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SUMMARIES FOR CARD INDEXES

Analytical applications of arsenazo III—II: Determination of thorium, uranium, protactinium, neptunium, hafnium and scandium: S. B. SAVVIN, *Talanta*, 1964, **11**, 1. (V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.)

Summary—The particular analytical utility of arsenazo III is its capacity for forming especially stable complexes with certain elements. This permits determinations to be carried out in strongly acid media (for quinquevalent and quadrivalent elements—Pa, Np^{IV}, Th, Zr, Hf, U^{IV}—up to 10*M* HCl or H_2SO_4), which ensures good reproducibility, ease of working, and little interference by anions. The high sensitivity (0·1–0·01 μg/ml, molar absorption coefficient 50–150 $\times$ 10^3) is a result of the good contrast effect of the reaction (pink $\rightarrow$ emerald-green, displacement of the absorption maximum 125 mμ), the nature of the spectrum, and the possibility of reaching extreme dilutions without dissociation of the complex.

Analytical applications of arsenazo III—III: The mechanism of complex formation between arsenazo III and certain elements: S. B. SAVVIN, *Talanta*, 1964, **11**, 7. (V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.)

Summary—The two functional-analytical groups of the molecule of Arsenazo-III are present in two almost isolated conjugated systems. Complex formation with the elements takes place through only one of these: this leads to the appearance of two absorption bands in the visible region of the spectrum. The composition of the complexes for Me^{II} and Me^{III} correspond to MeR; and for Me^{IV} to MeR or MeR_2 (according to the acidity and the concentrations of the components.) Elements whose ionic radii are less than 0·7–0·8 Å give no colour reaction with Arsenazo-III. The stabilities of the complexes formed by reagents of the type of Arsenazo-III (bis-azo derivatives of chromotropic acid) with elements depend on the nature of the Me—N bond, and are determined by the extent of the system of conjugated bonds of the molecule of the reagent and the nature of the substituent.

Аналитическое применение арсеназо III–II: Определение тория, урана, протактиния, нептуния, гафния, скандия: С. Б. Саввин. (Институт геохимии и аналитической химии им. В. И. Вернадского АН СССР, Москва, СССР.)

Резюме—Особенностью аналитического применения арсеназо III является его способность образовывать с элементами особо прочные комплексы. Это позволяет проводить определение в сильно-кислых средах (для пяти- и четырёхвалентных элементов—Pa, Np^{IV}, Th, Zr, Hf, U^{IV}—до 10 M HCl или H_2SO_4), что обеспечивает хорошую воспроизводимость, удобство работы, слабое влияние анионов. Высокая чувствительность (0,1 0,01 γ) мл, коэффициент молярного погашения 50–150.10^3) определяется хорошей контрастностью реакции (розовая → изумрудно-зелёная, смещение максимума в спектре поглощения 125 mμ), характером спектра и возможностью достигать высоких разбавлений без диссоциации комплекса.

Аналитическое применение арсеназо III–III: Механизм комплексообразования арсеназо III с элементами: С. Б. Саввин, *Talanta*, 1964, **11**, 7. (Институт геохимии и аналитической химии. В. И. Вернадского АН СССР, Москва, СССР.)

Резюме—Две функционально-аналитические группы молекулы арсеназо III входят в состав двух почти изолированных сопряженных систем. Комплексообразование с элементами происходит только по одной из них; это приводит к возникновению двух полос поглощения в видимой области спектра. Состав комплексов для Me^{II} и Me^{III} соответствует MeR, для Me^{IV} в зависимости от кислотности и концентраций компонентов возможен состав MeR и MeR_2. Элементы, ионный радиус которых < 0,7–0,8 Å, цветной реакции с арсеназо III не дают. Прочность комплексов, образуемых реагентами типа арсеназо III /бисазопроизводными хромотроповой кислоты/ с элементами зависит от характера связи Me—N и определяется протяженностью системы сопряженных связей молекулы реагента и природой заместителей.

A systematic scheme for the identification of polyatomic anions by infrared spectroscopy: FARAJ R. HABA and CECIL L. WILSON, *Talanta*, 1964, **11**, 21. (Department of Chemistry, The Queen's University, Belfast, Northern Ireland.)

Summary—Using infrared absorption spectroscopy, a systematic scheme has been established for the identification of the following 16 anions: ferrocyanide, ferricyanide, thiocyanate, arsenite, periodate, salicylate, benzoate, bromate, iodate, silicate, oxalate, tartrate, phosphate, arsenate, chromate and sulphate.

Re-activation analysis of vanadium: Y. KAMEMOTO and S. YAMAGISHI, *Talanta*, 1964, **11**, 27. (Division of Chemistry, Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan.)

Summary—Re-activation analysis is applied to the determination of vanadium. After the addition of vanadium carrier to the irradiated sample, vanadium-52 is separated radiochemically pure by extraction with benzene as vanadium oxinate. The γ-ray spectrum of the vanadium-52 is recorded; the height of the photopeak at 1·44 MeV is measured and compared with that of a vanadium standard. The chemical yield of the purification step is decided by re-irradiation of the separated vanadium oxinate solution and comparing the activity of the vanadium-52 with that of a further vanadium standard. The vanadium content of the sample is determined from the activity of the vanadium-52 induced by the first irradiation and corrected for the chemical yield from the second irradiation.

Separation of the oligophosphates: HERBERT L. ROTHBART, HENRY W. WEYMOUTH and WM. RIEMAN III, *Talanta*, 1964, **11**, 33. (Ralph G. Wright Chemical Laboratory, Rutgers—The State University, New Brunswick, N.J., U.S.A.)

Summary—Mixtures consisting of orthophosphate, its linear polymers up to and including tridecaphosphate, and three cyclic polymers have been separated by ion-exchange chromatography. One of the cyclic polymers (found in polyphosphate glasses of $\bar{n} \cong 10$) is probably pentametaphosphate. Its cyclic nature has been demonstrated by end-group titrations and by paper chromatography, but attempts to determine the number of phosphorus atoms in the ring failed because of the very small amount of the compound available. Evidence is presented in support of the common assumption that the linear phosphates above the tetramer are eluted in the sequence of their increasing degree of polymerisation.

