiert.

Résumé—On a etudié le du dosage volumétrique de l'or par iodométrie dans des conditions variées. Sans tenir compte de ces conditions, la stoéchiométrie de la réaction montre un poids atomique d'or pour deux poids atomiques relatifs à la formule du thiosulfate de sodium. On a décrit une modification de la méthode de dosage spectrophotométrique au bromoaurate; cette méthode est recommandée pour le dosage de quantités d'or de l'ordre de 15 μg ou plus. Un examen critique du dosage spectrophotométrique de l'or au moyen du violet de méthyle et du trichloréthylene est présenté. Cette méthode est recommandée pour des concentrations d'or variant de 0,5 à 2,0 p.p.m. On discute la stabilité en milieu acide des solutions d'or diluées.

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INVESTIGATION OF SOME HYDRAZINE DERIVATIVES AS REDUCTIMETRIC TITRANTS

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Summary—The possible application of benzoylhydrazine, phenylhydrazine, *p*-nitrophenylhydrazine, 2,4-dinitrophenylhydrazine, isonicotinic acid hydrazide and semicarbazide as reductimetric titrants has been studied. The stability of these substances in various media has been determined and causes of the stability and changes of titre of the solutions are discussed. Among the compounds investigated, isonicotinic acid hydrazide has been found to be the most suitable titrant, its solutions being stable and permitting the rapid and quantitative reduction of a number of inorganic systems.

ALTHOUGH hydrazine derivatives are characterised by relatively strong reductive effects, they have not as yet been applied for the quantitative reduction of various inorganic systems as has hydrazine itself.[4–6]

Reaction of hydrazine derivatives with oxidants mainly results in oxidation of the —NH·NH$_2$ group to nitrogen. For the sake of simplicity, the reaction may be illustrated by the oxidation of hydrazine itself. In an acid medium the following relation is valid:

$$N_2H_4 \rightarrow N_2 + 4H^+ + 4e \qquad (1)$$

and similarly for alkaline media:

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e \qquad (2)$$

Besides these fundamental reactions, side reactions may also take place under certain conditions. By analogy with hydrazine,[1] where side reactions generally lead to the formation of hydrazoic acid or ammonia, it may be assumed that these substances can also be formed in the case of hydrazine derivatives. For instance, in the oxidation of phenylhydrazine the following reaction may also take place:[2,3]

$$2C_6H_5{\cdot}NH{\cdot}NH_2 \rightarrow C_6H_5{\cdot}NH_2 + NH_3 + C_6H_5{\cdot}N{=}NH \qquad (3)$$

The non-stable phenyldi-imide is further decomposed to benzene and nitrogen:

$$C_6H_5{\cdot}N{=}NH \rightarrow C_6H_6 + N_2 \qquad (3')$$

The participation of side reactions depends on the character of the oxidising agent, pH of the solution and possibly also on the presence of any substance having a catalytic effect. It is therefore necessary to titrate under conditions when the side reactions do not take place or do not exceed the limits of experimental error.

The following substances were selected for study from among the derivatives of hydrazine, with respect to their solubility, reductive effects as determined beforehand and easy availability: phenylhydrazine chloride, *p*-nitrophenylhydrazine, 2,4-dinitrophenylhydrazine, benzoylhydrazine, isonicotinic acid hydrazide and semicarbazide chloride. Most of these substances are currently used for the detection and characterisation of the carbonyl group in aldehydes, ketones or in acetals. The aim of the present work was to find out whether these substances can be used as reductimetric titrants and further, whether they give the same effect or are possibly even more suitable than hydrazine itself.[4–6]

EXPERIMENTAL

Reagents

Solutions of isonicotinic acid hydrazide, benzoylhydrazine and semicarbazide chloride were obtained by dissolving the substances in water, phenylhydrazine chloride was dissolved in water and ethanol, and *p*-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine were dissolved in 2*N* hydrochloric acid. All of the substances and auxiliary reagents were of the highest purity.

Reagents

Potentiometric titration and other measurements were performed by means of the instruments Multoskop II and Multoskop V (Laboratorní přístroje, n.p., Prague, Czechoslovakia). Indicator electrodes were of platinum and silver, and the reference electrode was a saturated calomel electrode. pH measurements were performed with glass or antimony measuring electrodes.

RESULTS AND DISCUSSION

Stability of solutions

One of the main criteria for evaluating the usability of titrants is their stability. In the case of the hydrazine derivatives named, 0·1–0·001*N* solutions were prepared and their factors were immediately determined by potentiometric titration with potassium bromate, in the presence of potassium bromide, in a medium of hydrochloric acid.[7] The titre of the solutions was checked in the same way after periods of 10, 20, 40 and 60 min on the first day, and three times daily on successive days. Solutions were kept in stock bottles, exposed to light, at room temperature.

The results showed that the most stable among the substances investigated was isonicotinic acid hydrazide, whose titre remained unchanged after 25 days, whereas the titre of the other solutions had changed. The change was most marked in the case of phenylhydrazine chloride, its value having decreased in 5·5 days by 20%. More dilute solutions behaved similarly.

Because the titre of the isonicotinic acid hydrazide solution did not change even after 30 days, its stability was studied for a further period of several months. The titre was also checked iodometrically, bromometrically,[8] by titration of known amounts of potassium permanganate (see the determination of permanganate by isonicotinic acid hydrazide) and by means of titration with potassium hexacyanoferrate(III) in an alkaline medium.[9] It was found to remain unchanged even after 6 months.

The stability of isonicotinic acid hydrazide was further studied in acid and alkaline solutions. From the results in acid solutions, at concentrations of 0·5–1% of sulphuric acid, the titre of the solution remains unchanged for 1·5–2 months. A higher acidity has no great influence on the stability of the solution. On the other hand, alkaline solutions are decomposed soon after being prepared. It is an interesting fact that solutions of lower alkalinity are decomposed more readily than solutions of higher alkalinity. For instance, the titre of a 0·1*N* solution of isonicotinic acid hydrazide in 1% sodium hydroxide solution decreases after 4 days by 16·5% and after 15 days by 72·5%. The titre of the same solution in 0·5% sodium tetraborate solution decreases after 4 days by 15% and after 14 days by 51%, whereas when a 10% sodium hydroxide solution is used the titre decreases after 15 days only by 3·5%.

It must be added to the results mentioned above that at higher temperatures and especially at the boiling point alkaline solutions of isonicotinic acid hydrazide decompose far more rapidly. The decomposition depends on the duration of boiling, presence of aerial oxygen and oxygen dissolved in the solution and possibly also on the presence of catalysts. When solutions are kept in the absence of air, for instance in an atmosphere of nitrogen, the unwanted oxidation may be largely reduced. It has also been observed that in the presence of even small amounts of manganese^{IV}, copper^{II}, copper^{I} and iron^{III} oxides, platinum black, cerium^{IV} ions, *etc.*, rapid decomposition of isonicotinic acid hydrazide takes place.

The high stability of aqueous solutions of this substance is also caused, as has been determined experimentally,[10] by the presence of a nitrogen atom in the heterocycle, which causes compensation of the strongly reactive —CO·NH·NH$_2$ group. The lack of stability of this substance in alkaline or acid media is due to a change of this structure.

Redox potentials

To amplify the data on stability and to obtain a picture of the reduction effects of the hydrazine derivatives studied, their formal redox potentials in various media were measured on the basis of titration curves.

It is evident from the results obtained, that in acid media these substances are weaker reductants than in neutral or alkaline medium. For example, the following values of formal potentials were obtained for isonicotinic acid hydrazide (potentials apply to the hydrogen electrode): in 1*N* hydrochloric acid $E_f = 0·79$ V, in 0·1*N* hydrochloric acid $E_f = 0·78$ V, in 0·025*M* sodium tetraborate $E_f = 0·25$ V, and in 3*N* sodium hydroxide $E_f = -0·22$ V. Values found for other hydrazine derivatives are quite similar; for example, the potential of benzoylhydrazine was found to be $E_f = 0·70$ V in hydrochloric acid, and a value of $E_f = 0·67$ V has been found for semicarbazide chloride in 2*N* hydrochloric acid. Although the systems are irreversible and the E_f values measured do not conform to the Nernst equation, the above data still give a general idea of the character and chemical behaviour of the substances mentioned.*

Review of Determinations with Isonicotinic Acid Hydrazide

Because isonicotinic acid hydrazide proved to be the best of the reagents studied, on account of its stability, good solubility in water and reductive effects, only determinations performed with this titrant will be further described. Potentiometric indication was used in nearly all of the titrations.

Standardisation

The pure substance† may be used as a primary standard, otherwise the titre is determined bromatometrically[5,11,12] in a hydrochloric acid medium in the presence of

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* We have found the formal potentials for $N_2H_4·H_2SO_4$ solutions to be +0·65 V (in 1*N* HCl), −0·55 V (in 1*N* NaOH) and +0·35 V (in $NaHCO_3$ solution).

† Commerical samples must be recrystallised twice from ethanol, and dried to constant weight at 105° (m.p. 170–172°).

potassium bromide. Direct titration by potassium bromate in 8–12% hydrochloric acid, with potentiometric indication, is even more advantageous.

Halogens and their compounds

Chlorine, bromine and iodine are reduced by isonicotinic acid hydrazide to the corresponding halides according to the reaction:

$$2X_2 + C_5H_4N{\cdot}CO{\cdot}NH{\cdot}NH_2 + H_2O \rightarrow 4X^- + C_5H_4N{\cdot}COOH + N_2 + 4H^+ \quad (4)$$

where X = Cl, Br or I.

The determination of chlorine and bromine proceeds quantitatively at pH 1–5. Stabilisation of the potential is immediate and the point of equivalence is marked by a large potential change. Good results are obtained in the determination of active chlorine in chlorine water, calcium hypochlorite and chloramine-T, and in the determination of bromine in bromates and *N*-bromosuccinimide. The reaction is quantitative in media of 1–15% hydrochloric acid, 1–10% sulphuric acid, 1–84% phosphoric acid and 1–100% acetic acid. According to the medium selected, reduction of *N*-bromosuccinimide may proceed either to bromine or to bromide. In a medium of 50–60% phosphoric acid two potential changes are observed in the potentiometric titration, the first corresponding to the reduction $2Br^+ \rightarrow Br_2$, and the second to the reduction $Br_2 \rightarrow 2Br^-$.

Iodine is reduced quantitatively by isonicotinic acid hydrazide at pH 6·5–9. This medium may be obtained by the addition of sodium bicarbonate, borax or a phosphate buffer solution. The titration may be followed potentiometrically or visually by means of decolorisation of the originally yellow solution.

Bromate, iodate and periodate

The reduction of potassium bromate by isonicotinic acid hydrazide proceeds rapidly and quantitatively[10] in a medium of 5–30% hydrochloric acid, according to the equation:

$$2BrO_3^- + 3C_5H_4N{\cdot}CO{\cdot}NH{\cdot}NH_2 \rightarrow 2Br^- + 3C_5H_4N{\cdot}COOH + 3N_2 + 3H_2O \quad (5)$$

Potassium bromide need not be added to the solution titrated, because the bromine temporarily liberated is almost immediately reduced to bromide. A slower course of the reaction has been observed only in 20–30% hydrochloric acid; loss by the volatility of bromine was not more than 0·6%. The determination cannot be performed in media of other acids.

Iodate and periodate are reduced by isonicotinic acid hydrazide only very slowly.[10] We have not succeeded in hastening the reaction either by variation of the medium or by catalytic means, so that it is not suited to direct titration.

Bichromate, permanganate, vanadate and hexacyanoferrate(III)

Isonicotinic acid hydrazide reduces bichromate to chromium^{III} according to the equation:

$$2Cr_2O_7^{2-} + 3C_5H_4N{\cdot}CO{\cdot}NH{\cdot}NH_2 + 16H^+ \rightarrow$$
$$4Cr^{3+} + 3C_5H_4N{\cdot}COOH + 3N_2 + 11H_2O \quad (6)$$

The determination is quantitative at room temperature in media of 10–37% hydrochoric acid, under the catalytic action of copper^{II} sulphate (about 70 mg of $CuSO_4{\cdot}5H_2O$ for 1 to 50 mg of $Cr_2O_7^{2-}$). The end of the titration is indicated potentiometrically.*

The following reaction takes place between permanganate and isonicotinic acid hydrazide:

$$4MnO_4^- + 5C_5H_4N{\cdot}CO{\cdot}NH{\cdot}NH_2 + 12H^+ \rightarrow 4Mn^{2+} + 5N_2 + 5C_5H_4N{\cdot}COOH + 11H_2O \quad (7)$$

The quantitative course of the reduction is largely dependent on the medium. Precise results have been obtained in solutions containing 1–5% of sulphuric acid. It is, however, necessary to wait at least 5 min for the potential to become stable at the equivalence point; therefore it is better to heat the titration solution to a temperature of 70–80°. The potential then stabilises immediately and the reduction is very rapid, as may be observed also visually by the decolorisation of the violet permanganate solution.

When permanganate is reduced in an alkaline medium, manganate is first formed, then manganese^{IV} oxide. The potential change indicating the end of the first reaction cannot be observed, because the second reaction forming manganese dioxide proceeds at the same time. The reaction cannot be stopped at the first step even by the addition of a barium salt, nor by a variation of the potassium hydroxide concentration. It is similarly impossible to titrate to the second end-point, because traces of manganese dioxide already catalyse the decomposition of the titrant.

Vanadate is reduced by isonicotinic acid hydrazide to vanadyl ion only very slowly, so that the reaction cannot be applied for its direct determination.

On the other hand, potassium hexacyanoferrate(III) is reduced by the reagent very rapidly to hexacyanoferrate(II) according to the reaction;

$$4Fe(CN)_6^{3-} + C_5H_4N{\cdot}CO{\cdot}NH{\cdot}NH_2 + 4OH^- \rightarrow 4Fe(CN)_6^{4-} + C_5H_4N{\cdot}COOH{}^+N_2 + 3H_2O \quad (8)$$

This reaction takes place at room temperature, and is the basis of a titrimetric determination of hexacyanoferrate(III). Precise results have been obtained in 10–30% potassium or sodium hydroxide solutions. The reagent is not decomposed in the course of the titration (see *Stability of solutions*), because isonicotinic acid hydrazide reacts with the substance titrated earlier than its unwanted decomposition can take place.

Lead^{IV}, thallium^{III} and gold^{III}

Quadrivalent lead, tervalent thallium and tervalent gold may be titrated with isonicotinic acid hydrazide solutions with very good results. The reactions proceed according to the following equations:

$$2Pb^{4+} + C_5H_4N{\cdot}CO{\cdot}NH{\cdot}NH_2 + H_2O \rightarrow 2Pb^{2+} + C_5H_4N{\cdot}COOH + N_2 + 4H^+ \quad (9)$$

$$2Tl^{3+} + C_5H_4N{\cdot}CO{\cdot}NH{\cdot}NH_2 + H_2O \rightarrow 2Tl^{+} + C_5H_4N{\cdot}COOH + N_2 + 4H^+ \quad (10)$$

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* In the presence of copper^{II} as catalyst, solution of isonicotinic acid hydrazide may presumably be standardised against primary standard potassium dichromate.

$$4Au^{3+} + 3C_5H_4N{\cdot}CO{\cdot}NH{\cdot}NH_2 + 3H_2O \rightarrow 4Au + 3C_5H_4N{\cdot}COOH + 3N_2 + 12H^+ \quad (11)$$

The potentiometric titration of lead^{IV} proceeds well at room temperature in media of 1–10 % hydrochloric acid (optimum: 1–5 %). Media of other acids are not suitable (sulphuric, nitric, phosphoric and acetic acid) because hydrolysis occurs in dilute solutions of the acids, whereas in concentrated acids the course of the reaction is not stoichiometric.

Tervalent thallium may be determined in a medium of 1–5 % sulphuric acid, 1–15 % phosphoric acid or 1–50 % acetic acid. Because the reaction is too slow at room temperature, the titrated solution must be heated to 70–80°. The equivalence point is determined potentiometrically.

The determination of gold proceeds quantitatively at room temperature in dilute solutions of hydrochloric, sulphuric or phosphoric acid. The most suitable medium is that of hydrochloric acid. The titration may also be carried out on a microscale. It is possible to determine potentiometrically amounts down to 250 μg of gold in a volume of 40 ml. The method is, for instance, suitable for the analysis of drugs containing gold.[10]

Silver and mercury

Isonicotinic acid hydrazide has also been applied to the determination of silver and mercury. Silver is best reduced in ammonia solution in the presence of alkali metal hydroxides according to the equation:

$$4Ag[NH_3]_2^+ + C_5H_4N{\cdot}CO{\cdot}NH{\cdot}NH_2 + 4OH^- \rightarrow 4Ag + C_5H_4N{\cdot}COOH + N_2 + 8NH_3 + 3H_2O \quad (12)$$

There must be sufficient ammonia present to permit formation of the ammine complex with silver ions. A medium of ammonia itself, however, is not sufficient for quantitative reduction of silver, so that solutions must be used containing besides ammonia 20–35 % of an alkali metal hydroxide. Potentiometric titration is possible even in the presence of zinc, nickel, copper^{II}, lead, aluminium, cadmium and iron^{III} ions. Manganese^{II}, cobalt^{II} and mercury^{II} salts interfere. In all titrations a silver indicator electrode and saturated calomel reference electrode are used.