A systematic scheme for the identification of polyatomic anions by infrared spectroscopy: FARAJ R. HABA and CECIL L. WILSON, *Talanta*, 1964, **11**, 21. (Department of Chemistry, The Queen's University, Belfast, Northern Ireland.)

Резюме—Был разработан систематический метод для идентификации следующих 16 анионов при помоши инфракрасной абсорбционной спектроскопии (фероцианид, ферицианид, тиоцианат, арсенит, нерйодат, салицилат, бензоат, бромат, йодат, силикат, оксалат, тартарат, фосфат, арсенат, хромат и сульфат). Метод лучше класических химических методов для идентификации, так как он простой, быстрый и чувствительный.

Re-activation analysis of vanadium: Y. KAMEMOTO and S. YAMAGISHI, *Talanta*, 1964, **11**, 27. (Division of Chemistry, Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan.)

Резюме—Метод радиоактивационного анализа был применен для определения ванадия. После прибавления носителя для ванадия к облученому образцу, ванадий-52 выделяют в радиохимически чистой форме при помощи экстракции оксината ванадия бензолом. Снимеют γ-спектр ванадия-52; измеряют высоту фотопика при 1,44 Мэв и сравнивают её со стандартом ванадия. Содержание ванадия в образце определяют из активностей ванадия-52 возникшего при первом облучении и исправленного с помощью химического выхода определенного вторичным облучением

Separation of the oligophosphates: HERBERT L. ROTHBART, HENRY W. WEYMOUTH and WM. RIEMAN III, *Talanta*, 1964, **11**, 33. (Ralph G. Wright Chemical Laboratory, Rutgers—The State University, New Brunswick, N.J., U.S.A.)

Резюме—Было исследовано разделение смесей состоящих из ортофосфатов и их линейных полимеров включая тридекафосфаты и три циклические полимеры. Разделение этих соединий осуществлялось при помощи ионообменной хроматографии. Один из этих циклических полимеров (находящийся в полифосфатных стеклах $c\bar{n} \simeq 10$) является вероятно пентаметафосфатом. Его циклический характер был определен при помощи титрации конечных групп и хроматографией на бумаге. Так как количество исследованного соединения было незначительное неудалось определить число атомов фосфора в цикле. Было показано, что исследованные фосфаты элюируются в зависимости ина степени их полимеризации

Determination of trimetaphosphate ion in the presence of linear phosphates: HERBERT L. ROTHBART and WM. RIEMAN III, *Talanta*, 1964, **11**, 43. (Ralph G. Wright Chemical Laboratory Rutgers—The State University, New Brunswick, N.J., U.S.A.)

Summary—A method for the determination of trimetaphosphate in the presence of linear oligophosphates above the trimer has been developed. It has been demonstrated that ortho-, pyro- and triphosphate are incompletely precipitated by barium ion, while higher oligomeric linear phosphates are precipitated quantitatively. The latter species have been isolated from phosphate mixtures by anion-exchange chromatography, mixed with known quantities of cyclic phosphate, and precipitated with barium ion. A mean error of $+0{\cdot}8$ and a standard deviation of ± 3 μmole of phosphorus as the cyclic ion have been found for mixtures containing from 0 to 203 μmole of phosphorus as trimetaphosphate in the presence of 0 to 81 μmole of phosphorus as the linear polymers.

Titrimetric determination of quinol: U. A. TH. BRINKMAN and H. A. M. SNELDERS, *Talanta*, 1964, **11**, 47. (Chemical Laboratory, Free University, Amsterdam, The Netherlands.)

Summary—A critical review is presented of the literature on the titrimetric determination of quinol. For the standardisation of pure quinol solutions the cerimetric titration procedure can be recommended, but in the presence of various organic contaminants vanadate, hexacyanoferrate(III) plus zinc and dichromate are the best titrants.

The determination of thiourea using chloramine-T. G. ARAVAMUDAN and V. R. SATYANARAYANA RAO, *Talanta*, 1964, **11**, 55. (Department of Chemistry, Indian Institute of Technology, Madras-36, India.)

Summary—Chloramine-T oxidises thiourea quantitatively to urea and sulphate ion in neutral and alkaline media. The oxidation is completed within 2 min, even with a very small excess of the oxidant. Urea and ammonium ion do not interfere if the oxidation is carried out in an alkaline medium.

Determination of trimetaphosphate ion in the presence of linear phosphates: HERBERT L. ROTHBART and WM. RIEMAN III, *Talanta*, 1964, **11**, 43. (Ralph G. Wright Chemical Laboratory Rutgers—The State University, New Brunswick, N.J., U.S.A.)

Резюме—Был разработан метод определения триметилфосфата в присутствии линеарных олигофосфатов. Было показано что орто-, пиро-, и трифосфаты осаждываются неколичественно с ионом бария, в то же время высшие олигомерические линейные фосфаты осаждаются количественно. Это соединение было выделено из смеси фосфатов с помощью анионого обмена, к нему было прибавлено известное количество циклического фосфата, и осаждено с бариум ионом. Средняя ошибка $\pm 0{,}8\%$; стандартное откдонение ± 3 мк М фосфора при его определении в виде циклического иона в присутствии от 0 до 203 мкМ фосфора в виде триметафосфата и от 0 до 81 мкМ фосфора в виде линейного полимера

Titrimetric determination of quinol: U. A. TH. BRINKMAN and H. A. M. SNELDERS, *Talanta*, 1964, **11**, 47. (Chemical Laboratory, Free University, Amsterdam, The Netherlands.)

Резюме—Был представлен критический обзор литературы титриметрического определения квинола. Для стандартизации растворов чистого квинола рекомендуется цериметрическая титрация, но в присутствии органических веществ ванадаты, гексацианоферраты с цинком и дихлораты являются лучшими титрирующими веществами.

The determination of thiourea using chloramine-T. G. ARAVAMUDAN and V. R. SATYANARAYANA RAO, *Talanta*, 1964, **11**, 55. (Department of Chemistry, Indian Institute of Technology, Madras-36, India.)

Резюме—Хлорамин-Т количественно окисляет тиомочевину в нейтралной и щелочной среде образуя мочевину и сульфатый ион. Реакция протекает количественно в двух минутах и в присутствии очень малого избытка реактива. Мочевина а ион алюминия не мешают, если окисление происходит в щелочной среде.

Titration of anthranilic acid with electrolytically generated bromine: Application to coulometric determination of copper: L. G. HARGIS and D. F. BOLTZ, *Talanta*, 1964, **11**, 57. (Department of Chemistry, Wayne State University, Detroit 2, Michigan, U.S.A.)

Summary—Anthranilic acid when brominated by electrolytically generated bromine requires 3 moles of bromine per mole. Amperometric detection of the equivalence point is utilised. Small amounts of copper (0·5–2 mg) can be determined by precipitating copper anthranilate, dissolving the precipitate and titrating the liberated anthranilic acid with electrolytically generated bromine.

A simple separation of large quantities of 8-hydroxyquinoline from trace gallium: ALAN TOWNSHEND and LOUIS GORDON, *Talanta*, 1964, **11**, 60. (Department of Chemistry, Case Institute of Technology, Cleveland 6, Ohio, U.S.A.)

Summary—A simple method for the removal of large amounts of 8-hydroxyquinoline from aqueous solutions containing traces of gallium has been devised. It involves steam volatilisation of the organic compound, and gives >97% recovery of gallium as a non-volatile residue.

Titration of anthranilic acid with electrolytically generated bromine: Application to coulometric determination of copper: L. G. HARGIS and D. F. BOLTZ, *Talanta*, 1964, **11**, 57. (Department of Chemistry, Wayne State University, Detroit 2, Michigan, U.S.A.)

Резюме—Разход брома при бромовании антраниловой кислоты бромом возникавшим электролитически—тии молы брома/мол. Точка эквивалентности была исследована амперометрическии методом. Небольшие количества меди можно определить путем осаждения антранилата меди, растворением осадка и титрованием освобожденой антраниловой кислоты электролитически подготовленым бромом.

A simple separation of large quantities of 8-hydroxyquinoline from trace gallium: ALAN TOWNSHEND and LOUIS GORDON, *Talanta*, 1964, **11**, 60. (Department of Chemistry, Case Institute of Technology, Cleveland 6, Ohio, U.S.A.)

Резюме—Был разработан несложный метод метод разделения больщих количеств 8-гидроксиквинолина от следов галлия в водных растворах. Метод основан на испарении органического соединения с парами воды. Более чем 99% галия лия задержается в виде неиспарительного остатка.

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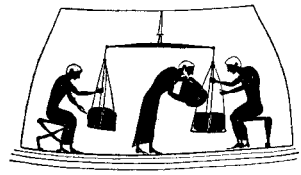

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Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA 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 language**, 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.

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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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The essential contents of each paper should be briefly recapitulated in a summary placed at the beginning of a paper, or at the end of a preliminary or short communication. This should be in the language of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

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[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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ADVISORY BOARD OF TALANTA

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

A. I. BUSEV N. TANAKA

L. B. ROGERS D. W. WILSON

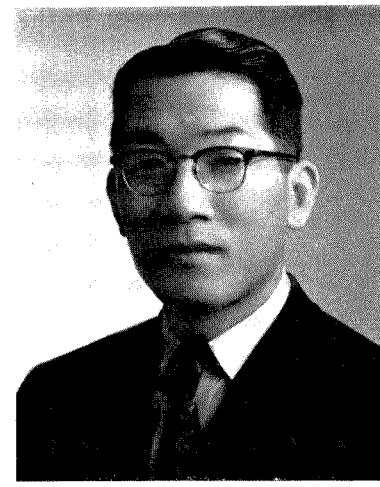
Also, they would like to record their sincere thanks for the help given by

C. E. CROUTHAMEL

who retires from the Advisory Board.

ALEKSEI IVANOVICH BUSEV (U.S.S.R.) was born in 1919. He defended a thesis for the degree of Candidate in Chemistry in 1946 and a thesis for the degree of Doctor in Chemistry in 1952. From 1953 to 1955 he worked as Lecturer and subsequently as Professor in the Chair of Analytical Chemistry, M.V. Lomonosov State University, Moscow. Since 1953 he has been a member of the Commission on Analytical Chemistry of the Academy of Sciences of the U.S.S.R. Professor Busev's most important work has been on organic analytical reagents and the analytical chemistry of the rarer metals. He has published a number of monographs on these metals.

Born in 1917, LOCKHART B. ROGERS (U.S.A.) studied at Wesleyan University for his B.A. (1939) and Princeton University for his Ph.D. (1942). Thereafter he held various positions before moving to Massachusetts Institute of Technology in 1948. In 1961 he was appointed Professor and Head of the Analytical Chemistry Division at Purdue University. He is a past Secretary-Treasurer and past Chairman of the Division of Analytical Chemistry of the American Chemical Society. His main research interests are in analytical separations (electroanalytical, gas chromatographic) and trace analysis (polarography, coulometry and fluorimetry).



NOBUYUKI TANAKA (Japan) was born in 1920 and educated at University of Tokyo, where he received his B.S. (1941). He was appointed Assistant Professor at University of Tokyo in 1947 and obtained his Dr.S. there in 1948. From 1952 to 1954 he worked as a Research Fellow with Professor I. M. Kolthoff at University of Minnesota (U.S.A.). Since 1955 he has been Professor of the Department of Chemistry at Tohoku University, Sendai. His fields of research include co-ordination chemistry, electrode kinetics and electroanalytical chemistry.

DAVID W. WILSON (U.K.) graduated at Queen's University of Belfast, and obtained his M.Sc. there, having been on the Lecturing Staff for a short time before World War II. After a period in the Armaments Research Department of the Ministry of Supply, followed by a year on the Staff of the Northampton Polytechnic in London, he moved to Sir John Cass College where he eventually became Head of the Chemistry Department in 1962. He is associated with his brother, the Editor-in-Chief of TALANTA, as joint editor of the multi-volume work *Comprehensive Analytical Chemistry*. He is closely connected with the Society for Analytical Chemistry, being a past Secretary and now Chairman of its Microchemistry Group, and also an Assistant Secretary of the Society.