In an alkaline medium in the presence of an excess of iodide bivalent mercury is reduced according to the equation:

$$2[HgI_4]^{2-} + C_5H_4N{\cdot}CO{\cdot}NH{\cdot}NH_2 + 4OH^- \rightarrow 2Hg + C_5H_4N{\cdot}COOH + 8I^- + N_2 + 3H_2O \quad (13)$$

The reaction is rapid and quantitative, if the titrated solution contains sufficient alkali metal hydroxide (20–35 %). The determination may be performed even in the presence of large amounts of nitrate, sulphate, carbonate, fluoride, chloride and bromide. Cyanide and ammonium salts interfere.

Optical conditions for the titration of all systems mentioned above are summarised in Table I.

Other substances

Cerium^{IV} salts are reduced in an acid medium by isonicotinic acid hydrazide very rapidly to cerium^{III} salts. Although a large potential change occurs at the equivalence point, the reactions are not quantitative. The results depend to a large measure on the

TABLE I.—OPTIMAL CONDITIONS FOR TITRATIONS WITH ISONICOTINIC ACID HYDRAZIDE

Compound	Amount titrated, *mg*	Optimal medium	Inflexion potential (against S.C.E.), *mV*	Average error, ±%	Notes
Cl_2	0·14–350	HCl, pH 1–5	810	0·55	
Chloramine-T	30–120	15–25% H_3PO_4	520	0·33	60–70°
Br_2	0·3–350	HCl, pH 1–5	740	0·28	
N-bromosuccinimide	2–70	1–15% HCl			
		1–10% H_2SO_4			
		1–84% H_3PO_4	840; 600	0·34	
		1–100% CH_3COOH			
I_2	1–250	pH 6·5–8	180	0·45	
BrO_3^-	0·2–60	5–15% HCl	580	0·24	
$Cr_2O_7^{2-}$	10–100	10–37% HCl	550	0·38	
MnO_4^-	5–50	1–5% H_2SO_4	900	0·16	70°
$Fe(CN)_6^{3-}$	10–300	10–30% KOH	−40	0·44	
Pb^{4+}	1–200	1–5% HCl	760	0·48	
Tl^{3+}	10–230	1–5% H_2SO_4			
		1–15% H_3PO_4	560	0·58	70–80°
Au^{3+}	0·25–6	HCl			
		H_2SO_4, pH 0–1	630	0·36	
		H_3PO_4			
$Ag[NH_3]_2^+$	10–250	25–35% NaOH	−180	0·54	Ag indicator electrode
$[HgI_4]^{2-}$	10–300	30–35% NaOH	−290	0·56	

pH of the solution. Attempts have been made to carry out this titration in buffer solutions, but even then it did not proceed stoichiometrically, so that the determination of cerium^{IV} ions by means of isonicotinic acid hydrazide cannot be carried out.

The reduction of bivalent copper is also not quantitative, because in an alkaline medium in the presence of complex-forming substances either copper^{I} oxide or metallic copper is formed, depending on the reaction conditions. These products cause catalytic decomposition of isonicotinic acid hydrazide. No reduction was observed in an acid medium.

Selenate and tellurate are reduced by isonicotinic acid hydrazide very slowly, even in media of optimum acidity. Selenate is reduced quantitatively only when the sample is boiled with excess reagent for 20 min. Reduction of tellurate is even slower. For these reasons the reaction cannot be employed for the direct titration of these substances. Only indirect determinations are possible.

CONCLUSIONS

Based on the data on stability of solutions, redox potentials and the quantitative course of reactions of the investigated hydrazine derivatives with various inorganic systems it is concluded that isonicotinic acid hydrazide is the most suitable reductimetric titrant of the group. Compared with the parent substance, hydrazine,[4–6] isonicotinic acid hydrazide is at least equal in its action, yielding an even broader range of application (bichromate, permanganate). A number of reactions proceed rapidly and quantitatively, without unwanted side effects, so that they may be applied as direct titrations.

Successful titrations may also be carried out using solutions of semicarbazide chloride, benzoylhydrazine or 2,4-dinitrophenylhydrazine, but the low stability of these reagents hinders their broader application. The least suitable titrants of the group studied are *p*-nitrophenylhydrazine and phenylhydrazine chloride where, beside the low stability of the reagents, the course of the reactions is not stoichiometric.

Zusammenfassung—Es wurden die Anwendungsmöglichkeiten von Benzoylhydrazin, Phenylhydrazin, p-Nitrophenylhydrazin, 2,4-Dinitrophenylhydrazin, Isonikotinsäurehydrazid und Semikarbazid als massanalytische Reagenzien untersucht. Es wurde die Beständigkeit dieser Stoffe in verschiedenen Medien untersucht, und es werden die Beständigkeit und die Ursache der Faktoränderungen der Masslösungen diskutiert. Unter den genannten Stoffen zeigte sich Isonikotinsäurehydrazid als das geeignetste Reagens, da seine Lösungen beständig sind und zur raschen und quantitativen Reduktion einer ganzen Reihe von anorganischen Systemen herangezogen werden kann.

Résumé—On a étudié les possibilités d'application comme produits de titrage en réductimétrie de la benzoylhydrazine, de la phénylhydrazine de la nitrophénylhydrazine, de la dinitro-2,4-phénylhydrazine et de semicarbazide et de l'hydrazide de l'acide isonicotinique. La stabilité de ces substances dans des milieux variés a été déterminée; les causes de cette stabilité et les changements de titres sont discutés. Parmi ces composés, l'hydrazide de l'acide isonicotinique semble être le meilleur réactif; ses solutions sont en effet stables et permettent la réduction rapide et quantitative d'un grand nombre de systèmes minéraux.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XII*

SUCCESSIVE DETERMINATION OF THORIUM, RARE EARTHS AND SOME OTHER ELEMENTS

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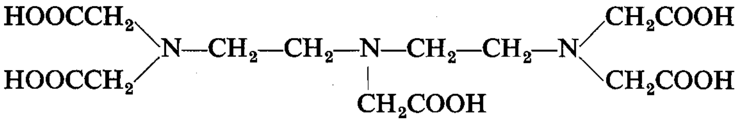
Summary—The successive determination of thorium and rare earths with diethylenetriaminepenta-acetic acid (DTPA) and triethylenetriaminehexa-acetic acid (TTHA) is described. Such a determination cannot be carried out with the commonly used EDTA or diaminocyclohexanetetra-acetic acid (DCTA). By combined titrations with DTPA and TTHA it is possible to determine successively not only thorium and rare earths, but also some bivalent elements which might be present in the material to be analysed.

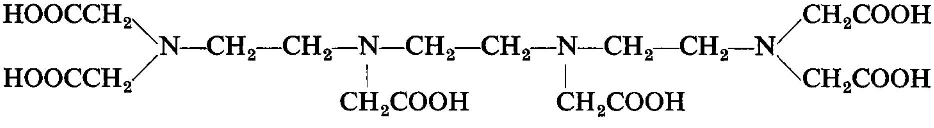
THE high stability constant of the thorium complex with EDTA ($pK_{ThY} = 23{\cdot}2$) enables a highly selective complexometric determination of thorium to be made in the presence of most bivalent metals and other rare earths with the exception of scandium ($pK_{ScY} = 23{\cdot}1$). The direct titration is best carried out at pH 2·5–3 with Xylenol Orange as indicator.[1] A further determination of the mentioned elements ($pK_{Me} = 16$–18) at pH 5–6 cannot be carried out because of the colour reaction of the thorium-EDTA complex with Xylenol Orange. A similar reaction occurs with Methylthymol Blue or Pyrocatechol Violet. By increasing the pH a less stable hydroxycomplex of thorium is formed, which dissociates sufficiently to undergo a sensitive colour reaction with the indicator. The resulting coloration makes any further titrations impossible. For the same reason the use of DCTA is unsuccessful.

Thorium and rare earths can be separated from other elements by precipitation with sodium hydroxide in the presence of triethanolamine (TEA) in the same way as can titanium.[2] One could then determine thorium and some of the rare earths successively in the same solution provided a suitable titrimetric reagent was available to eliminate the disturbing influence of thorium. Attention was turned to compounds related to EDTA, such as diethylenetriaminepenta-acetic acid (DTPA) and triethylenetetraminehexa-acetic acid (TTHA).



$$(HOOCCH_2)_2N{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_2COOH}{\underset{|}{N}}{-}CH_2{-}CH_2{-}N(CH_2COOH)_2$$

(DTPA)



$$(HOOCCH_2)_2N{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_2COOH}{\underset{|}{N}}{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_2COOH}{\underset{|}{N}}{-}CH_2{-}CH_2{-}N(CH_2COOH)_2$$

(TTHA)

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* Part XI: *Talanta*, 1963, **10**, 383.

From our preliminary experiments it appeared that neither the thorium-DTPA nor the thorium-TTHA complexes offer a colour reaction with Xylenol Orange at pH 5–5·5. This can be explained by the high stability of the respective complexes. The stability constant of the thorium-DTPA complex, as measured by Bogucki and Martell,[3] is $pK_{ThY} \simeq 27$; that for the thorium-TTHA complex has not yet been measured. Further experiments with DTPA and TTHA showed that both reagents not only enable a complexometric determination to be made of thorium, but also a subsequent determination of rare earths and some other bivalent elements which may be present in a sample.

EXPERIMENTAL

Reagents

0·05M solution of EDTA: Prepared by dissolving 18·61 g of the disodium salt (CHELATON III, Lachema, Brno, Czechoslovakia) in redistilled water and diluting to 1 litre. The strength was checked complexometrically with a standard solution of 0·05*M* lead nitrate using Xylenol Orange as indicator.

0·05M solution of DTPA: Prepared by dissolving 19·65 g of the free acid (Geigy, Basel, Switzerland) in 130–150 ml of hot 1*M* sodium hydroxide solution and diluting to 1 litre with redistilled water. The strength was checked as for the EDTA solution.

0·05M solution of TTHA: Prepared by dissolving 24·73 g of the free acid (Geigy, Basel, Switzerland) in 130–150 ml of hot 1*M* sodium hydroxide solution and diluting to 1 litre. The strength was checked as for the EDTA solution.

Other 0·05*M* solutions were prepared from reagent-grade chemicals and their strengths checked complexometrically.

Successive Determination of Thorium and Rare Earths (or Some Other Elements) with DTPA

Thorium can be determined by direct titration with DTPA at pH 2·5–3 just as well as with EDTA. The colour change from red to yellow with Xylenol Orange is very sharp. After subsequent adjustment of the pH with urotropine to 5·0–5·5 it is possible to proceed in the titration of lanthanum, praseodymium, neodymium, cerium and some bivalent elements which may be present (see Table I). This method is, however, limited by the amount of thorium. At a content of 30 mg of thorium in a volume of 150–200 ml the colour change during the second titration is not sharp and the consumption of DTPA is a little higher than the theoretical. On the other hand, a very sharp colour change and correct results are obtained if, after the titration of thorium has been completed, more than sufficient further DTPA is added to complex the second element and the excess is back-titrated with standard 0·05*M* lead nitrate solution.

Procedure

Dilute to 150–200 ml an acid solution containing 10–200 mg of thorium and other elements as indicated in Table I. Adjust the pH to 2·5–3 with dilute aqueous ammonia or nitric acid. Add Xylenol Orange indicator solution and titrate slowly with 0·05*M* DTPA solution to a clear yellow end-point. Add a further amount of DTPA (more than enough to complex the second element), adjust the pH to 5–5·5 with solid urotropine (universal indicator paper) and titrate the excess of DTPA with 0·05*M* lead nitrate solution until the yellow coloration of the solution turns to red-violet.

Remarks

Iron, nickel and copper interfere with the determination of thorium. Iron can be reduced to the bivalent state and copper masked with thiourea.

All of these interferences can be also eliminated by the precipitation of thorium and rare earths as hydroxides in the presence of triethanolamine.[2] Scandium and bismuth are quantitatively cotitrated.

TABLE I. DETERMINATION OF THORIUM AND RARE EARTHS (OR SOME OTHER METALS) WITH DTPA (AND EDTA)

0·05*M* Th taken, *ml*	0·05*M* RE or other metal taken, *ml*	0·05*M* Th found, *ml*	Excess 0·05*M* DTPA added, *ml*	Back titre with 0·05*M* Pb, *ml*	0·05*M* RE or other metal found, *ml*
0·99	1·04 La	1·00	3·00	1·98	1·02 La
19·70	1·04 La	19·75	5·00	4·00	1·00 La
0·99	26·00 La	1·00	30·00	4·03	25·97 La
0·99	0·89 Ce	1·00	4·00	3·12	0·88 Ce
0·99	8·85 Ce	1·00	12·00	3·16	8·84 Ce
9·85	0·89 Ce	9·82	0·85	direct	0·85 Ce
4·93	13·28 Ce	4·95	20·00	6·90	13·10 Ce
9·85	0·98 Pr	9·90	3·00	2·04	0·96 Pr
4·93	4·89 Pr	4·92	10·00	5·12	4·88 Pr
9·85	0·92 Nd	9·81	5·00	4·07	0·93 Nd
0·99	9·15 Nd	0·95	9·13	direct	9·13 Nd
14·78	13·72 Nd	14·85	20·00	6·35	13·65 Nd
			with 0·05*M* EDTA		
4·93	8·85 Ce	4·95	9·84	0·99	8·85 Ce
4·93	26·00 La	4·92	26·57	0·49	26·08 La
0·99	10·40 La	1·00	10·50	direct	10·50 La
1·02	18·30 Nd	1·03	18·12	direct	18·12 Nd
15·35	0·92 Nd	15·35	2·95	2·13	0·82 Nd
9·85	4·82 Zn	9·87	6·89	2·13	4·76 Zn
0·99	14·88 Pb	1·02	14·91	direct	14·91 Pb

Phosphates, oxalates and sulphates also interfere. For the second titration DTPA can be replaced by EDTA. This is advantageous especially at higher concentrations of lead and zinc, *etc.* A very interesting phenomenon has been observed. If a pure solution of thorium is titrated with DTPA, then a solution of EDTA added and the pH adjusted with urotropine, a violet coloration appears which makes further titrations impossible. This interference can be eliminated in a simple way. After the titration of thorium with DTPA, first add urotropine and then the EDTA solution. The solution remains in the presence of only thorium, clearly yellow. The first reaction can be explained by the fact that the thorium-DTPA complex changes in an acidic medium partly into a thorium-EDTA complex which, after addition of urotropine, forms with the indicator a colour complex even in the presence of an excess of EDTA:

$$\underset{\text{colourless}}{\text{ThDTPA}} \rightarrow \underset{\text{colourless}}{\text{ThEDTA}} \rightarrow \underset{\text{red-violet}}{\text{ThXO}}$$

Successive Determination of Thorium, Rare Earths and Some Other Elements with TTHA

Triethylenetriaminehexa-acetic acid behaves similarly to DTPA. Therefore it can be used instead of DTPA according to the procedure described above. It was previously reported[4] that TTHA forms 1:2 complexes with some elements, but only 1:1 complexes with the rare earths. This can be utilised with advantage for the determination of the ternary mixture Th-RE-Me, where RE is a rare earth (or their sum) and Me is a bivalent heavy metal (or their sum). For the determination one needs two aliquots of the test solution. In the first aliquot one determines successively thorium (pH 2·5–3) and RE plus Me (pH 5·5–6) by titration with DTPA. In the

TABLE II. DETERMINATION OF THORIUM, RARE EARTHS AND SOME OTHER ELEMENTS WITH DTPA AND TTHA

0·05*M* solution taken, *ml*			0·05*M* Th found, *ml*	Sum (A) of RE plus Me with 0·05*M* DTPA, *ml*	Sum (B) of RE plus Me with 0·05*M* TTHA, *ml*	0·05*M* solution found, *ml*	
Th	RE	Me				RE	Me
1·02	3·12 La	5·95 Pb	1·05	9·06	6·13	3·20 La	5·96 Pb
5·12	4·58 Nd	4·82 Zn	5·10	9·44	6·93	4·42 Nd	5.02 Zn
10·23	12·48 La	4·98 Cd	10·18	17·50	14·95	12·40 La	5·10 Cd

Calculation: (A − B) × 2 = Me, A − Me = RE.

second aliquot one again determines successively thorium and RE plus Me, but with TTHA. In the second case the consumption for Me drops by one half so that the amount of Me can be easily calculated. Table II shows the results of some of these determinations.