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ANALYTICAL APPLICATIONS OF ARSENAZO III—II*

DETERMINATION OF THORIUM, URANIUM, PROTACTINIUM, NEPTUNIUM, HAFNIUM AND SCANDIUM

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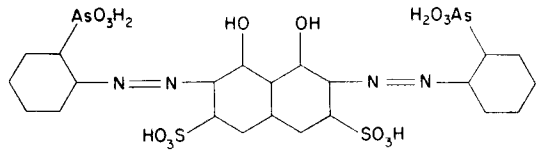
Summary—The particular analytical utility of arsenazo III is its capacity for forming especially stable complexes with certain elements. This permits determinations to be carried out in strongly acid media (for quinquevalent and quadrivalent elements—Pa, Np^{IV}, Th, Zr, Hf, U^{IV}—up to 10*M*HCl or H_2SO_4), which ensures good reproducibility, ease of working, and little interference by anions. The high sensitivity (0·1–0·01 μg/ml, molar absorption coefficient 50–150 $\times$ 10^3) is a result of the good contrast effect of the reaction (pink $\rightarrow$ emerald-green, displacement of the absorption maximum 125 mμ), the nature of the spectrum, and the possibility of reaching extreme dilutions without dissociation of the complex.

THE reagent arsenazo III, produced[1] in 1959, is widely used at the present time for determining thorium,[1–10] uranium,[1,2,11–13] zirconium,[2,14–16] hafnium,[17] protactinium,[18] scandium,[19,20] neptunium,[21,22] and the rare earth elements.[19] Some of the papers mentioned,[3,4,6,8,13,14] having been considered in a previous review[2] are not discussed in the present paper.



PROPERTIES OF ARSENAZO III

Arsenazo III is a dark red powder, moderately soluble in water to give a pink solution. The solutions are stable for an unlimited time in air. Arsenazo III gives colour reactions (violet, blue, and green) in the range from pH 4 to 10*M* HCl or H_2SO_4 with more than 20 elements.[2] The main distinguishing characteristic of the reagent is its capacity for forming particularly stable metal chelate complexes, their stability exceeding that of the corresponding arsenazo I complexes by more than two or three orders of magnitude.[23]

The high stability of the complexes permits the elements to be determined in strongly acid media at high dilution and in the presence of complex-forming anions—phosphates, sulphates, fluorides, complexone III, and the like. All this permits the analysis to be considerably simplified, making it more reliable and selective. In many cases, it is not necessary to isolate in the pure state the element to be determined; the determination is carried out directly on a solution obtained by dissolving in acids the sample to be analysed.

* Part I—see ref. 2.

The sensitivity of the colour reactions is of the order of 0·1–0·01 μg/ml of the element. The molar absorption coefficient for multiply charged elements is of the order of 50–150 $\times$ 10^3. Methods for ensuring the necessary selectivity of the reactions have been discussed previously.[2]

METHODS FOR DETERMINING THE ELEMENTS

Thorium

Methods have been previously been described for determining micro-amounts down to 0·01 μg of thorium,[3] thorium in zircons,[4] in rocks (down to 0·0001% of Th),[6] and in Nb-containing products, *etc.*[8]

In the determination of thorium in the presence of zirconium, oxalic acid is added to bind the latter[1]; the determination is carried out in 2·5–3*M* HCl. In the absence of zirconium, the determination is carried out in 1:1 HCl ($\sim$6*M* HCl) and no oxalic acid is added. The maximum sensitivity is found in 8*M* HCl. In view of the high acidity, the presence of oxidising agents, for example, nitric acid or chlorine, which are sometimes present in technical acids, is inadmissible (decomposition of the reagent). It is best to use distilled hydrochloric acid. Sometimes powerful reducing agents (for example, Ti^{III}) which also decompose the reagent, may be formed in the process of decomposing and treating the material to be analysed. In this case these must be oxidised by adding, for example, a small crystal of $KMnO_4$ followed by ascorbic acid to decolorise the solution.

In recent papers a method has been described for determining thorium in silicate rocks with a high content of Zr, Ti, rare-earth elements, and the like. The method is based on the separation of Zr, Ti, and the rare-earth elements by ion exchange on KU-2 cation-exchange resin in the H form. Titanium is not sorbed from 1*M* HCl; the rare-earth elements are eluted by 2*M* HCl, and Zr by a 0·5% solution of oxalic acid. The thorium is then eluted quantitatively by means of a saturated solution of ammonium oxalate, and is determined photometrically with arsenazo III in 5*M* HCl without separation of the oxalates. The sensitivity of the method is 10^{-3}–10^{-4}%, and the relative error is $\pm$4%; 6–8 parallel determinations can be completed in 10 hours.[7]

A method has been reported for determining thorium in metallic tungsten, and in natural and other materials.[9] The concentration and photometric determination of thorium in natural waters in which it is present in ultra-high dilution has been described.[5] The thorium is co-precipitated with methyl violet tannate, and the precipitate is filtered off and decomposed by wet ashing. The residue is dissolved in 6*M* HCl, and phenylarsonic acid is added to precipitate the zirconium. The thorium is determined photometrically in hydrochloric acid solution containing lithium chloride (to bind UO_2^{2+}) and oxalic acid. The smallest amount of thorium which can be determined in 5–20 litres of river water is 0·5–1 μg.

Uranium

Uranium may be determined after its preliminary reduction[11] to U^{IV}. An extraction-photometric method consisting of the extraction with butanol of the diphenylguanidinium salt of the complex of UO_2^{2+} with arsenazo III, from a solution containing complexone III, has been described.[13] A method has been developed for determining uranium in rocks, minerals, and solutions of complex

composition. UO_2^{2+} is extracted with a 20% solution of tributyl phosphate in carbon tetrachloride from a solution containing ammonium nitrate and Complexone-III; the uranium is re-extracted with a solution of arsenazo III and is determined photometrically. The method permits the determination of uranium when its concentration in the solution to be analysed is 0·002 μg/ml and above.[12]

UO_2^{2+} is determined photometrically at pH 1·5–3·5 and U^{IV} in 6–9*M* HCl.[1,2]

Zirconium

Zirconium is determined under approximately the same conditions as thorium—in 6–9*M* HCl.[2] If a high sensitivity is not required, the determination of Zr can be carried out at a lower acidity, for example, in 2*M* HCl. Various methods of determining it in ores, in concentrates, and in Al, Cu, Mg, Ti, Nb, and Fe alloys have been described.[14–16]

Hafnium

Hafnium is determined under approximately the same conditions and with the same selectivity as zirconium.[2] When Zr and Hf are present simultaneously, a two-pH method is possible.[2,24]

The method of determining Zr in metallic Hf is as follows: 10–20 g of metallic hafnium are dissolved in HF. The solution is fumed off with H_2SO_4. The residue is dissolved in 4*M* HCl and is transferred to a 500-ml measuring flask. An aliquot is taken containing not more than 50 μg of Hf, the solution is heated and, after cooling, 2 ml of a 0·05% solution of arsenazo III is added. The solution is made up to 50 ml with 4*M* HCl and is subjected to photometry. The content of zirconium is found from a calibration curve. Th, U^{IV}, and Ti^{IV} interfere with the determination. The accuracy of the method is ±20% at a Zr content of 0·5% and ±10% at a Zr content of 1%.[17]

Scandium

The determination of scandium is carried out in a fairly acid medium—pH 1–2—, *i.e.*, under conditions where no formation of polynuclear scandium cations takes place. This is of particularly great importance for Sc—almost as much as for Zr—to ensure reproduceability of the results and the reliability of the determinations.[19]

A method has been described for the photometric and complexonometric determination of Sc with arsenazo III as metal indicator.[20] The possibility of working in an acid medium ensures that the reaction takes place rapidly and, at the same time, that the selectivity is greater.

Lanthanum and the lanthanides

In weakly acid solutions with a pH of the order of 1·5–3·5, Y, La, and the lanthanides form an intense blue-green coloration with arsenazo III. The sensitivity is 0·01 μg/ml of the element. A method for determining the individual rare-earth elements has been described by Savvin and Muk.[19]

Protactinium

Arsenazo III gives a colour reaction with Pa^{V} over a wide range of acidities—from slight acidity up to 5*M* H_2SO_4, 10*M* HCl or more. The complex is green, and it is stable for more than 1 day. The reaction may also be carried out by an extraction-photometric method: the complex of Pa with arsenazo III is extracted almost completely by an equal volume of isoamyl alcohol from sulphuric acid solutions with concentrations of the acid greater than 2*M*. In order to increase

the selectivity of the determination of the protoactinium, the organic phase is used for the photometric measurements.[18]

The molar absorption coefficient of the Pa–arsenazo III complex is 22×10^3 at $\lambda = 660$ mμ; in the range of concentrations investigated (0·3–3·1 μg/ml of Pa), Beer's law is applicable. The accuracy of the determination is $\pm 3{\cdot}5\%$. With a slight excess of reagent, the composition of the complex is 1:1.

The possibility of extracting the Pa–arsenazo III complex from strongly acid media ensures that the determination of protactinium is highly selective. Other elements reacting with arsenazo III either do not pass into the extract at all (Fe, Ti, La, and the like) or are extracted to only a slight extent (Th, U, Zr). The effect of Th, U, and Zr is eliminated by washing the extract with a solution of oxalic acid in 3·5*M* H_2SO_4. The oxalic acid does not affect the formation and extraction of the complex of Pa with arsenazo III. Mention must be made of the favourable action of sulphuric acid itself, which binds many elements in the form of stable complexes, and, consequently, increases the selectivity of the determination of protactinium.

The chemical analogue of protactinium—niobium—does not react with arsenazo III under these conditions. There is therefore a possibility of determining protactinium in the presence of elements (Nb, Zr, *etc.*) which are always present in uranium ore, and which accompany protactinium when it is isolated.

The procedure is as follows:[18] 0·2–1 ml of the initial sulphuric acid solution containing 1–10 μg of Pa is placed in a 5-ml tube with a ground-in stopper and is treated with 0·8 ml of a $10^{-4}M$ aqueous solution of arsenazo III and concentrated H_2SO_4 in such an amount that the final acidity is 3·5–4*M* with respect to H_2SO_4. Extraction is carried out with 2 ml of isoamyl alcohol previously saturated with 3·5*M* H_2SO_4.

After separation of the layers, the extract is transferred into a centrifuge tube and the aqueous phase is extracted with a further 1 ml of isoamyl alcohol. The extracts are combined and centrifuged in order to achieve complete separation of the phases. After centrifuging, the extract is transferred to a 10-mm cuvette and is examined photometrically at 660 mμ against an extract of the reagent alone obtained under the same conditions as the extract of the material to be analysed. The content of protactinium is found from a calibration curve (Fig. 1).

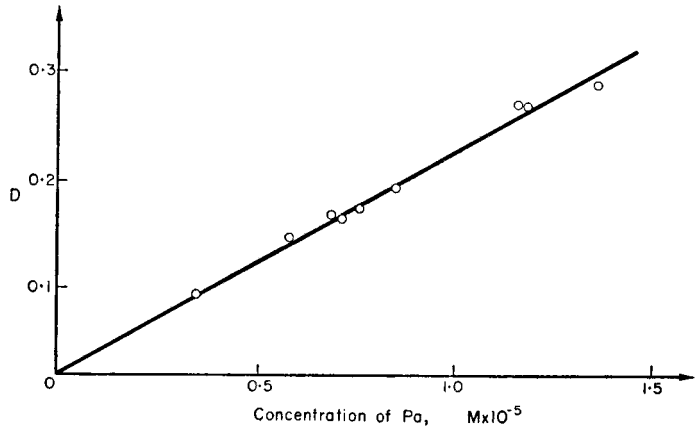


FIG. 1.—Calibration curve for the determination of protactinium. (Concentration of arsenazo III, $2{\cdot}3 \times 10^{-5}M$.)

When Pa is determined in the presence of Th, U^{IV}, and Zr, the extract is washed before centrifuging with one or two 1-ml portions of a 0·5*M* solution of oxalic acid in 3·5*M* H_2SO_4. The amount of reagent is increased by a factor of 1·5–2.

Neptunium

A method has been described for determining quadrivalent neptunium with arsenazo III.[21] Np^{IV} with arsenazo III in 1–5*M* HNO_3 forms a green complex, an excess of reagent causing the colour to change to violet. At a concentration of nitric acid of more than 5*M* the coloration of the complex is pale blue and in 8*M* acid it is dark blue. Colorations are formed instantaneously, and are stable for at least some hours. In the presence of iron sulphamate no decomposition of the reagent in concentrated nitric acid solutions takes place. Over the range 4–6*M* HNO_3 the intensity of the coloration changes little with a change in the acidity. The molar absorption coefficient at 665 mμ is approximately 100,000.