Acknowledgements—The authors thank Dr. A. Krebser (Geigy, Basel, Switzerland) for providing the samples of DTTPA and TTHA, and Dr. G. Werner, (Institute of Inorganic Chemistry, Karl-Marx-University, Leipzig, DDR) for the samples of pure rare earths.

Zusammenfassung—Die aufeinanderfolgende Bestimmung von Thorium und seltenen Erden mit einer Lösung der Natriumsalze von Diathylentriamin-pentaessigsäure (DTPA) und Triäthylentriamin-hexaessigsäure (TTHA) wird beschrieben. Solche Bestimmungen sind mit den üblichen EDTA oder DCTA nicht möglich. Durch kombinierte Titration mit DTPA und TTHA ist es möglich, außer Thorium und seltenen Erden auch einige im Analysenmaterial anwesende zweiwertige Elemente nacheinander zu bestimmen.

Résumé—On décrit les dosages successifs du thorium et des métaux des terres rares par des solutions de sel de sodium des acides diéthylène-triamine-pentacétique (DTPA) et triéthylène-triamine-hexacétique TTHA). De tels dosages ne sont pas possibles avec les réactifs habituellement utilisés comme l'EDTA ou le DCTA. Par ces dosages combines au moyen du DTPA et du TTHA il est possible de doser non seulement le thorium et les métaux des terres rares, mais aussi certains éléments bivalents pouvant egalement être presents dans le materiel à analyser.

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A NEW PRINCIPLE OF ACTIVATION-ANALYSIS SEPARATIONS—IV*

SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF SILVER

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Summary—A substoichiometric determination of traces of silver in germanium dioxide and in metallic lead has been developed. It consists of simultaneous irradiation of a standard and test sample in a nuclear reactor followed by dissolution and addition of silver carrier. After adjusting the pH, the samples are extracted with the same substoichiometric amount of dithizone in carbon tetrachloride and the activities of the organic extracts measured. This single-step separation procedure is fully satisfactory because of its high selectivity. Moreover, substoichiometry avoids the necessity of determining the chemical yield. The procedure developed could be adapted without difficulty for the determination of traces of silver in other materials.

INTRODUCTION

ACTIVATION analysis is frequently used for the determination of traces of silver in various materials.[1,2,3,4,5] The procedure in current use consists of neutron activation, radiochemical separation, determination of the chemical yield and measurement of the activity of the radioactive silver isolated.

By irradiation of silver with neutrons the following radio-isotopes are formed as a result of (n, γ) reactions:

$$^{107}\text{Ag}(\text{n}, \gamma)^{108}\text{Ag}$$

$$^{109}\text{Ag}(\text{n}, \gamma)^{110}\text{Ag}$$

$$^{109}\text{Ag}(\text{n}, \gamma)^{110\text{m}}\text{Ag}$$

Because the first two radionuclides have very short half-lives (2·3 min and 24·2 sec, respectively), only the 270–day $^{110\text{m}}$Ag is of value for practical use. This β and γ emitter is produced from ^{109}Ag (natural abundance 48·65 %) with an activation cross section of 3·2 barns. The nuclear interference from ^{110}Cd (n, p) $^{110\text{m}}$Ag and from ^{113}In(n, α) $^{110\text{m}}$Ag must be considered only if cadmium and indium are present in large amounts. These nuclear properties enable the activation determination of traces of silver to be made in various materials, *e.g.*, silicon,[1] aluminium,[2] galena,[3] platinum sponge[4] and rocks.[5] The simplest radiochemical separation procedure commonly used includes the following steps: (1) precipitation of silver as AgCl, (2) scavenging with $Fe(OH)_3$ precipitation after dissolution of AgCl in ammonia, (3) reprecipitation

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* Part III: see reference 8.

of silver as Ag_2S, and (4) converting the latter to $AgIO_3$ (or AgCl) for weighing and measuring of the activity. However, more complicated schemes (including up to 12 separation steps) have been described.[4,5]

The purpose of the present paper is to show that using the substoichiometric separation principle[6,7,8] for determination of silver it is possible to reduce the number of separation steps and to avoid the necessity of determining the chemical yield. Hence the time of analysis is substantially reduced.

From the theory of the substoichiometric separation principle[6] the optimal conditions for separation and determination of silver have been deduced. Silver should be very selectively isolated by dithizone-carbon tetrachloride extraction from 0·1*M* sulphuric acid. This proposed procedure has been verified by the determination of traces of silver in germanium dioxide and in metallic lead. Its application to other matrices should be possible without difficulty.

EXPERIMENTAL

Apparatus

Scintillation counter: Well-type with NaI(Tl) crystal.
Mechanical shaker
Glass test-tubes: With ground stopper, 40-ml volume.

Reagents

All reagents used were of AnalaR purity.

Dithizone solution: $2 \times 10^{-4}M$ in carbon tetrachloride.
Silver carrier solution: $10^{-3}M$ silver nitrate slightly acidified with nitric acid.

Irradiation

Samples of germanium dioxide, metallic lead and a comparative standard of silver nitrate were sealed in quartz ampoules and simultaneously irradiated in a nuclear reactor at a neutron flux of 5×10^{12} neutrons . cm^{-2}. sec^{-1} for 3 days. The radiochemical procedure was started after allowing 2 weeks for cooling of the irradiated samples.

Development of the method

Two ml of silver carrier solution were extractively titrated in 0·1*M* sulphuric acid with dithizone solution. This amount of silver carrier solution was found to correspond to approximately 12 ml of the dithizone solution. These standardised solutions were used in all further experiments. The same titration was carried out also in the presence of the dissolved germanium dioxide.

For investigating the reproductibility of the substoichiometric separation a series of solutions containing various amounts (2, 3, 4 and 5 ml) of silver carrier was prepared and these solutions were extracted with a substoichiometric amount of dithizone solution (4 ml). The extinctions of the organic extracts showed that exactly the same amount of silver was always isolated. From these experiments the time necessary for reaching equilibrium in the extraction was also determined (10 min).

A further test of the substoichiometric separation principle was carried out as follows: To a series of solutions containing 2·0 ml of silver carrier various amounts of irradiated silver (0·4 to 2·0 μg) were added. After adjusting the acidity to about pH 1, the solutions were simultaneously extracted with a substoichiometric amount of dithizone solution (4 ml). The activities of the same volume of organic extract were measured in a scintillation counter. From Fig. 1 it is evident that the isolated activity is directly proportional to the amount of irradiated silver present.

Procedure

Germanium dioxide. The irradiated germanium dioxide sample was dissolved in 3 ml of 8*M* sodium hydroxide solution, then 4*M* sulphuric acid added until a white precipitate appeared. This precipitate was dissolved with a few drops of the sulphuric acid, the acidity of the solution adjusted to pH 1 and 2·00 ml of silver carrier solution added. After extracting with 4 ml of dithizone solution for 10 min, the activity (a) of 3 ml of the organic extract was measured. To an appropriate amount (y_s) of irradiated silver nitrate standard sample 2·0 ml of the same silver carrier solution were added and this solution treated simultaneously and in exactly the same way as the test sample. From the activity (a_s) of 3 ml of the organic extract, the amount of silver present in the test sample was calculated using the relation[6]

$$y = y_s \frac{a}{a_s} \qquad (1)$$

Silver-free lead. The irradiated metallic lead (Merck "Pro Analysi" grade) was dissolved in 15 ml of nitric acid (1 : 2). To this solution 2·00 ml of silver carrier solution were added. After evaporation to dryness the residue was dissolved in 10 ml of 0·1*M* nitric acid and the extraction carried out in exactly the same way as in the case of germanium dioxide.

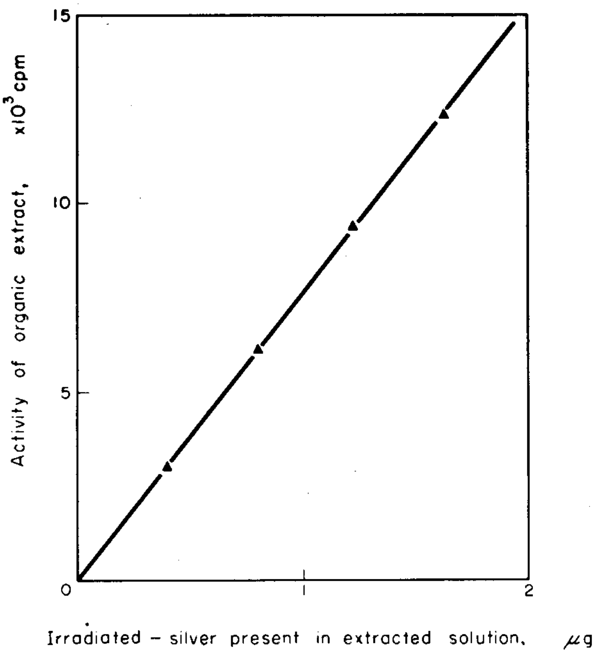

FIG. 1

RESULTS AND DISCUSSION

The results of the analyses are summarised in Table I. The analysed germanium dioxide samples contained less than 7×10^{-6}% of silver and the metallic lead (silver-free) $1{\cdot}7 \times 10^{-4}$% of silver. The sensitivity of the determination could be further increased by using a higher neutron flux, and increasing the weight of the analysed sample and/or the irradiation time (an increased interference from the presence of cadmium and indium might now have to be taken into consideration—see *Introduction*). However, the main purpose of the present work was to develop and verify the new separation method for the determination of silver by activation analysis.

The procedure described is very selective. Using an excess of dithizone only palladium, mercury, gold, silver, copper and bismuth are extracted from 0·1*M* sulphuric acid by carbon tetrachloride. Germanium and lead are, of course, not extracted under these conditions. Under our conditions, the nuclear properties of copper and bismuth preclude their interference. From the known extraction constants of metal dithizonates[6,9] it follows that palladium, mercury and gold will be extracted by the first portion of the carbon tetrachloride solution of dithizone. To eliminate possible interference from the above three metals, a second successive extraction with 4 ml of dithizone solution was carried out. In the second extract only the activity of radiosilver can be expected. However, in our case no difference between the activities of the first and second extracts were found and thus it can be concluded that palladium, mercury and gold are not present in detectable amounts in the test sample.

TABLE I—SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF SILVER

Material analysed, *g*	Germanium dioxide		Metallic lead
	0·0975	0·1048	0·4971
Amount of irradiated silver standard added to irradiated material, μg	—	1·224	—
Activity* obtained from test sample (a)	120	20392	14368
Amount of silver in irradiated standard sample (y_s), μg	1·224	1·224	0·612
Activity* obtained from standard sample (a_s)	20552	20552	10492
Amount of silver found, μg	0·007	1·215	0·838
%	7×10^{-6}	—	$1{\cdot}7 \times 10^{-4}$

* All activities are expressed in cpm and are the mean values from 4 measurements corrected for background.

CONCLUSION

A substoichiometric determination of traces of silver by neutron-activation analysis has been developed. The substoichiometric method enables a substantial reduction to be made in the number of separation steps used in current radiochemical procedures. This method also avoids the necessity of determining the chemical yield. The procedure developed for the analysis of germanium dioxide and metallic lead could be adapted without serious difficulties for the determination of traces of silver in other materials.

Acknowledgements—The authors thank Dr. V. Majer for his interest in this work and Dr. R. Přibil for critical discussion.

Zusammenfassung—Eine substöchiometrische Methode zur Bestimmung von Silberspuren in GeO_2 und silberfreiem R.G. wurde ausgearbeitet. Standard und Analysenprobe werden im Kernreaktor bestrahlt, gelöst und mit Träger versetzt, Nach Einstellung des p_H werden beide Lösungen mit unterstöchiometrischen Mengen Dithizon in CCl_4 extrahiert. Diese einstufige Abtrennung reicht wegen ihrer hohen Selektivität völlig aus. Ferner erspart die Anwendung des Unterschusses die Bestimmung der chemischen Ausbeute.

Die Methode kann ohne Schwierigkeiten der Silberbestimmung in anderen Materialien angepaßt werden.

Résumé—On décrit une méthode substoéchiométrique de dosage de l'argent dans GeO_2 et dans les échantillons R.G. contenant de l'argent libre. Cette méthode consiste en une irradiation de l'échantillon à analyser et d'un échantillon de référence dans un réacteur nucléaire suivie d'une mise en solution et de l'addition d'un traceur. Après mise au point des conditions de pH, les deux échantillons sont extraits par des quantités substoéchiométriques de dithizone dans le tétrachlorure de carbone. Ce procédé de séparation en une seule étape est tout à fait satisfaisant en raison de sa très haute sélectivité. De plus, la méthode substoéchiométrique supprime la nécessité de déterminer le rendement chimique. La méthode décrite peut également être adaptée sans difficultés au dosage de l'argent contenu dans d'autres types d'échantillons.

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ANALYSIS OF MIXTURES OF MONO- AND DI-ALKYL ORTHOPHOSPHATES

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Summary—Quantitative separations of mixtures of mono- and di-alkyl orthophosphates by salting-out chromatography on special Dowex 50-X4 resins of low capacity are described. Dimers of some of the mono-alkyl esters have also been isolated.

SEVERAL different methods for the separation of mono- and di-alkyl orthophosphates have been investigated. Plimmer and Bunch[1] and Kumler and Eiler[2] employed fractional crystallisation of the barium salts. Extraction with organic solvents was first employed by Stewart and Crandall.[3] Their method was improved by Peppard *et al.*[4,5] Higgens and Baldwin[6] separated phosphoric acid, mono- and di-n-butyl phosphates on a column of Dowex 2-X8 in the chloride form. Plapp and Casida[7] achieved a partial separation of phosphoric acid and mono- and di-methyl phosphates by gradient elution from a column of Dowex 1X-8. Recently, two groups of Italian investigators[8,9] have used ion exclusion[10,11] to achieve a partial separation of phosphoric acid, mono-n-butyl phosphate and di-n-butyl phosphate. A 180-cm column of Dowex 50-X8 was required. A small quantity of a dimer of mono-n-butyl phosphate was incompletely separated from the phosphoric acid. Cesarano and Lepscky[9] suggested that the same technique could be used for the separation of other alkyl orthophosphates. There is evidence to indicate that water will not be an effective eluent for the separation of the lower molecular weight esters.[12,13] Elution with aqueous salt solutions should be more effective.

The use of aqueous salt solutions as an eluent for the separation of water-soluble non-electrolytes on an ion-exchange resin was first suggested by Sargent and Rieman.[14] These authors called their new method "salting-out chromatography." The method has been applied to the separation of alcohols,[15] ethers,[16] aldehydes and ketones,[17] amines,[18] and organophosphorus acids.[12,13]

The usual procedure employed in the development of a separation by ion-exchange or salting-out chromatography involves initial studies with pure compounds. The results of these investigations are used to calculate the optimum conditions for a quantitative separation.

Several of the components believed to be present in the mixture of mono- and di-alkyl orthophosphates were not available. Synthesis of the desired compounds was considered too time consuming. Isolation from commercially available mixtures by solvent extraction was not attempted because the fate of some of the minor components, *e.g.*, dimers of the mono-alkyl esters, was uncertain. The procedure that was adopted consisted of preliminary elutions of each mixture, analysis of the elution diagram, and calculation of the column height necessary for quantitative separation.

In this paper the basic equation of the plate theory[19]

$$U^* = CV + V \tag{1}$$

was used to calculate C values. The symbol U^* represents the volume of eluate collected from the addition of the sample to the peak of the elution curve; V is the interstitial volume of the column; and C is the distribution ratio, defined as the quantity of sample constituent in the resin of any plate divided by the quantity of the same constituent in the interstitial solution of the same plate at equilibrium. Optimum column heights were calculated with the equations of the plate theory.

The eluents used in this study, lithium chloride and/or hydrochloric acid, have been found to be the most effective for the separation of organophosphorus compounds.[12,13] The interstitial volumes of the special resins used in this investigation, equilibrated with the aforementioned eluents, have also been determined by Rieman and his co-workers.

EXPERIMENTAL WORK

Materials

Mixtures of the mono- and di-alkyl esters of orthophosphoric acid were supplied by the Victor Chemical Company, Chicago, Illinois, U.S.A.

Resins of low capacity* were used throughout this investigation. These resins were in every way identical to Dowex 50-X4, except that their capacities were lower than the usual value of 5·2 meq per g. Each low-capacity resin consisted of spheres that passed through a 325-mesh screen and were cross-linked with 4% nominal divinylbenzene.

All eluents were prepared by dissolving reagent-grade chemicals in distilled water.

Polypropylene test tubes (19 × 115 mm) were obtained from Van Waters and Rogers Inc., San Francisco, California, U.S.A.