Since other quadrivalent elements—U^{IV}, Pu^{IV}, Th, Zr—also form coloured compounds in strongly acid media, these must be removed. This is achieved by extracting the elements with appropriate organic solvents, the NpO_2^+ ions, which are not readily extracted, remaining in the aqueous phase. The neptunium is then reduced to Np^{IV} and is determined with arsenazo III.

For the extraction of U, Pu and Th, Chudinov and Yarkoplev[21] have used a 0·25*M* solution of di-2-ethylhexyl orthophosphate in carbon tetrachloride, which extracts these elements from 0·5*M* nitric acid with a partition coefficient of the order of 100–1000. When quinquevalent neptunium stabilised with sodium nitrite is extracted under the same conditions, only about 2% of the original amount of Np passes into the organic phase. At a ratio of Np to interfering elements of about 1:2000, extraction must be carried out three times to eliminate the latter completely. About 10% of the original amount of Np is lost during the extraction process.

The stabilisation of Np^V is carried out by oxidising it to NpO_2^{2+} with potassium permanganate, and subsequently reducing it to NpO_2^+ with sodium nitrite. Oxidising agents (for example, potassium dichromate) and large amounts of reducing agents interfere with this operation, and they must therefore be removed beforehand.

The following cause no interference in the determination of 1–10 μg of Np: 4 mg of Pu, 3 mg of U, 0·5 mg of La, 2 mg of Th, 1 mg of Zr, 0·2 mg of Cr, and up to 5 mg of Mg, Al, Ca, Co, and other elements. The lower limit for the determination of Np is 0·04 μg/ml (D = 0·02 at l = 20 mm, photoelectric colorimeter, red filter). The accuracy of the determination is between 1% and 7% relative.

In the reaction of Np^V with arsenazo III a green coloration[22] is produced over the pH range 4·4–7·4. The complex has a 1:1 composition, and its molar absorption coefficient is 70,800. Complex-forming substances weaken the coloration. Since the coloration of the complex vanishes on acidification to pH 3, it may be concluded[22] that no change in the valency of the Np compound takes place during complex formation.

Zusammenfassung—Der besondere analytische Nutzen von Arsenazo-III besteht in seiner Fähigkeit, mit bestimmten Elementen besonders stabile Komplexe zu bilden. Das erlaubt Bestimmungen in stark sauren Medien (bei fünf- und vierwertigen Elementen—Pa, Np(IV), Th, Zr, Hf, U(IV)—bis 10 m HCl oder H_2SO_4), was gute Reproduzierbarkeit, leichtes Arbeiten und geringe Störung durch Anionen garantiert. Die hohe Empfindlichkeit (0,1–0,01 μg/ml, molarer Extinktionskoeffizient 50–150 . 10^3) rührt vom guten Kontrasteffekt der Reaktion (rosa–smaragdgrün, Verschiebung des Absorptionsmaximums um 125 mμ), der Natur des Spektrums und der Möglichkeit, extreme Verdünnungen zu erreichen, ohne daß die Komplexe dissoziieren.

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ANALYTICAL APPLICATIONS OF ARSENAZO III—III*

THE MECHANISM OF COMPLEX FORMATION BETWEEN ARSENAZO III AND CERTAIN ELEMENTS

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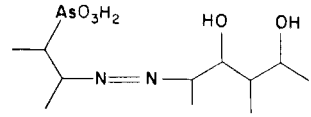
Summary—The two functional-analytical groups of the molecule of arsenazo III are present in two almost isolated conjugated systems. Complex formation with the elements takes place through only one of these: this leads to the appearance of two absorption bands in the visible region of the spectrum. The composition of the complexes for Me^{II} and Me^{III} correspond to MeR; and for Me^{IV} to MeR or MeR_2 (according to the acidity and the concentrations of the components.) Elements whose ionic radii are less than 0·7–0·8 Å give no colour reaction with arsenazo III. The stabilities of the complexes formed by reagents of the type of arsenazo III (bis-azo derivatives of chromotropic acid) with elements depend on the nature of the Me—N bond, and are determined by the extent of the system of conjugated bonds of the molecule of the reagent and the nature of the substituent.

IN recent years the attention of investigators has been attracted to analytical reagents forming particularly stable complexes with elementary cations. Among these are reagents such as complexone III (EDTA) and its analogues, forming colourless complexes and reagents giving coloured complexes—arsenazo III and its analogues, bis-azo derivatives of chromotropic acid containing various salt-forming groups.[1,2] The theory of the analytical action of reagents of the type of complexone III has been studied in relatively great detail, but that of reagents of the type of arsenazo III quite inadequately. Some preliminary observations on the mechanism of complex formation between arsenazo III and various elements have been made by the present author.[3]

The functional-analytical group responsible for the formation of complexes between arsenazo III and elements (as with the other reagents of the arsenazo class, *i.e.*, those containing arsenic and an azo group) is the following:

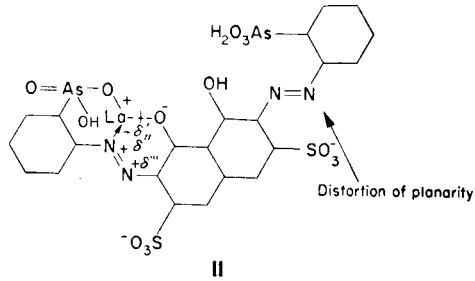


Two such groups are present in the reagent arsenazo III.