Elution

The preparation of columns for ion-exchange and salting-out separations has been described in a recent treatise.[20] The resin, having a capacity of 3·82 meq per g, was equilibrated with each eluent by passing approximately 1 litre of this solution through the column. The eluent was then drained to the top of the resin bed. A sample of 1·00 ml was pipetted on to the top of the resin bed and was allowed to drain into the resin. At this point, collection of the effluent was initiated. The sample was then completely washed into the resin with the aid of three small portions of the first eluent (3–4 ml). After each addition the solution was permitted to drain into the resin. All eluent changes were made after draining the previous eluent completely into the resin bed. The columns were maintained at a temperature of 50 ±2°. Flow rates were adjusted to the desired value by variation of the hydrostatic head of the eluent. Small fractions (3·18 ml) were collected with the aid of a siphon pipette[21] and a Misco fraction collector.

Analysis of eluate fractions

The organophosphorus compounds were oxidised with ammonium persulphate in strongly alkaline solution. This oxidation procedure is described in previous papers.[12,22] The oxidations were carried out in polypropylene test tubes in order to avoid interference from silica.[23] The resulting orthophosphate was determined by the phosphovanadomolydate method.[24] All absorbance measurements were made with a Beckman DU spectrophotometer with 1-cm Corex cells.

RESULTS AND DISCUSSION

Fig. 1 is the elution diagram of a freshly prepared solution of the mono- and di-methyl esters of orthophosphoric acid. The four peaks, in order of appearance, are from orthophosphoric acid, mono-methyl ester, the dimer of mono-methyl ester, and di-methyl ester. These compounds were identified in several ways. The yellow phosphovanadomolybdate complex is formed only when phosphorus is present as

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* The Dow Chemical Company, Midland, Michigan, U.S.A.

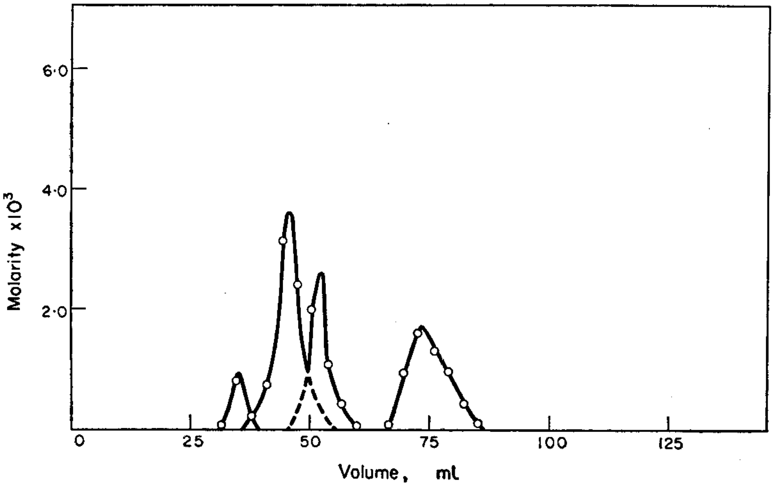

FIG. 1.—Elution of mono- and di-methyl orthophosphate mixture with 4·0 *M* LiCl and 1·0*M* HCl.
(16·7 cm × 2·76 cm² Dowex 50W-X4, 325 mesh, 3·82 meq per g linear flow rate 0·17 cm per min.)
The order of appearance of the components in the effluent is the same as that given in Table I.

orthophosphate. The amount of phosphorus containing compound under the first peak, corresponded, within experimental error, with the amount of orthophosphoric acid in the sample. This was considered as sufficient proof of the identity of the least strongly retained component. The *C* value of the last compound to appear in the eluate checked, within experimental error, with the *C* value of di-methyl orthophosphate.[12] The second and third peak still had to be identified.

Fig. 2 is the chromatogram that was obtained when the same mixture was eluted

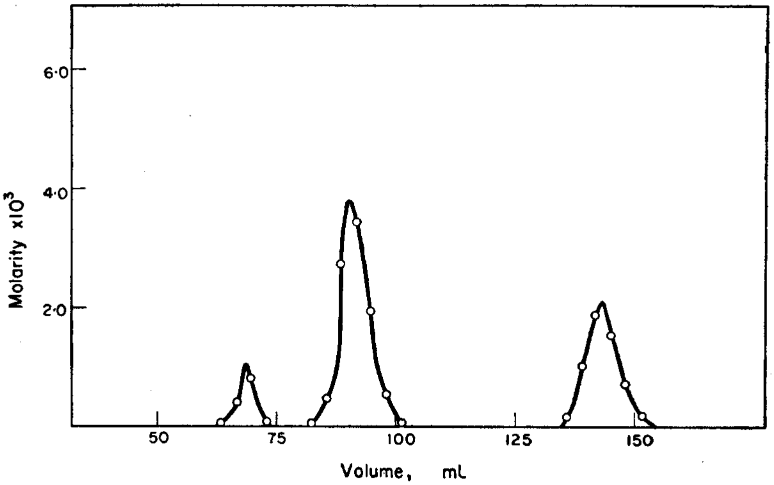

FIG. 2.—Separation of mono- and di-methyl orthophosphate mixture with 4·0*M* LiCl and 1·0*M* HCl.
(33·4 cm × 2·76 cm² Dowex 50W-X4, 325 mesh, 3·82 meq per g linear flow rate 0·17 cm per min.)
The compounds, in order of appearance, are orthophosphoric acid, mono-methyl orthophosphate and di-methyl orthophosphate.

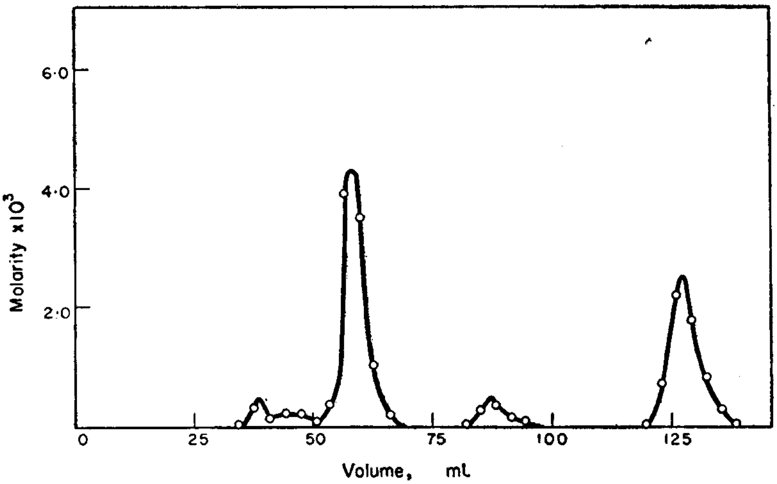

Fig. 3.—Separation of mono- and di-ethyl orthophosphate mixture with 2·0*M* LiCl and 1·0*M* HCl.
(20·2 cm × 2·76 cm² Dowex 50W-X4, 325 mesh, 3·82 meq per g linear flow rate 0·16 cm per min.)
The order of appearance of the components in the effluent is the same as that given in Table I.

from a longer column. Only three peaks are evident; apparently the dimer had been hydrolysed on the longer column. The amount of mono-methyl ester under the second peak corresponded to the amount of dimer and mono-methyl ester found under the second and third peaks of the first chromatogram. This interpretation was further substantiated by the fact that samples that had been prepared and stored at room temperature for thirteen weeks gave only three peaks. Without additional kinetic

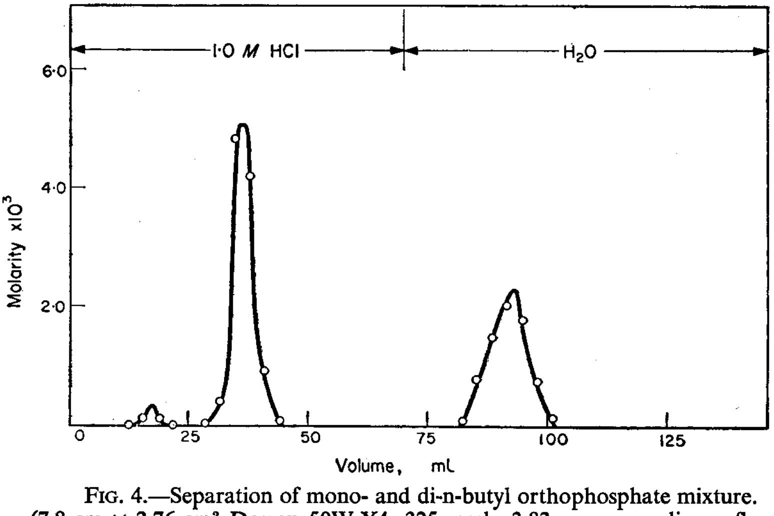

Fig. 4.—Separation of mono- and di-n-butyl orthophosphate mixture.
(7·8 cm × 2·76 cm² Dowex 50W-X4, 325 mesh, 3·82 meq per g linear flow rate 0·20 cm per min.)
The order of appearance of the components in the effluent is the same as that given in Table I.

data it is not possible to estimate how much of the dimer, present in the freshly prepared sample, hydrolysed on the shorter column.

Fig. 3 shows a quantitative separation of a mono- and di-ethyl orthophosphate mixture. Four major peaks are evident. They are orthophosphoric acid, mono-ethyl ester, the dimer of mono-ethyl ester, and di-ethyl ester, respectively. The identity of the various peaks was established with methods similar to those applied to the analysis of the first chromatogram. The small peak appearing between the orthophosphoric acid and the mono-ethyl ester has not been identified.

TABLE I.—ANALYSIS OF MONO- AND DI-ALKYL ORTHOPHOSPHATES

	Elution Number					
	1	2	3	4	5	6
Mono- and di-methyl orthophosphates						
Phosphorus taken, *mg*	1·612	1·612	1·612	1·612	1·612	1·685
Phosphorus found, *mg*, as						
H_3PO_4	0·142	0·142	0·142	0·132	0·130	0·142
$MeOPO(OH)_2$				0·898	0·905	0·967
	0·922*	0·930*	0·876*			
Dimer of $MeOPO(OH)_2$						
$(MeO)_2OPOH$	0·523	0·520	0·531	0·540	0·546	0·563
Recovery, %	98·4	98·8	96·1	97·4	98·1	99·2
Mono- and di-ethyl orthophosphates						
Phosphorus taken, *mg*	1·741	1·741	1·741			
Phosphorus found, *mg* as						
H_3PO_4	0·062	0·054	0·055			
Unknown	0·019	0·013	0·029			
$EtOPO(OH)_2$	0·887	0·889	0·895			
Dimer of $EtOPO(OH)_2$	0·105	0·102	0·100			
$(EtO)_2OPOH$	0·650	0·638	0·624			
Recovery, %	99·0	97·4	97·8			
Mono- and di-n-butyl orthophosphates						
Phosphorus taken, *mg*	1·824	1·824	1·824			
Phosphorus found, *mg*, as						
H_3PO_4	0·030	0·033	0·036			
$n\text{-}BuOP(OH)_2$	1·035	1·038	1·030			
$n\text{-}(BuO)_2OPOH$	0·718	0·716	0·715			
Recovery, %	97·8	98·0	97·6			

Elutions 1, 2 and 3 were performed on a 16·7-cm column and 4, 5 and 6 on a 33·4-cm column.
* These quantities represent the total amount of mono-methyl ester and dimer.

Fig. 4 shows a separation of a mixture of mono and di-n-butyl orthophosphates. The three peaks, in order of appearance, are those of orthophosphoric acid, n-butyl ester and di-n-butyl ester. Any dimer of n-butyl ester that may have been present in the original mixture must have been hydrolysed on the column. Table I lists the recoveries obtained from 12 separate analyses.

Acknowledgements—The authors are grateful for the financial assistance received from the Sacramento State College Foundation.

Zusammenfassung—Die quantitative Trennung von Mischungen aus Mono- und Dialkylorthophosphaten durch Aussalz-Chromatographie auf speziellen Dowex 50-X4-Harzen niedriger Kapazität wird beschrieben., Auch Dimere der Monoalkylester wurden isoliert.

Résumé—On decrit des séparations quantitatives de phosphates mono- et dialcoylés par chromatographie de relarguage sur résines spéciales Dowex 50–X4. et l'isolement de quelques dimères d'esters monoalcoylés.

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INTERNATIONAL COMPARISON OF ANALYTICAL METHODS FOR NUCLEAR MATERIALS—I

ACCURACY AND PRECISION OF SOME TECHNIQUES IN ROUTINE TRACE ANALYSIS*

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Summary—The results of an international comparison designed to show the accuracy and precision of some techniques of trace analysis used routinely are given. The techniques are emission spectrography, absorption spectrophotometry, polarography and neutron activation. A common sample, an aqueous solution containing approximately 5 ppm of copper and manganese and 15 ppm of chromium and mercury has been analysed by 9 different laboratories. The statistical analysis of the results (551 in all) shows, with the limitations as to generality imposed by the design of the experiment, that the expected precisions of a single determination in the routine application of each of the techniques are: spectrography, ±40%; polarography, ±25%; activation, ±20% and spectrophotometry, ±10% at the 0·05-probability level. The accuracy follows the same pattern though the spread of results within a technique is wider. When all results are considered together the precision is ±25%.

INTRODUCTION

ONE of the most characteristic aspects of present day analytical chemistry is the growing importance of the determination of impurities at very low concentrations in materials of interest to modern industry. Trace analysis is today no longer a very specialised activity applied almost exclusively in the study of particular chemical problems but represents an important part of the daily routine work of many analytical laboratories.

Some papers have appeared in which the accuracy and precision of a particular trace determination have been studied.[1] These, however, seldom refer to results obtained in routine work, but are generally the consequence of a careful study made by one investigator in one laboratory trying to diminish all statistical influences not inherent to the method itself. When the variations in routine results of different origin are compared, it very frequently happens that these are many times bigger than those reported by the originator of the method. A recent survey made in Japan on results obtained for many elements[2] is an excellent example of this fact.

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In connection with a programme of international comparison of analytical methods applied to nuclear materials, it was considered of interest to compare on a wide basis the magnitude of the differences which appear in routine practice in the case of the most important techniques used in trace analysis. The comparison would contribute information as to the degree of agreement between laboratories and would help to give a quantitative meaning to the accuracy and precision of trace analysis as a whole when applied as a routine activity.

As a first step, the results obtained by 9 different laboratories, ours included, have been compared, using 4 different techniques, in the determination of copper, chromium, manganese and mercury in an aqueous solution containing these elements in the 0 to 20-ppm range of concentration. These conditions were deliberately chosen so that any interference from the matrix would be a minimum and the variation in results could largely be attributed to the techniques used. No attempt was made to establish the best method for each element studied, because a different design of the comparison experiment would be necessary for this purpose.

The work was arranged to try to reproduce as far as possible the conditions prevailing in routine analysis. The participants were asked to make the determinations by emission spectrography, absorption spectrophotometry, polarography and neutron activation, but no particular method was specified in each technique. They were also asked to perform only those analyses for which they had methods available prior to the intercomparison and not to take special measures to deal with the case. The results, therefore, represent the application of the techniques in each laboratory using methods that the laboratory itself considers satisfactory from its previous experience.

The participating laboratories were selected arbitrarily through personal contacts, but taking into consideration that only laboratories with some years of active experience in the use of trace techniques for routine purposes should participate.

This paper reports the results obtained. Now that some information is available on the degree of agreement which can reasonably be expected in simple situations such as this, it is planned to continue the work with samples of nuclear materials representing real analytical situations.

EXPERIMENTAL

The sample was prepared from 4 stock solutions, each containing the element in the form of a nitrate. The stock solutions were prepared and standardised as follows:

Copper^{II} nitrate solution: 0·9823 g of electrolytic copper were dissolved in a quartz dish with nitric acid (1 + 1) and diluted with water to 500 ml: 1 ml = 1·964 mg of copper.

Chromium^{III} nitrate solution: Approximately 35 g of crystallized chromium^{III} potassium sulphate were dissolved in water and chromium^{III} hydroxide was precipitated from this solution with aqueous ammonia. The precipitate was washed with dilute ammonia solution until no sulphate was detected in the washings, then dissolved in nitric acid 1 + 1 and diluted with water to 500 ml. The concentration of chromium in the solution was determined by complexometric back-titration with 0·05M EDTA solution, using 0·05M standard zinc solution and Erio-T as indicator. The determination was repeated 5 times independently. The following results were obtained: 6·58, 6·62, 6·65, 6·63 and 6·57 mg of chromium/ml; average = 6·61 ± 0·042 mg of chromium/ml.

Manganese^{II} nitrate solution: Approximately 2·9 g of crystallised manganese^{II} chloride were dissolved in water and manganese^{II} carbonate was precipitated from this solution with ammonium carbonate solution in the presence of hydroxylamine. The precipitate was washed with water until no chloride was detected in the washing, then dissolved in nitric acid (1 + 1) and diluted with water to 500 ml. The concentration of manganese in the solution was determined by complexometric back-titration with 0·05*M* EDTA solution, using 0·05*M* standard zinc solution and Erio-T as indicator. The determination was repeated 5 times independently. The following results were obtained: 1·70, 1·72, 1·70, 1·69 and 1·70 mg of manganese/ml; average = 1·70 ± 0·013 mg of manganese/ml.

Mercury^{II} nitrate solution: 3·0387 g of purest mercury were dissolved in nitric acid (1 + 1) in a quartz dish and diluted with water to 500 ml: 1 ml = 6·077 mg of mercury.

To prepare the sample, 50 ml of each stock solution were pipetted successively to a 1000-ml volumetric flask and diluted to the mark. 50 ml of this new solution, containing the 4 elements with the addition of 10 ml of 2*M* nitric acid, were diluted to 1000 ml. This operation was repeated as many times as was necessary to obtain the desired amount of sample.

The final sample was 0·02*M* in nitric acid and contained the elements in the following concentrations, calculated from the results quoted and the dilutions performed:

Cu: 4·92 ± 0·01 μg/ml; Cr: 16·5 ± 0·1 μg/ml;
Mn: 4·25 ± 0·033 μg/ml; Hg: 15·2 ± 0·01 μg/ml.

These numbers were taken as the "true values" of the concentrations throughout the experiment. The confidence in these true values appeared satisfactory, because the concentrations of copper and mercury were defined by the weight of the pure metals, those of chromium and manganese were determined accurately by titration at relatively high concentrations and all dilutions were made in volumetric glassware previously checked. A rough calculation indicated that the maximum error introduced by cumulative errors in glassware and analytical balance would be well below 0·5% and therefore negligible. All of the reagents were Merck-Darmstadt *pro analysi* and only demineralised water was used.

The samples were sent in bottles of Jena G-20 glass which were carefully washed and rinsed and afterwards steamed for some hours. This treatment was intended to minimise errors from adsorption on the walls. At the same time, some bottles were kept as controls in the laboratory and their content analysed 7 months after the initiation of the experiment, when all results had been received. These determinations made clear that no significant alteration had occurred, as can be seen from Table I, where results obtained with polythene control bottles have also been included.

TABLE I.—STABILITY OF THE SAMPLE
(Values given are averages of 5 independent spectrophotometric determinations, expressed in ppm)

	Date of determination		
	True values April 1962	November 1962 (stored in glass)	November 1962 (stored in polythene)
Copper	4·92	4·98	4·93
Chromium	16·5	16·6	16·3
Manganese	4·25	4·35	4·30
Mercury	15·2	15·3	13·7

The participating laboratories were requested to determine each element 5 times by each technique and to report the individual results. The general instructions, summarised in the introduction to this paper, were aimed at warranting that the results would correspond to routine work as far as possible. On the whole, these instructions were carried out satisfactorily. Laboratories which had no checked method for a particular determination or which lacked the equipment required for certain techniques, made only those determinations that were possible within their routine work. The methods used were reported by the majority of the participants and showed that there was appreciable variation in most cases. The available information is summarised in Table II. This is included here for reference purposes only, because the results were treated without discrimination against methods within each technique, in agreement with the original purpose.

The total number of determinations received was 551 from a theoretical total of 720 (80 determinations × 9 laboratories).

TREATMENT OF RESULTS AND DISCUSSION

The individual results were normalised with reference to the corresponding true values of the concentrations taken as 100 in order to permit a direct comparison of the results obtained for different elements independently of their absolute values. The histogram obtained by plotting all of the individual normalised results at 1 % intervals against the corresponding frequency of occurrence is shown in Fig. 1.

Fig. 2 and Table III show the normalised data and the confidence limits of these data at the 0·05-probability level. When expressing the results in this way, the number of determinations from which each average was calculated is taken into consideration and therefore all data are put on an equal basis.

TABLE II—METHODS USED

Technique	Method	Number of determinations				
		Cu	Cr	Mn	Hg	Total
Spectrography	Graphite, dc or ac arc, gallium carrier	10	10	10	10	40
	Graphite, spark	15	10	10	5	40
	Copper, spark	—	5	5	5	15
	Graphite, no details	5	5	5	—	15
	No information	4	4	4	2	14
						124
Spectrophotometry	Neocuproïne	15	—	—	—	15
	8-Hydroxyquinoline (oxine)	5	—	—	—	5
	Sodium diethyldithiocarbamate	15	—	—	—	15
	Sym-D-diphenylcarbazide	—	30	—	—	30
	8-Hydroxyquinaldine (2-methoxyline)	—	5	5	—	10
	Oxidation to permanganate	—	—	35	—	35
	Dithizone	—	—	—	35	35
	No information	8	8	8	3	27
						172
Polarography	Sodium chloride + EDTA	5	—	—	5	10
	Ammonium chloride + aqueous ammonia	5	—	—	—	5
	Potassium chloride	5	10	4	—	19
	Nitric acid	10	—	—	5	15
	Calcium chloride	—	5	—	—	5
	Hydrochloric acid	—	5	—	—	5
	EDTA	5	—	—	—	5
	Sodium or potassium cyanide	—	—	15	—	15
	Sodium hydroxide	—	9	—	—	9
	Potassium hydroxide + triethanolamine	—	—	10	—	10
	Potassium nitrate	—	—	—	10	10
	No information	2	2	2	2	8
						116
Activation	Direct γ-spectrometry	20	5	20	20	65
	Same after separation of mercury	—	10	—	—	10
	Radiochemical separation	10	10	5	—	25
	Analysis of decay curve	—	—	5	—	5
	No information	9	9	8	8	34
						139
Total number of determinations		148	142	151	110	551

The formulae used for the calculations[3] were the following (x_i = individual

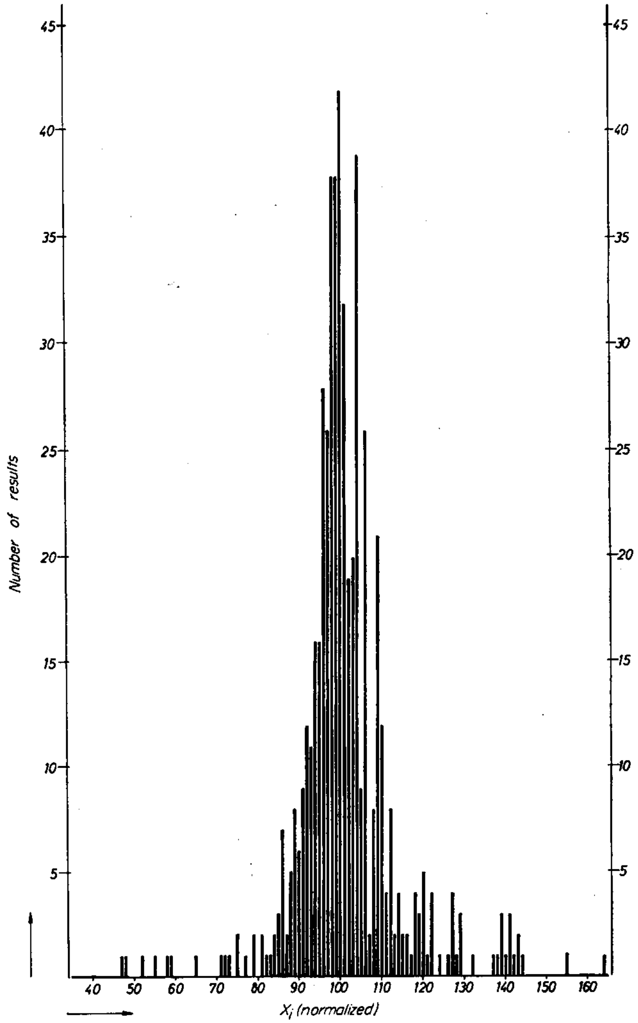

FIG. 1.—Frequency of occurrence for all of the results obtained plotted at 1% intervals.

results; n = number of results; t = Student's factor for n − 1 degrees of freedom at the 0·05-probability level):

Average: $\bar{x} = \frac{\Sigma x_i}{n}$

Standard deviation of single determination: $s = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n - 1}}$

Standard deviation of average: $\bar{s} = \frac{s}{\sqrt{n}}$

Confidence limits of single determination: $x_i(95\%) = \bar{x} \pm ts$

Confidence limits of average: $\bar{x}(95\%) = \bar{x} \pm t\bar{s}$

Table III.—Normalised results and confidence limits
(n = number of determinations; $\bar{x}$ = average; ts = standard deviation of single determination at 0·05-probability level;
t$\bar{s}$ = standard deviation of average at the same probability level)

Element	Lab.	Technique															
		Spectrography				Spectrophotometry				Polarography				Activation			
		n	$\bar{x}$	ts	t$\bar{s}$	n	$\bar{x}$	ts	t$\bar{s}$	n	$\bar{x}$	ts	t$\bar{s}$	n	$\bar{x}$	ts	t$\bar{s}$
Cu	A	5	88·2	34·7	15·5	5	100·0	2·4	1·1	5	97·5	26·0	11·7	—	—	—	—
	B	5	121·9	52·2	23·3	5	101·2	2·4	1·1	5	110·9	21·3	9·7	5	101·6	11·1	5·0
	C	3	100·9	118·0	68·8	3	103·1	3·0	1·7	2	105·7	108·0	77·5	8	103·7	10·3	3·8
	D	5	102·0	39·7	17·7	5	99·1	2·8	1·2	5	97·2	3·1	1·4	5	110·1	3·1	1·4
	E	5	95·1	7·4	3·3	5	97·5	11·6	5·3	5	95·9	5·7	2·6	10	99·4	9·8	3·2
	F	5	134·1	64·1	29·4	5	100·8	5·0	2·2	—	—	—	—	1	54·8	—	—
	G	5	92·7	24·7	11·1	5	102·8	17·2	7·8	5	102·8	13·3	5·8	5	129·0	23·9	10·5
	H	—	—	—	—	5	99·6	3·9	1·7	5	95·1	6·0	2·7	5	95·4	25·7	11·7
	I	1	71·1	—	—	5	99·1	8·6	3·9	—	—	—	—	—	—	—	—
	All	34	104·3	42·9	7·3	43	100·5	6·2	1·0	32	100·5	15·5	2·8	39	104·2	28·1	4·4
Cr	A	5	104·2	18·3	8·0	5	99·8	3·7	1·6	5	103·0	11·8	5·3	—	—	—	—
	B	5	103·5	26·6	11·1	5	97·3	8·9	3·9	5	90·0	9·6	4·2	5	91·4	7·2	3·3
	C	3	84·0	24·5	14·2	3	100·4	5·2	3·0	2	100·6	63·5	45·8	8	101·8	7·5	2·6
	D	5	97·5	10·0	4·4	5	99·0	1·4	0·6	5	91·6	20·8	9·2	5	94·3	10·0	4·4
	E	5	95·5	12·2	5·6	5	102·9	5·3	2·7	4	98·2	3·2	1·6	10	96·2	9·3	2·9
	F	5	90·9	20·3	9·2	5	97·8	13·6	6·1	—	—	—	—	1	100·0	—	—
	G	5	98·2	39·7	17·8	5	101·8	13·9	6·1	5	101·5	9·2	4·2	—	—	—	—
	H	—	—	—	—	5	100·1	1·9	0·8	5	100·2	1·4	0·6	5	99·2	23·0	10·5
	I	1	103·0	—	—	5	93·1	10·8	4·9	—	—	—	—	—	—	—	—
	All	34	97·2	19·1	3·2	43	99·1	7·9	1·2	31	97·6	12·7	2·2	34	97·0	11·2	2·0

TABLE III (*Continued*)

Element	Lab.	Technique															
		Spectrography				Spectrophotometry				Polarography				Activation			
		n	$\bar{x}$	ts	$t\bar{s}$	n	$\bar{x}$	ts	$t\bar{s}$	n	$\bar{x}$	ts	$t\bar{s}$	n	$\bar{x}$	ts	$t\bar{s}$
Mn	A	5	107·8	13·0	5·8	5	103·0	5·8	2·6	5	94·1	0·0	0·0	—	—	—	—
	B	5	108·2	33·6	15·0	5	104·6	3·1	1·4	5	127·5	22·9	10·3	5	98·3	8·7	3·9
	C	3	109·0	172·0	99·8	3	96·0	7·4	4·3	2	103·5	135·0	96·5	7	102·7	9·2	3·4
	D	5	104·5	16·9	7·5	5	100·6	3·7	1·6	5	141·1	8·6	3·9	5	118·4	8·8	3·9
	E	5	102·6	9·7	4·4	5	98·3	6·1	2·7	4	100·0	26·0	13·0	10	107·2	3·8	1·1
	F	5	112·9	54·1	24·4	5	100·2	3·1	1·4	—	—	—	—	1	115·3	—	—
	G	5	113·4	43·0	19·1	5	114·8	12·4	5·6	5	121·8	16·2	7·2	5	96·4	18·6	8·3
	H	—	—	—	—	10	106·5	3·6	1·1	5	98·8	16·4	7·2	5	97·6	23·0	10·5
	I	1	58·8	—	—	5	108·2	0·0	0·0	—	—	—	—	—	—	—	—
	All	34	106·9	34·4	5·9	48	104·1	10·0	1·6	31	113·6	37·2	6·5	38	104·1	17·0	2·8
Hg	A	5	100·0	15·0	6·7	5	97·8	5·4	2·4	5	94·7	10·7	4·7	—	—	—	—
	B	5	55·6	17·8	8·0	5	89·3	4·4	1·9	—	—	—	—	—	—	—	—
	C	1	47·4	—	—	3	95·2	6·8	3·9	2	90·8	95·0	67·3	7	114·4	7·8	2·9
	D	5	101·4	23·6	10·5	5	106·2	5·0	2·2	5	98·3	10·7	4·7	5	95·1	6·5	3·0
	E	—	—	—	—	5	98·1	3·9	1·7	—	—	—	—	10	103·1	11·7	3·6
	F	—	—	—	—	5	103·4	3·1	1·4	—	—	—	—	1	122·4	—	—
	G	5	91·8	43·0	19·1	5	100·0	2·8	1·2	5	84·6	3·7	1·6	—	—	—	—
	H	—	—	—	—	5	99·2	3·7	1·6	5	99·2	9·2	4·2	5	99·0	17·1	7·8
	I	1	105·2	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	All	22	86·1	46·1	9·8	38	98·8	10·5	1·8	22	94·0	13·5	2·9	28	104·4	17·8	3·3

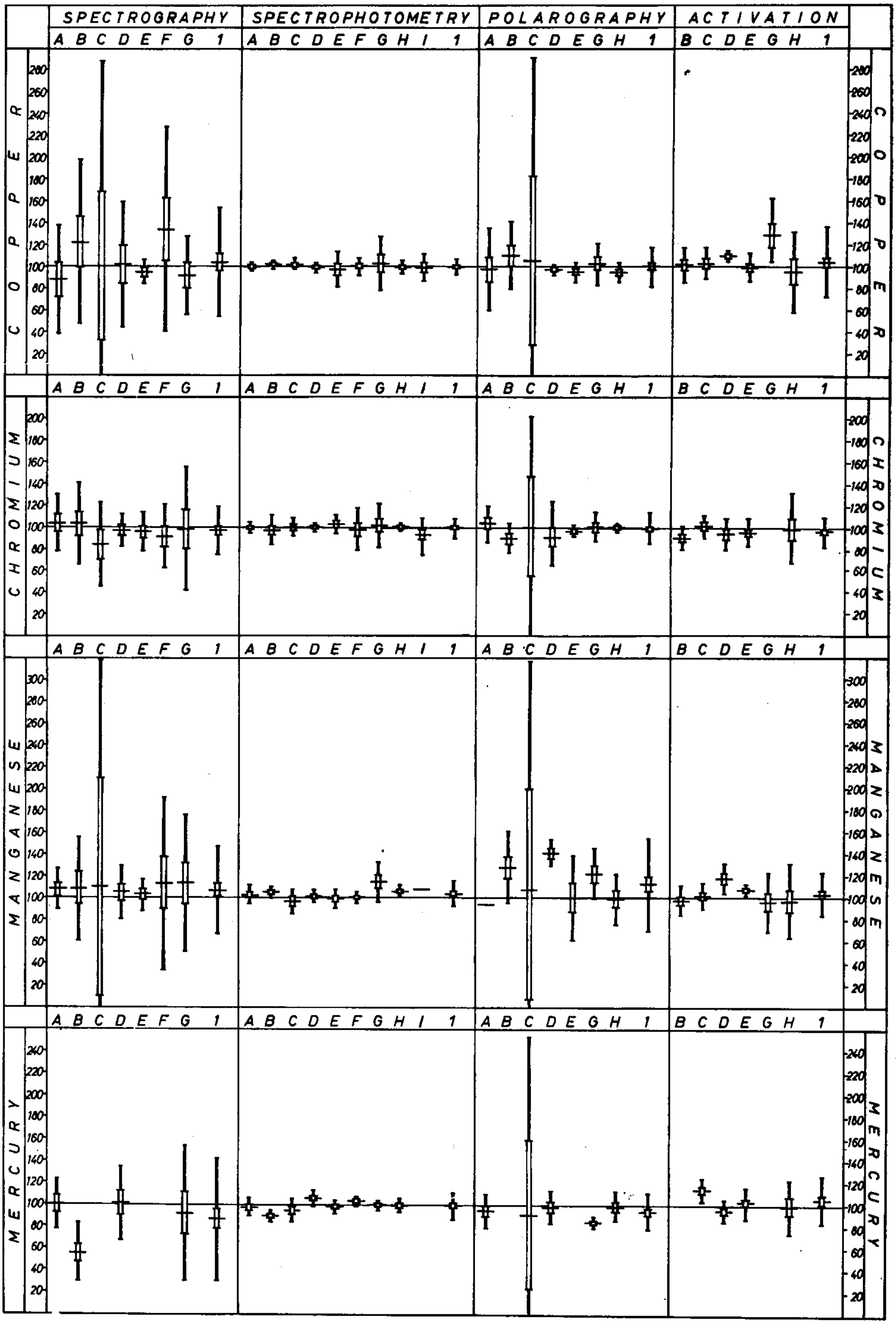

Fig. 2.—Laboratory averages and confidence limits at the 0·05-probability level for each element and each technique. The continuous horizontal lines correspond to the normalised true values (= 100). In each plot, the average is shown by the longer black horizontal line, the confidence limits of this average by the white region and those of a single determination by the total height of the plot. The plots have not been prolonged below the zero line when the calculated lower confidence limit fell below it. (A, B, *etc.*, = each laboratory; 1 = all laboratories combined).