Now that further experimental material is available, the mechanism of the formation of complexes of the elements with the functional group is fairly clear.[4–18] Analogies can be drawn with similar reactions between simple inorganic compounds and other organic compounds having the same grouping.[4,13,14] Elements such as UO_2^{2+}, Th, U^{IV}, Zr, Hf, TR form a direct covalent bond with an AsO_3H_2 group and an OH group. For Al, Ti, and some other elements, chromotropic acid is also

* Part II—see ref. 2

specific and for Zr even one azo group together with a labile hydrogen atom. Depending on the nature of the reagent and, for a given reagent depending on the conditions, complex formation may take place at different groups. Earlier, for example, by analogy with the corresponding complexes of arsenazo I and thoron I[6,11–13] the following structure was proposed for the complex between La and arsenazo III:



II

A special role is played by the Me—N co-ordinate link. Besides the considerable increase in stability resulting from the formation of two six-membered rings possessing almost aromatic properties, complex formation leads to the transfer to the chromophoric centre of the molecule—the azo group—of some charge, resulting in a marked deepening of the colour of the complex. The same effect is favoured by the transfer of some negative charge to the residue of the hydroxyl group of the naphthalene ring of the reagent.[4,5] The dipole arising at the ends of the system of conjugated bonds, including the chromophoric centre—the azo group—(the magnitude of which depends to some extent on the nature of the metal and the conditions) causes a marked change in the colour of the reagent, *i.e.*, the corresponding colour reaction. A metal cation therefore here plays the role of a peculiar extremely powerful positive auxochrome. This is in complete agreement with modern views, developed, in particular, for azo dyes,[9,15,16] on the theory of the colour of organic compounds.

In the case of arsenazo III, this scheme, which is generally accepted in the literature, is again but only one of the two functional groups is capable of reaction.

Coloration of the reagent and coplanarity

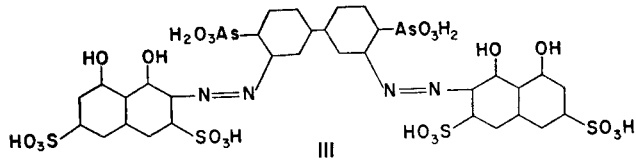
The bis-azo derivatives of chromotropic acid, in contrast to its mono derivatives, and as a result of the conjugation of the two parts of the molecule and the associated planar structure, usually possess deep colours—violet and dark blue. These compounds are unsuitable as photometric reagents. The pink coloration of arsenazo III in acid solutions is the result of a disturbance of the planar structure and the conjugation (consequent on the presence in the *o*-position to the azo group of such voluminous substituents as AsO_3H_2 groups.) The same colour effect is found in the case of certain other substituents: $—NO_2$ and $—SO_4H$.

The steric hindrance due to the arsono group is also shown by the considerable difficulty in synthesizing arsenazo III if this is carried out by the methods usually used for azo-coupling reactions.

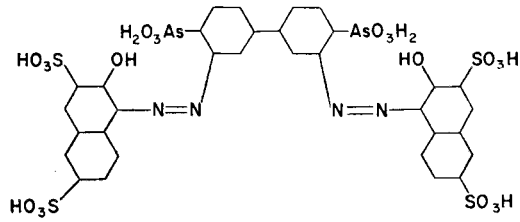
The coloration of arsenazo III in alkalis (dark blue) and in concentrated H_2SO_4 (green) is connected, in the first place, with the ionisation of the hydroxyl groups of the naphthalene nucleus and, in the second place, with the protonisation of the azo groups; this agrees well with views given in the literature.[4–6]

Absorption spectra of the reagent and the complexes

In acid solutions the absorption maximum of arsenazo III in the visible region is located at 540 mμ. The absorption spectra of complexes of arsenazo III with the elements have two maxima in the visible region—$\lambda_1 = 665$ mμ and $\lambda_2 = 610$ mμ (Figs. 1 and 2). The latter circumstance is quite unexpected: with the overwhelming majority of photometric reagents and with all reagents of the arsenazo–thoron group, including the bifunctional reagents arsenazo II and thoron II [Reagents (III) and (IV)], only one absorption band is found in the visible region. It is an



III



IV

essential feature that the characteristic shape of the spectra of the complexes of arsenazo III is retained for all the elements investigated over wide ranges of pH and ratios of the concentrations of the metal and the reagent (Fig. 2). Hence this cannot be a consequence of the simultaneous presence in the solution of two different complexes of dissimilar composition or structure. The two maxima can only be connected with the presence of two weakly interacting (dissociated) chromophoric systems in a single molecule of the reagent, different in magnitude or present in different ionic states. Similar phenomena—*i.e.*, the presence of two absorption bands in the visible region—are known for certain complex cyanine dyes having two dissociated chromophoric systems.[17]

In the case of a molecule of arsenazo III not bound in a complex, which is obviously symmetrical, both chromophoric systems, consisting in the present case of functional-analytical groups, are identical, and their absorption spectra coincide, giving a single maximum. Complex formation at *one* group disturbs the symmetry of the molecule and if the system (molecule) does not consist of a single optical unit, *two* absorption maxima appear. The maximum corresponding to the greater depth of colour, $\lambda_1 = 665$ mμ, we ascribe to the functional-analytical group directly linked with the metal and the second maximum at $\lambda_2 = 610$ mμ to the chromophoric centre (conjugated system) not directly connected with the element but, owing to a definite and, apparently, considerable, influence of the first functional-analytical group passing into a different ionic state. To be precise, we assume the transfer of some positive charge to the azo group, more in the first case and less in the second.

It is interesting that the absorption spectrum of the reagent in concentrated

H_2SO_4, where protonisation of the azo group takes place, has a single maximum at the same wavelength as in the case of a complex—665 mμ. In dilute H_2SO_4, protonisation is apparently possible at only one azo group; the symmetry is disturbed and two maxima appear, the first remaining at the same wavelength, 665 mμ. Both for the reagent and for a complex, the first maximum is considerably higher than the second. In alkaline solutions where no protonisation of the azo group takes place, the depth of the coloration is less, the absorption maximum being between 580 and 610 mμ.

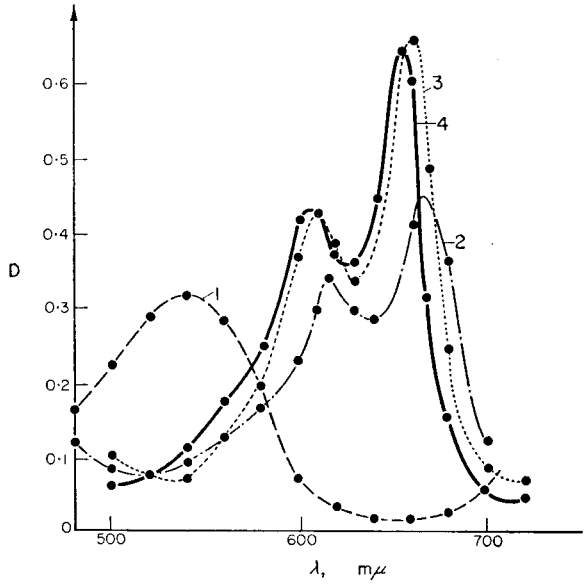


FIG. 1.—Absorption spectra.