It is obvious from the figure and the table that the sets of results containing only 2 or 3 determinations are of little significance, because the confidence limits at the probability level chosen are very wide. With this limitation, their inclusion improves the completeness of the picture.

The data illustrates the general pattern of the results and gives immediate information as to the agreement between laboratories for the same determination. Its examination shows, even when disregarding the sets with small numbers of determinations, that spectrophotometric results showed the best agreement and spectrographic the poorest, with polarography and activation between the two extremes. When the different elements analysed are compared, it can be seen that the results for copper and chromium show less spread and that their averages are nearer to the true value than those for the other two. In particular, the results for manganese appeared to be high by all techniques. It was first thought that the true value was incorrect but redetermination of the original stock solution of this element by complexometric titration and by gravimetry confirmed the value of the concentration. Further investigation by spectrophotometry (permanganate) directly on the sample solution showed that consistently high results were obtained when the working curve was made using pure manganese solutions but that the results approached the true value when this curve was prepared from solutions containing in addition to manganese the other elements present in the sample. Most probably the interference is from chromium. This phenomenon could affect all of the techniques for the determination of manganese if the standards used were calibrated by spectrophotometry, as is often done. In this respect there is no information from the laboratories concerned so that one cannot say with certainty that this is the explanation for the fact that manganese results were generally high. However, this particular behaviour is worth reporting, even if it has no relevance to the purpose of this paper, because it constitutes a warning as to the care necessary for obtaining accurate standards.

The accuracy and the precision of the techniques used have been plotted in Figs. 3 and 4. In these figures the normalised results obtained by one technique for the 4 elements have been combined.

Fig. 3 shows the distribution of the individual results when compared with the true value. It gives, therefore, a picture of the accuracy obtained with each technique. The figure shows the high accuracy of spectrophotometric results when compared with those obtained by the other techniques. It can be seen that 50% of the spectrophotometric results had an accuracy better than ±2% and that 95% of them were within the 0–10% interval. Spectrophotometry is followed by neutron-activation analysis and polarography which show a similar pattern with a little less than 30% of the results being within the 0–2% interval and about 75% within the 0–10% interval. Spectrographic results were, as would be expected from general experience, much less accurate. Only for 20% of the results was the accuracy better than ±2% and 60% of them fell within the 10% accuracy limit. It is also seen that in spectrography the maximum errors were larger; some results differed 70% from the true value while maximum deviations of 40% and 50% from the true value were found in polarography and activation analysis and not more than 20% in absorption spectrophotometry.

In Fig. 4 the deviation of each individual normalised result from the corresponding laboratory average for each element by each technique has been plotted against its frequency of occurrence. This excludes from the total picture the effects of systematic

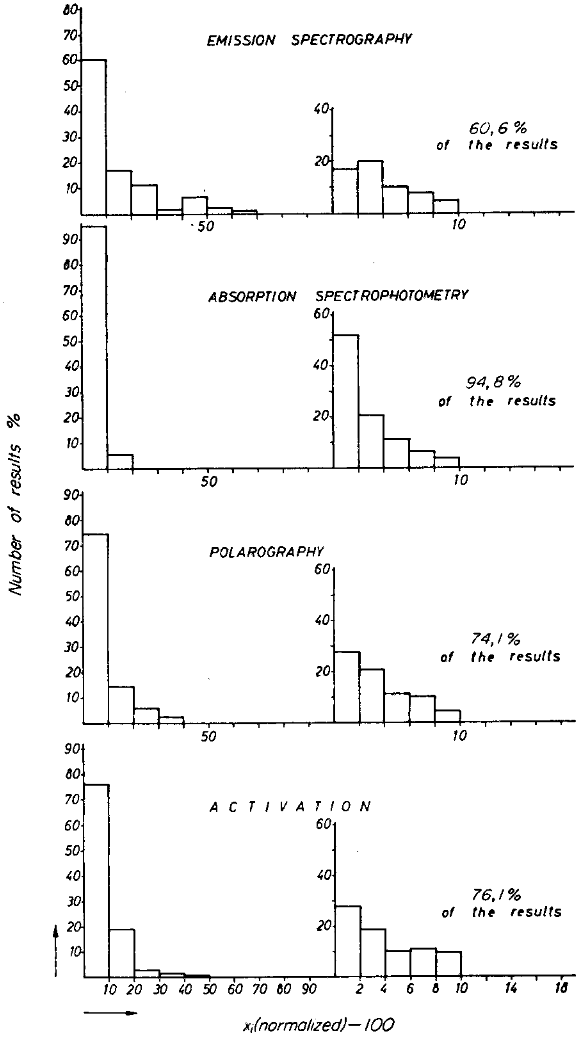

Fig. 3.—Accuracy of the normalised results. The histograms on the left side include all values reported; those on the right side show in detail (at 2% intervals) the first interval of the plots on the left.

errors, retaining at the same time the random variations present in the determinations made by one laboratory. Therefore, the figure gives a picture of the over-all precision of the results obtained by each technique in all laboratories.

It is seen again that spectrophotometry was by far the leading technique, because 84% of the results were within a ±2% deviation and no result showed a deviation of more than 10%. For about 50% of the polarographic and activation results the value was ±2% and the maximum deviation was in the range of 16%–18%. The spectrographic results showed deviations of up to ±28% and only 28% were within a ±2% deviation. It is also interesting to observe that this histogram shows much better agreement in results than is the case for the accuracy. For example, over 95% of the activation analysis results fall inside the ±8% precision limits while only about 64%

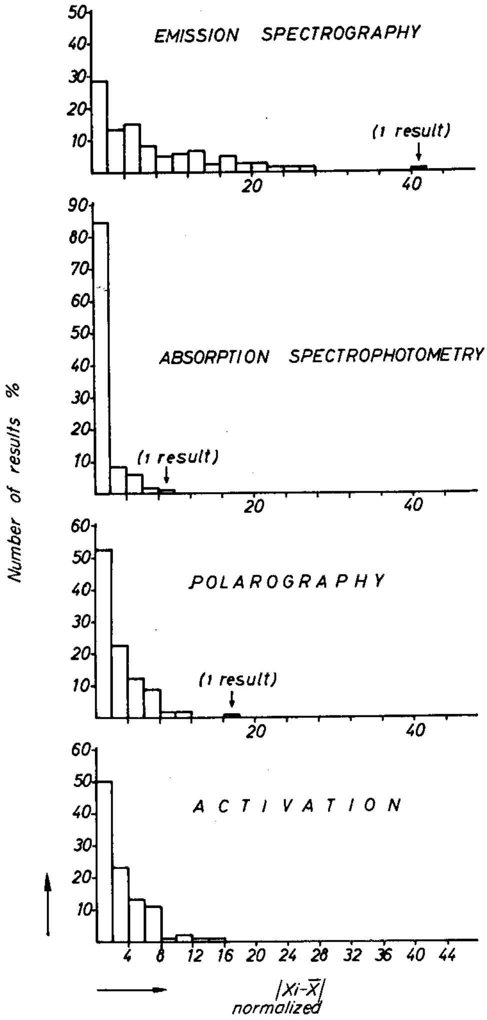

FIG. 4.—Precision of the normalised results, plotted at 2% intervals.

of them fall inside the same accuracy limits (Fig. 3). The histograms for the other three techniques are similar, showing that the internal consistency of a technique in one laboratory was better than between different laboratories. At the same time, they provide a measure of the degree to which the differences in systematic errors in different laboratories can be held responsible for the discrepancies observed.

The general evaluation of the techniques, as obtained from the results reported, is given in Table IV. The table shows the average value of all of the determinations of the 4 elements made by each technique with its corresponding confidence limits and also the values obtained when all the techniques are combined.

The values of the table can be taken as a measure of the accuracy and precision attainable in routine trace analysis. No absolute generality is claimed for this statement because the conclusions have been drawn from a particularly simple situation in which no interfering matrix was present and only 4 analytically well developed elements and 4 widely used techniques were considered. There is no doubt, however, that the numbers have meaning at least as orientation figures because they are based on a sufficiently large number of individual results to be statistically significant. The Student's factor used for over 120 determinations is 1·96 which corresponds theoretically to an infinite number.

The table shows that high accuracy and precision can be reached for the averages, even when many laboratories and techniques are involved, at the expense of increasing the number of determinations well beyond the normal practice in routine determinations. This becomes evident when comparing the values of the 3rd and 5th column of Table IV with averages in Table III for smaller numbers of determinations. Even in the case of spectrophotometry none of the averages in Table III, with about 40 determinations for each element, has an accuracy and precision better than ±1% Only combining the 170 odd results in Table IV permitted an improvement on this figure.

TABLE IV—GRAND AVERAGES BY TECHNIQUES (NORMALISED)
[Standard deviation (S.D.) at the 95% Confidence level]

Technique	Number of Detn.	Average	S.D. of single Detn.	S.D. of Average
Spectrography	124	99·8	37·8	3·3
Spectrophotometry	172	100·8	9·8	0·8
Polarography	116	102·0	26·1	2·4
Activation	139	102·5	20·4	1·8
All	551	101·3	24·3	1·0

From the point of view of agreement between individual determinations in everyday practice, the most significant data of Table IV are those in column 4, *i.e.*, the the standard deviations of a single determination estimated from all pertinent results. The values correspond to the standard deviation of a determination of any element in any laboratory. It can be seen that the expected precision is about 40% for spectrography, 25% for polarography, 20% for activation and 10% for spectrophotometry at the 0·05-probability level chosen. This means that differences of up to 80% in spectrography, 50% in polarography, 40% in activation and 20% in spectrophotometry between single determinations in two laboratories should be considered statistically possible, although the probability of the two extremes being obtained in one particular case is very small. Of course, this statement would not apply if special measures between the two laboratories had been taken to reach better agreement. When all of the techniques were combined, the standard deviation of a single determination was 25%. With the limitations as to generality pointed out above, this value can be taken as the overall precision attainable in routine trace analysis as a whole.

Acknowledgements—The collaboration of W. Rutkowski and E. Bähnk (Seibersdorf), E. Ricci (Argentina), K. Champion, J. Cosgrove, L. Dale, D. Dixon, T. M. Florence and M. Thackray (Australia), Mme. Cittanria, Mlle. Rabanel and M. Simenauer (France), T. Nakai, K. Motojima, H. Hashitani, Y. Kamemoto, T. Nakajima and H. Okashita (Japan) and other scientists and analysts not identified by name in the reports is gratefully acknowledged.

Zusammenfassung—Es werden die Resultate eines internationalen Vergleiches, der die Genauigkeit und Präzision einiger in der Spurenanalyse routinemässig verwendeter Techniken zeigen sollte, angegeben. Diese Techniken waren Emissionsspektographie, Absorptionsspektrophotometrie, Polarographie und Aktivierungsanalyse. Eine gemeinsame Probe, eine wässrige Lösung mit einem ungefähren Gehalt von 5 ppm Cu und Mn and 15 ppm Cr und Hg wurde von 9 verschiedenen Laboratorien analysiert. Die statistische Auswertung der Resultate (im ganzen 551) ergab, innerhalb der durch das Experiment begrenzten Allgemeingültigkeit, folgende Zahlen für die bei jeder Technik zu erwartende Präzision einer einzelnen routinemässigen Bestimmung: Spektrographie: ±40%, Polarographie: ±25%, Aktivierungsanalyse: ±20% und Spektrophotometrie: ±10% bei einem Wahrscheinlichkeitsgrad von 95%. Die Zahlen für die Genauigkeit verhielten sich ähnlich, obwohl die Streuung der Resultate innerhalb einer Technik grösser war. Die Präzision aller Resultate zusammen betrug ±25%.

Résumé—Résultats sont donnés d'une comparaison internationale conçue pour montrer la précision et l'exactitude de quelques techniques utilisées habituellement dans l'analyse des traces. Ces techniques sont la spectrographie d'émission, la spectrophotométric d'absorption, la polarographie et la radioactivation. Un échantillon courant, en solution aqueuse et contenant approximativement 5 p.p.m. de Cu et Mn, et 15 p.p.m. de 6r et Hg a été analysé par 9 laboratoires diffèrents. L'analyse statistique des résultats, (551 en tout), montre, avec la limitation à la généralisation dûe aux améliorations des expériences, que pour une détermination simple et s'éffectuant de la manière habituelle à chacune de ces techniques, les précisions attendues sont: spectrographie ±40%, polarographie ±25%, activation ±20% et spectrophotométrie ±10%. La justesse montre des résultats analogues bien que l'étalement des résultats soit plus important à l'intérieur d'une même technique. La prise en considération des résultats globaux montre une précision de ±25%.

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SHORT COMMUNICATIONS

Polarographic behaviour of dinitrochlorohydrin and diglycerinetetranitrate

(*Received* 15 *November* 1962. *Accepted* 14 *March* 1963)

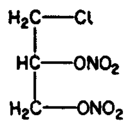
In an earlier paper[1] the polarographic determination of nitroglycerine and dinitroglycol was described and a reduction mechanism for nitroglycerine was suggested. The polarographic behaviour of dinitrochlorohydrin and diglycerinetetranitrate has now been investigated. Only the first compound appears to behave in a similar way to nitroglycerine.

EXPERIMENTAL

The Differential Cathode Ray Polaroscope (Nash & Thompson Ltd, Surbiton, Surrey, England) has been used throughout the investigations with a single cell. Dinitrochlorohydrin (DNClH) and diglycerinetetranitrate (DGTN) were prepared in the manner described by Davis.[2]

Dinitrochlorohydrin

DNClH has been investigated in the same concentration range as was used for nitroglycerine and dinitroglycol (100–400 μg/ml).[1] However, the solubility of DNClH in aqueous solutions of ammonium chloride-potassium chloride, used as base electrolyte, meant that the addition of methanol was unnecessary. The polarograms (start potential −0·2 V) were recorded in the usual way. Fig. 2 shows more clearly than does Fig. 1 that two waves are formed in the ammonium chloride-potassium chloride base solution. The addition of 10% pyridine to the base electrolyte containing DNClH resulted in the formation of single waves (as with nitroglycerine[1]) as shown in Figs. 3 and 4.



$$\begin{array}{l} H_2C—Cl \\ \quad | \\ HC—ONO_2 \\ \quad | \\ H_2C—ONO_2 \end{array}$$

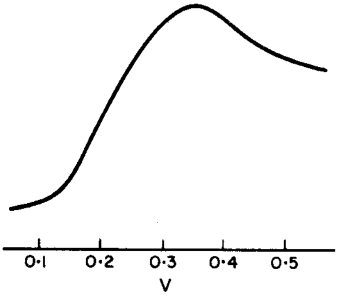


Fig. 1.—Direct current (300 μg of dinitrochlorohydrin)

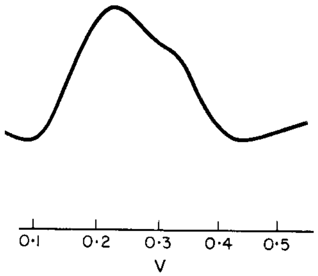


Fig. 2.—Derivative current (300 μg of dinitrochlorohydrin)

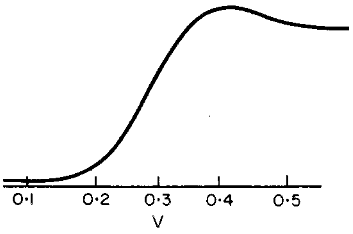


Fig. 3.—Direct current (300 μg of dinitrochlorohydrin)

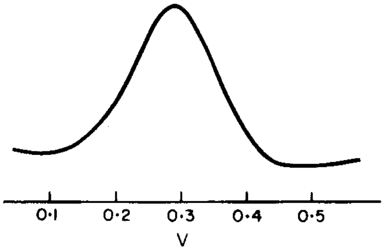


Fig. 4.—Derivative current (300 μg of dinitrochlorohydrin)

Diglycerinetetranitrate

DGTN is insoluble in the aqueous base electrolyte and the addition of 30% of methanol is necessary to ensure solubility. Polarograms with direct presentation show two poorly defined waves (see Fig. 5). Derivative presentation distinctly shows the presence of two waves in the potential range 0–0·5 V (Fig. 6). Two ill-defined waves at potentials between −0·6 and −1·0 V were also observed.

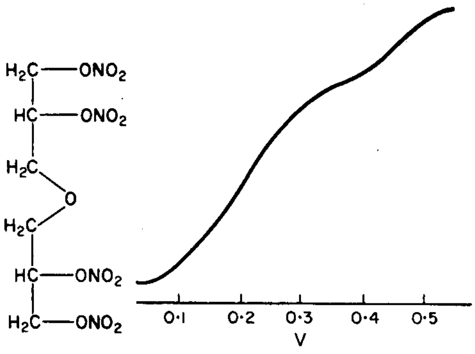


Fig. 5.—Direct current (200 μg of diglycerinetetranitrate).

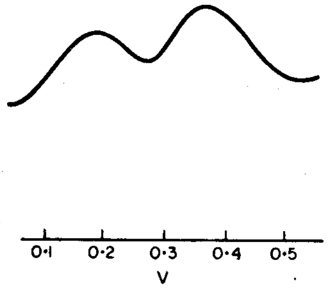


Fig. 6.—Derivative current (200 μg of diglycerinetetranitrate).

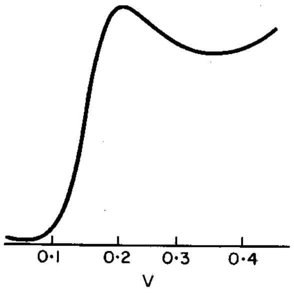


Fig. 7.—Direct current (200 μg of nitroglycerine).

The addition of 10%, 20% and 30% of pyridine to the ammonium chloride-potassium chloride base solution did not show any significant alteration in the reduction waves.

For comparison a typical nitroglycerine wave (start potential −0·05 V) is shown in Fig. 7.

DISCUSSION

The results obtained show that the polarographic behaviour of nitroglycerine and dinitrochlorohydrin is similar. Nitroglycerine is, however, reduced at the peak potential −0·27 V, whereas dinitrochlorohydrin is reduced at the peak potential −0·5 V. The addition of pyridine to diglycerinetetranitrate has no effect on its reduction (*cf.*, the addition to dinitroglycol which results in the disappearance of both of its waves[1]).

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Summary—The polarographic behaviour of dinitrochlorohydrin and diglycerinetetranitrate has been investigated. Only the first compound behaves in a similar way to nitroglycerine.

Zusammenfassung—Das polarographische Verhalten von Dinitrochlorohydrin und Diglyzerintetranitrate wird untersucht. Nur die erstere Verbindung verhält sich ähnlich wie Nitroglyzerin.

Résumé—Le comportement polarographique de la dinitrochlorohydrine et du tétranitrate de diglycérol a été étudié. Seulement le premier de ces composés se comporte d'une maniere semblable à la nitroglycérine.

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Spectrophotometric determination of hexanitrodiphenylamine in microgram quantities

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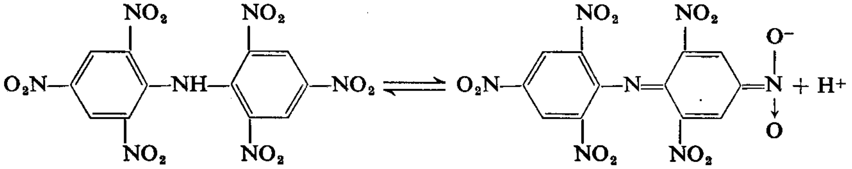
No general method appears to be known for the determination of nitro compounds by spectrophotometry, although specific methods for the determination of some individual nitro compounds have been reported.[1,2,3,4] During the course of other work it was noticed that when a concentrated solution of potassium citrate was added to an acetic acid solution of hexanitrodiphenylamine, an intense orange colour developed which appeared yellow on dilution. Further investigations showed that potassium citrate was in no way specific for the development of the colour and that the colour was only pH dependent. The intensity of absorption was maximal at pH > 4 and decreased with increasing acid content. The solution was completely colourless in strongly acidic solution. It appears that with a rise in pH above 4, the colour is derived from the anion formed by the release of a proton from the hexanitrodiphenylamine as follows:



I II

Several other resonating structures like II would also exist for the anion. The effect of increasing acid content would be to suppress the above ionisation which reaches its maximum when the pH of the solution is above 4. Adjustment of the pH could be made with alkali solutions, but in the present work all of the determinations were made using potassium citrate solution.

Under the experimental conditions mentioned above hexanitrodiphenylamine exhibits a broad absorption band in the region 320–500 mμ with λ_{max} at 418 mμ. At 418 mμ the Beer-Lambert Law was found to be valid for 2–14 μg of hexanitrodiphenylamine/ml of the final solution. Results on six different samples showed that recoveries were from 98·56 to 100·66% of the theoretical in the above range. No change in the intensity of the absorption was found for up to at least 60 min.

EXPERIMENTAL

Reagents

Hexanitrodiphenylamine stock solution: Prepared by dissolving about 10 mg of the compound (Organic Reagents for Metals, Hopkin and Williams Ltd., England) in 60–70 ml of warm glacial acetic acid (AnalaR, B.D.H. Ltd., England) and diluting to 100 ml with distilled water.

70% *Potassium citrate solution:* Prepared from AnalaR potassium citrate (B.D.H. Ltd., England).

Apparatus

Absorbance measurements were made at room temperature with a Beckman model DU spectrophotometer using matched 1·005-cm Corex cells and pH measurements were made with a Leeds and Northrup pH meter.

Procedure

Treat the hexanitrodiphenylamine solution with 6·0 ml of the potassium citrate solution, then dilute to 50·0 ml with distilled water. Measure the absorbance of this solution at 418 mμ and compare with a calibration curve derived from the absorbances of known samples at 418 mμ.

Acknowledgement—One of the authors(J. P. S.) thanks the Ministry of Scientific Research and Cultural Affairs, Government of India, for the award of a Scientific Research Training Scholarship.

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Summary—A spectrophotometric method for the determination of microgram quantities of hexanitrodiphenylamine is described. Conditions for the colour development are stated and it is suggested that the colour arises from the anion formed by the ionisation of hexanitrodiphenylamine in solutions of pH above 4.

Zusammenfassung—Hexanitrodiphenylamin färbt sich in essigsaurer Lösung bei pH > 4 intensiv orange mit $\lambda_{max} = 418 \pm 2$ mμ. Das Lambert-Beer'-sche Gesetz gilt bei 418 mü für 2 – 14 ug/ml. Die meisten Nitroverbindungen sind in essigsaurer Lösung unter den Versuchsbedingungen farblos und die Bestimmung von Hexanitrodiphenylamin erscheint neben solchen Verbindungen möglich. Das in Lösung sauer reagierende Hexanitrodiphenylamin ist oberhalb pH 4,0 maximal dissoziiert; sein Anion wird als Resonanzhydrid mehrerer Grenzstrukturen beschrieben.

Résumé—L'hexanitrodiphenylamine en solution dans l'acide acétique à des pH supérieurs à 4 donne une couleur orange intense et présente un max. à 418 ± 2 mμ. La loi de Beer et Lambert est valable à 418 mμ pour des solutions de 2 à 14 mg par ml. La plupart des composés nitrés en solution dans l'acide acétique sont incolores dans les conditions experimentales utilisées, et la détermination de l'hexanitrodiphenylamine semble possible par ce moyen, même en présence de tels compòsés. L'hexanitrodiphenylamine, qui se comporte comme un acide en solution, présente un maximum d'ionisation au-dessus de pH 4, et l'anion formé semble être un hybride de résonance entre plusieurs structures possibles.

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Coprecipitation of microgram amounts of beryllium and thorium with organic reagents

(*Received* 14 *March* 1963. *Accepted* 12 *April* 1963)

ORGANIC coprecipitants have been reported in recent years for concentrating micro and submicro amounts of metal ions.[1–6] Kuznetsov[1,2] has studied these coprecipitants extensively and suggested possible mechanisms of the phenomenon. Following the lines of Kuznetsov's studies, the recovery of micro amounts of beryllium and thorium by organic coprecipitants has been investigated and the details are presented in this communication.

COPRECIPITATION OF BERYLLIUM WITH METHYLENE BLUE AND TANNIC ACID

Beryllium can be quantitatively recovered from dilute solutions at pH 8–10 by methylene blue and tannic acid. Ammonium chloride is added to coagulate the precipitate which otherwise tends to pass through a filter paper. Though the above reagents are precipitated in the presence of ammonium chloride at a pH lower than 8–10, beryllium does not coprecipitate at any pH below 8. In the range of concentration of the reagents and ammonium chloride studied neither of the reagents is precipitated alone.

Special reagent

Standard beryllium solution: Prepared from beryllium sulphate as recommended by Sandell.[7] The working solution contains 10 μg of beryllium/ml.

Procedure

Add aliquots of the beryllium solution to 250 ml of distilled water in a Pyrex beaker, add 1 g of ammonium chloride and adjust the pH to between 8–10. Add a few drops of 10% tannic acid solution followed by 20 ml of 1% methylene blue solution, stir the solution well, then add 7 ml of tannic acid slowly. Allow the precipitate to settle, filter through a Whatman No. 541 filter paper and wash with 0·5% ammonium chloride solution at pH 8. Dry the precipitate under an infrared lamp and ignite at 500°.

Heat the residue to dense fumes with perchloric acid and make to a known volume with distilled water. Take a suitable aliquot and determine the beryllium fluorimetrically[7] using morin. A standard solution of quinine sulphate in 0·1*N* sulphuric acid is used as the reference solution. The final recoveries are corrected for a corresponding blank. Some results are given in Table I.

The application of the above method for determining microgram amounts of beryllium in sea water and in biological materials (*e.g.*, urine) is under investigation.

TABLE I.—RECOVERY OF BERYLLIUM FROM PURE SOLUTION

Beryllium added, μg	Beryllium recovered, μg
10·0	9·8
10·0	10·0
10·0	10·1
10·0	10·3
10·0	10·0
5·0	5·0
5·0	5·0
5·0	4·8
5·0	4·8
5·0	4·8
1·0	1·0
1·0	1·0

COPRECIPITATION OF THORIUM WITH METHYL VIOLET AND SPADNS

Thorium when present in a concentration range of 10^{-7}–10^{-8} g can be collected quantitatively by coprecipitating with methyl violet and SPADNS [sodium 2-(4-sulphophenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonate] in an alkaline medium. Various pH ranges were tried and the recovery of thorium was found to be complete at pH 8. Recovery of thorium at this level of concentration was determined using ^{234}Th-tracer.

Special reagents

Standard thorium solution: Prepared from thorium nitrate as recommended by Sandell.[8] The working solution contains 10 μg of thorium/ml.

^{234}Th—tracer: Carrier-free ^{234}Th was separated from 1-yr old pure U_3O_8 using an anion-exchange separation from a chloride medium.[9] To an aliquot of the chloride solution of the tracer known amounts of thorium solution were added and isotopic exchange effected by repeated evaporations with concentrated hydrochloric acid.

Procedure

Add aliquots of the thorium solution containing 1–10 μg of thorium and a known activity of ^{234}Th to 250 ml water and adjust the pH to 8. Add a few drops of 0·5% SPADNS solution and 30 ml of 1% methyl violet solution.

Precipitation is completed by adding 20 ml of 0·5% SPADNS solution. Collect the precipitate on a Whatman No. 541 filter paper, dry and ignite at 500°.

Take up the residue in concentrated hydrochloric acid and transfer to a small glass planchette, evaporate to dryness and count using a G.M. counter.

Some results are given in Table II.

TABLE II.—RECOVERY OF THORIUM FROM PURE SOLUTION

Thorium added, μg	Thorium recovered, %
10·0	99
10·0	101
10·0	97
5·0	97
1·0	99

The applicability of the above method for determining thorium in sea water is being studied.

Acknowledgement—The author wishes to thank Messrs. S. R. Desai and M. Sankar Das for valuable discussions and Dr. V. T. Athavale for his keen interest in the work.

K. SUDHALATHA

Analytical Division
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Summary—Methods for coprecipitating microgram amounts of beryllium and thorium using organic coprecipitants are reported. The former is coprecipitated with methylene blue and tannic acid at pH 8–10, while the latter is coprecipitated with methyl violet and SPADNS at pH 8.

Zusammenfassung—Methoden zur Mitfällung von Mikromengen Be^{2+} und Th^{4+} mit organischen Mitfällungsreagentien werden angegeben. Be^{2+} wird mit Methylenblau und Gallusgerbsäure bei pH 8 – 10 gefällt, Th^{4+} mit Methylviolett und SPADNS bei pH 8.

Résumé—On donne une méthode pour la coprécipitation de microquantités de Be^{2+} et Th^{4+} utilisant des coprécipitants organiques. Le premier est précipité au moyen de bleu de méthylène et d'acide tannique à pH 8–10, et le second est précipité par le violet de méthyle et le SPADNS à pH 8.

REFERENCES

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[2] *Idem*, *Radioisotopes in scientific research: Proceedings of the 1st UNESCO International Conference.* Pergamon Press, London, Vol. II, p. 264.

[3] R. L. Mitchell in J. H. Yoe and H. J. Koch, *Trace analysis.* Wiley, N.Y., 1957, p. 398.

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[5] E. E. Pickett and B. E. Hankins, *Analyt. Chem.*, 1958, **30**, 47.

[6] E. E. Pickett and W. P. Tappmayer, *ibid.*, 1962, **34**, 1709.

[7] E. B. Sandell, *Colorimetric determination of traces of metals.* Interscience Publishers Inc., N.Y., 3rd Ed., p. 311.

[8] *Idem*, *ibid.*, p. 846.

[9] K. A. Kraus and F. Nelson, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, 1955, 7, Session 9B.1, p/837, p. 113.

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

NOTICES

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

BUNDESREPUBLIK DEUTSCHLAND

9. bis 14. *September* 1963; **Hauptversammlung der Gesellschaft Deutscher Chemiker:** Heidelberg (Die Hauptvorträge sind in *Talanta*, 1963, **10**, Juni, ii, schon angedeutet worden).

GDCh-Fachgruppe "Analytische Chemie"

Vortragstagung über "*Analytische Methoden in medizinisch-biologischer Forschung und Praxis: Moderne analytische Methoden und Probleme auf dem Gebiete der Eiweißchemie*"

Montag. 9. *September*	
H. ZAHN	"*Zum heitigen Stand der Proteinchemie*"
K. SCHREIER	"*Angeborene Anomalien des Eiweißstoffwechsels und deren analtische Probleme*"
F. TURBA, H. FASOLD und G. GUNDLACH	"*Neuere Methoden zur Trennung und Reinigung von Proteinen*"
W. GRASSMANN und L. STRAUCH	"*Ein neues chromatographisches System zur Trennung von Fermenten und Proteinen*"
W. APPEL	"*Carboxymethylsephadex als Trägermaterial zur Auftrennung von Polypeptiden*"
K. WIRTH und B. HESS	"*Serumeiweißchromatographie in der klinischen Diagnostik*"
W. WÖRNER und H. MARTIN	"*Die hochspannungselektrophoretische Trennung der Lactatdehydrogenase auf Cellulose-Acetatefolie und ihre klinische Bedeutung*"
K. HANNIG	"*Neue Anwendungen der trägerfreien Elektrophorese*"
H. STEGEMANN und G. FUCHS	"*Die Bedeutung der Proteine für den Einbau von Transplantatknochen in vivo*"
V. LOESCHCKE und H. STEGEMANN	"*Die Gewinnung und Verteilung der Proteine aus Kartoffelknollen*"
Dienstag, 10 *September*	
B. HESS	"*Grundlagen der Bestimmung von Enzymaktivitäten*"
H. GREILING	"*Der Vergleich der Isoenzyme der Lactatdehydrogenase in der Synovialflüssigkeit und im Blutserum*"
H. W. GOEDDE	"*Bestimmung genetisch bedingter atypischer Serum* (Pseudo) *-Cholinesterasen*"
H. STEGEMANN, W. VOGT und K. D. FRIEDBERG	"*Eigenschaften und Reaktionen von Anaphylatoxin*"
R. RICHTERICH	"*Zuverlässigkeit von Laboratoriumsmethoden: Eiweiß- und Enzymanalytik*"
H. SCHÖN	"*Klinische Analyse, ihre Aufgaben und Probleme*"

IRELAND

Thursday–Friday 5–6 *September* 1963; Joint Meeting on **Modern Aspects of Chromatography:** *Institute of Chemistry of Ireland* and *Society for Analytical Chemistry, Scottish Section:* Rupert Guinness Hall, Dublin (see *Talanta*, 1963, **10**, July).

UNITED KINGDOM

July 1965: The *Society for Analytical Chemistry* has announced that it will hold a five-day *Conference* on all aspects of analytical chemistry at the University of Nottingham. The programme will consist of original papers,

British Standards Institution has announced the following *Amendment Slips:*

B.S. 676: 1953: *Flasks with graduated necks. Amendment No.* 2 *PD* 4900.

B.S. 700: 1962: *Graduated pipettes, Amendment No.* 1 *PD* 4909.

B.S. 2511: 1954: *Determination of water by the Karl Fischer method. Amendment No.* 2 *PD* 4897.

B.S. 3266: 1960: *Determination of conductivity, pH, water-soluble matter, chloride and sulphate in aqueous extracts of textile materials. Amendment No.* 1 *PD* 4834.

UNITED STATES OF AMERICA

Sunday–Friday 8–13 *September* 1963: **145th National Meeting:** *American Chemical Society:* New York, N.Y.

The programme for the **Division of Analytical Chemistry** is:

MONDAY MORNING, 9 *September*

General Papers

MAE I. FAUTH, MIKKEL FRANDSEN and BERNICE R. HAVLIK: *Titration Characteristic of Hexahydro-*1,3,5-*trinitro-s-triazine (RDX) and Octahydro-*1,3,5,7-*tetranitro-s-tetrazine (HMX) in non-aqueous Solvents.*

RAY E. HUMPHREY and JERRY M. HAWKINS: *Reduction of Aromatic Disulphides with Triphenylphosphine.*

BYRON KRATOCHVIL and DAVID A. ZATKO: *Ruthenium 2,2′-bipyridine Complexes as Fluorescent Oxidation-Reduction Indicators.*

THEODORE KUWANA, BARRY EPSTEIN and EDDIE SEO: *Electrochemical Generation of Solution Luminescence.*

DONALD E. LEYDEN and A. L. UNDERWOOD: *Equilibrium Studies with Dowex Chelating Resin A-*1.

D. L. LEUSSING: *Schiff Base Complexes: A Numerical Study, using a High Speed Computer, of the Nickel(II)-Pyruvate-Glycinate System.*

CARL R. STRAUSS, HENRY G. GUAY and H. JAMES HARWOOD: *Analysis of Tertiary Butyl Sulphides.*

RAYMOND B. SEYMOUR, EZEQUIEL R. RIVERA and FAITH I. SMITH: *Classification and Identification of Pure Aromatic Hydrocarbons.*

MONDAY AFTERNOON, 9 *September*

Symposium on Reflection Techniques in Analytical Spectroscopy

N. J. HARRICK: *Frustrated Total Internal Reflections: Application to Optical Spectroscopy.*

R. E. KELLER and B. KATLAFSKY: *Attenuated Total Reflections Infrared Analysis of Aqueous Solutions.*

STANLEY E. POLCHLOPEK: *Analytical Applications of Attenuated Total Reflectance.*

PAUL A. WILKS, Jr.: *Multiple Internal Reflection Techniques for the Identification of Gas Chromatograph Fractions and other Applications.*

TUESDAY MORNING, 10 *September*

Symposium on Electrode Reaction Mechanisms

RUDOLPH A. MARCUS: *Theory of Electron Transfers in Electrochemical and Chemical Redox Systems.*

RALPH N. ADAMS: *Anodic Oxidation Studies of Organic Molecules.*

TUESDAY AFTERNOON, 10 *September*

Symposium on Electrode Reaction Mechanisms (continued)

WILLIAM H. REINMUTH: *Faradaic Non-Linearity. Theory and Applications.*

HERBERT A. LAITINEN and PETER R. RHODES: *Anodic Properties of Carbon Indicator Electrodes.*

WEDNESDAY MORNING, 11 *September*

Symposium on Gas Chromatography

A. G. ALTENAU and L. B. ROGERS: *Characterisation of New Adsorbents for Gas Chromatography.*

J. CALVIN GIDDINGS: *Theory of Gas Solid Chromatography: Potential for Analytical Use and the Study of Surface Kinetics.*

DANIEL E. MARTIRE, L. Z. POLLARA and PHILLIP T. FUNKE: *Prediction of Activity Coefficients and G.L.G. Solvents Selectivities.*

H. W. HABGOOD and W. E. HARRIS: *Homologous Series Relationships in Programmed Temperature Gas Chromatography.*

H. F. MARTIN, J. L. DRISCOLL and B. J. GUDZINOWICZ: *Method for Calculating Gas Chromatographic Relative Retention Times for Phenolthiazine Derivatives on Non-Polar Liquid Stationary Phases.*

WEDNESDAY AFTERNOON, 11 *September*

Symposium on Gas Chromatography (continued)

BARRY L. KARGER and W. D. COOKE: *Effect of Column Length on Resolution.*

BARRY L. KARGER and W. D. COOKE: *Gas Chromatography Under Normalised Time Conditions Effect of Particle Size on Resolution.*

MORTON BEROZA: *Determining Chemical Structure Using Carbon-skeleton Chromatography:* A New *Technique.*

DONALD T. SAWYER and HOWARD PURNELL: *Considerations for Idealising Preparative Gas Chromatography.*

WILLIAM W. WEST: *Poly (Phenyl Ethers) as Liquid Phases for the Gas Chromatographic Separation of Complex Hydrocarbon Mixtures.*

W. B. INNES and W. E. BAMBRICK: *Rapid Hydrocarbon Analysis by Chromatography and Chemical Absorption.*

THURSDAY MORNING, 12 *September*

SECTION A

Symposium on Recent Advances in Instrumental Methods of Analysis

(Joint with Division of Chemical Education)

SECTION B

General Papers

HARRY B. MARK, JR.: *Chronopotentiometric Behaviour of Hydroquinone in Concentrated Acid Solutions.*

D. G. DAVIS and M. E. EVERHART: *Chronopotentiometry of the Bromide-Bromine Couple at Platinum and Carbon-Paste Electrodes.*

STEPHEN W. FELDBERG and CLEMENS AUERBACH: *A Model for Current Reversal Chronopotentiometry with Kinetic Complications.*

HARVEY B. HERMAN and ALLEN J. BARD: *Cyclic Chronopotentiometry. Electron Transfer followed by a Chemical Reaction.*

EMANUEL SOLON and ALLEN J. BARD: *Electrochemistry of Diphenylpicrylhydrazyl.*

GEORGE M. CAMPBELL and LARRY C. HALL: *A Chronopotentiometric and Chemical Rate Study of the Third Order Disproportionation of* $EuCl_2$, $YbCl_2$ *and* $SmCl_2$ *in Molten KCl-LiCl Eutectic.*

P. S. MCKINNEY and W. B. SCHAAP: *Resistance Compensation in Electrolytic Cells.*

THURSDAY AFTERNOON, 12 *September*

SECTION A

Symposium on Recent Advances in Instrumental Methods of Analysis

(Joint with Division of Chemical Education)

SECTION B

General Papers

J. E. HESSE and D. E. WANNER: *Determination of Certain Trace Element Impurities in Sodium Chloride to the P.P.B. Level by Extraction of Thiocarbamates and Emission Spectroscopy.*

R. KO: *Determination of Tantalum in Plutonium.*

BEN D. HOLT and JOHN E. STOESSEL: *Macro Determination of Oxygen in Metal Oxides by Inert Gas Fusion.*

R. P. WEBERLING, J. F. COSGROVE and D. J. BRACCO: *Analysis of Small Samples of Mixed Alkaline Earth Carbonates.*

R. S. BOTTEI, BR. AMBROSE and F. S. C. TRUSK: *Fluorometric Determination of Tungsten.*

JOHN M. CORLISS and ERNA J. W. RHODES: *Combustion Separation of Phosphorus in the Microdetermination of Sulphur.*

T. G. MUNGALL, J. H. MITCHEN and D. E. JOHNSON: *Determination of Microgram Amounts of Carbon in Sodium Metal.*

FRIDAY MORNING, 13 *September*

General Papers

J. P. YOUNG: *Windowless Spectrophotometric Cell for Use with Corrosive Liquids.*

S. S. YAMAMURA and J. H. SIKES: *Determination of Ammonia and Hydrazine in Nuclear Reactor Loop Samples.*

HISASHA KUBOTA, R. F. APPLE and H. L. HOLSOPPLE: *Arsenazo III, a Sensitive Spectrophotometric Reagent for Lanthanides and Actinides.*

C. H. LIU and SAMUEL SHEN: *Argentometric Titrations of Sulphide in Alkaline Ammoniacal Solutions.*
W. L. BELEW, D. J. FISHER, M. T. KELLEY and J. A. DEAN: *Polarographic Determination of the Concentration of Metal Complexes in the Organic Phase Following Solvent Extraction.*
MICHAEL N. SOLTYS and GEORGE H. MORRISON: *Determination of Microstoichiometry of Sodium-Vanadium Bronzes by "Instrumental", Activation Analysis.*
A. J. DURBETAKI and C. MILES: *Near Infrared and Nuclear Magnetic Resonance Spectroscopy in the Analysis of Polybutadiene Polymers.*

FRIDAY AFTERNOON, 13 *September*

General Papers

SOL GILMAN: *Mechanism of Electrochemical Oxidation of CO and Methanol on Platinum—I: Interpretation of the CO and "Oxygen" Adsorption Data obtained at Constant Potential.*
SOL GILMAN: *Mechanism of Electrochemcial Oxidation of CO and Methanol on Platinum—II: CO Adsorption and Desorption and Simultaneous Surface Oxidation at Constant Potential.*
L. WISH and S. C. FOTI: *Radiochemical Separation of Silver, Cadmium and Rhodium by Solvent Extraction.*
T. F. BRODASKY: *Reproducibility and Correlation of R_f on Paper and Thin Layer Plates.*
PAUL D. GARN: *Thermal Analysis—Another Critique.*
J. H. ATKINS: *A Rapid and Precise Method for Determining Surface Areas.*
C. T. LYNCH, K. S. MAZDIYASNI, J. S. SMITH and W. J. CRAWFORD: *Infrared Spectra of Transition Metal Alkoxides.*
JOHN P. DELEY, RALPH J. GIGI and ANTHONY J. LIOTTI: *Identification of Laminate Components via Attenuated Total Reflectance.*

Monday–Wednesday 16–18 *September* 1963: General Meeting on **Practice of Gas Chromatography:** *Committee E-19 on Gas Chromatography of American Society for Testing and Materials:* Hotel Dennis, Atlantic City, New Jersey (see *Talanta*, 1963, **10**, July).

A directory giving the locations of approximately 850 testing laboratories equipped and prepared to undertake testing in a commercial basis, **Directory of Testing Laboratories, Commercial and Institutional—STP 333,** has just been published by the *American Society for Testing and Materials* and is available from ASTM Headquarters, 1916 Race Street, Philadelphia, 3, Pa. (Prices if prepaid: $1.50; to ASTM members: $1.00).

A set of reliable, unique four-letter codes or CODEN for the titles of scientific periodicals, **Coden for Periodical Titles—STP 329,** has just been published by the *American Society for Testing and Materials.* It is designed to perform three important functions: (1) facilitate the storage and retrieval of information, (2) aid in the preparation of bibliographies or compilations of references, and (3) enable general communication involving references to published material. (From ASTM Headquarters, prices if prepaid: $20.00; to ASTM members: $16.00)

Four new radioactivity standards, calcium-45, chlorine-36, iodine-125 and cerium-139, are now available from the **National Bureau of Standards.** Two previously available radioactivity standards, krypton-85 and a contemporary carbon for radiocarbon dating, as well as five rock standards, have been reissued as part of a continuing Bureau programme to provide standard reference materials.

All orders for the radioactivity standards should be addressed to Miss E. ZANDONINI, Radioactivity Standard Samples, Radioactivity Section, National bureau of Standards, Washington 25, D.C.

YUGOSLAVIA

Monday 30 *September–Friday* 4 *October* 1963: **XI Colloquium Spectroscopicum Internationale:** Beograd.

Further information may be obtained from the General Secretary to the Organising Committee, Dr. VLADIMIR M. VUKANOVIĆ, Prirodno-matematički fakultet, Fizičko-hemijski zavod, Beograd, Studentski trg 16, Blok "C", Jugoslavija.

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

PAPERS RECEIVED

Analytical application of arsenazo-III.—II: Determination of thorium, uranium, protactinium, neptunium, hafnium and scandium: The mechanism of the complex-formation of arsenazo-III with elements: S. B. SAVVIN. (30 *January* 1963)

The precipitation of metal chelates from homogeneous solution: F. H. FIRSCHING. (31 *May* 1963)

Spectrophotometric determination of palladium with 1-thioglycerol and a study of palladium complex formation with four similar thio-organic compounds: R. W. BURKE and JOHN H. YOE. (31 *May* 1963)

A new oxidimetric reagent: Potassium dichromate in a strong phosphoric acid medium—I: G. GOPALA RAO and P. KANTA RAO. (3 *June* 1963)

Reactivation analysis of vanadium: Y. KAMEMOTO and S. YAMAGISHI. (5 *June* 1963)

Untersuchung des Wirkungsmechanismus von Redoxindikator 2-Hydroxy-4-amino-4'-methoxydiphenylamin und seine Anwendungen: L. ERDEY and I. KASA. (11 *June* 1963)

A new specific spot test for malonic acid: V. ANGER and S. OFRI. (11 *June* 1963)

Spot tests for pyridine aldehydes, pyridine-2-aldehyde, phenyl hydrazine, phenylhydrazones and osazones: F. FEIGL and L. BEN-DOR. (11 *June* 1963)

A data logging absorptiometer for routine uranium analysis: NORMAN P. WILBURN and WESLEY L. NICHOLSON. (14 *June* 1963)

The stability constant of the complex of Zr(IV) with EDTA: M. KYRŠ and R. CALETKA. (16 *June* 1963)

Die Bestimmung kleiner Fluormengen—III: Schnelle Bestimmung von Fluor mit Zr-Xylenolorange in Naturwässern—I: ROMAN VALACH. (17 *June* 1963)

Die Bestimmung kleiner Fluormengen—IV: Schnelle Bestimmung von Fluor mit Zr-Xylenolorange in Naturwässern—II: ROMAN VALACH. (17 *June* 1963)

Die Bestimmung kleiner Fluormengen—V: Schnelle Bestimmung von Fluor mit Zr-Xylenolorange in Naturwässern—III: ROMAN VALACH. (17 *June* 1963)

Ion exchange in non-aqueous solvents: Adsorption behaviour of uranium and other elements on strong base anion-exchange resin from acid-organic solvent media.. Methods for the separation of uranium: J. KORKISCH and S. URUBAY. (19 *June* 1963)

Selective determination of trace amounts of cobalt using the sorption of $\mathbf{Co(Phen)_3^{2+}}$ on silica: FRANTIŠEK VYBRA. (20 *June* 1963)

Some observations on the zero-current behaviour of antimony indicator electrodes: E. BISHOP and G. D. SHORT. (21 *June* 1963)

Spectrophotometric determination of chromium (III) with Chrome Zzurol S: Colorimetric studies—V: M. MALAT and M. HRACHOVCOVA. (24 *June* 1963)

Use of masking agent in chelatometric titration—III. β-Mercaptopropionic acid as a masking agent: KOICHI YAMAGUCHI and KEIHEI UENO. (24 *June* 1963)

Thermogravimetric and differential thermal analysis of europium (III) oxalate and some europium (II) salts: A. GLASNER, E. LEVY, M. STEINBERG and W. BODENHEIMER. (24 *June* 1963)

The extraction of the zirconium-Alizarin—S complex with butanol: C. DRĂGULESCU, T. SIMONESCU, SEPTIMIA POLICEC. (25 *June* 1963)

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