(1) Arsenazo-III, $0{\cdot}5 \times 10^{-5}M$;
(2) Zirconium–arsenazo III complex in $9M$ HCl;
(3) Uranyl–arsenazo III complex, pH 1·5;
(4) Lanthanum–arsenazo III complex, pH 3
(SF-4 spectrometer: 10-mm cell: recorded against water)

There is, of course, also the possibility that the extremely large bathochromic effect on complex formation (from pink to green, displacement of the maximum by 125 mμ) is also connected in part with some divergence of the molecule from the non-coplanar state because of the "drawing together", as it were, of the benzene and naphthalene nuclei by the forces of the chemical bond between the metal and the complexing agent; and especially through the quite strongly expressed aromatic character of the two six-membered rings formed with the participation of the metal.

Composition of the complexes

With elements forming doubly charged cations (UO_2^{2+}, Cu, Pb, *etc.*) arsenazo III forms only complexes with a 1:1 composition. This is confirmed by data on the spectrophotometric titration of an element and the reagent, by curves of isomolar series (graphs not given here), and also by the non-dependence, in practice, of the nature of the spectrum of the complex (two absorption bands) on the Me:R ratio

in the reaction medium. For example, for molar ratios UO_2^{2+}:R of 1:1 and 10^5:1 the nature of the spectrum remains unchanged; even a 10^5-fold excess of the metal does not give rise to the formation of a complex of the composition Me_2R which, because of its symmetry, would have one absorption maximum. The two absorption maxima are retained at any acidity at which the existence of a given complex is possible.

With elements forming triply charged cations, arsenazo III again forms complexes with a 1:1 composition. This is confirmed by the same methods. With elements

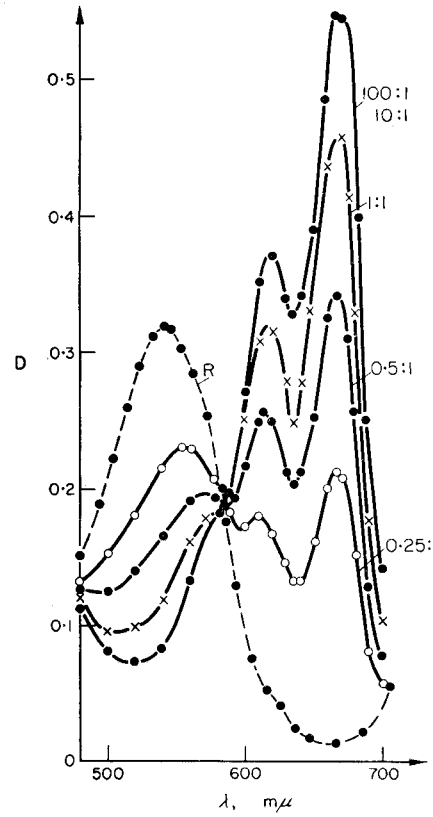


FIG. 2.—Absorption spectrum of thorium–arsenazo III complex at various M:Re ratios
(8*M* HCl: concentration of reagent $0{\cdot}9 \times 10^{-5}M$)

forming a quadruply charged cation arsenazo III forms complexes both of the composition MeR and MeR_2. A greater ratio of R to Me is impossible, not so much because valency saturation has been reached, but because of steric considerations which do not permit the co-ordination about Me^{IV} of more than two molecules of so large a ligand. However, Nemodruk and Kochetkova[18] have discussed the possibility of the formation of more highly saturated complexes.

In the spectrophotometric titration of elements forming quadruply charged cations, the point of inflection corresponding to the 1:1 and 1:2 (and, even more, the 1:3 and 1:4) compositions are not clearly expressed; the results obtained by this method are difficult to interpret. It is possible, however, to use the method

of determining the absorption of the saturated complexes. It can be seen from Fig. 3 that at a 100–1000-fold excess of thorium (composition known to be 1:1) D = 0·520. The same number of moles of thorium with a 10–20-fold excess of reagent give D = 1·15, *i.e.*, approximately twice as great. In the second case, the formation of a complex ThR_2, having a molar absorption coefficient approximately twice that of ThR may be assumed. This follows from the fact that at a high acidity, when the Th^{4+} ion has appeared quite strongly, the ionic state determining the coloration of the two co-ordinated molecules of arsenazo III is similar, and corresponds to the ionic state of the residue of the arsenazo III molecule in the 1:1 complex.

The same state of affairs is found for zirconium. At an arsenazo III concentration of $0{\cdot}9 \times 10^{-5}M$ and an excess of zirconium in $9M$ HCl, D = 0·5. At a zirconium concentration of $0{\cdot}9 \times 10^{-5}M$ and an excess of reagent in $9M$ HCl, the extinction is approximately twice as high, at D = 1·1.

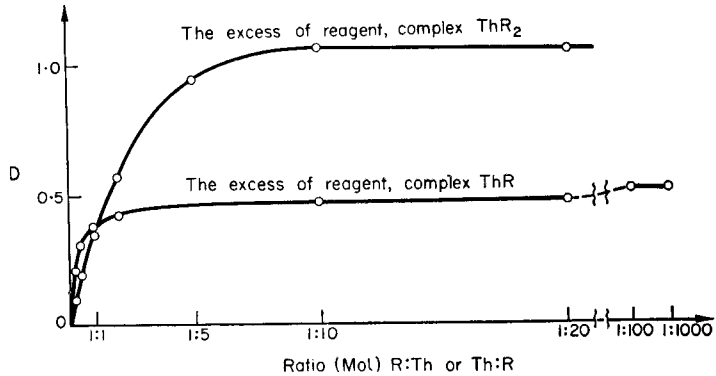


FIG. 3.—Spectrophotometric titration producing saturated complexes for the thorium–arsenazo III system
(Concentrations of MeR and MeR_2, $2{\cdot}2 \times 10^{-7}M$: recorded against reagent)

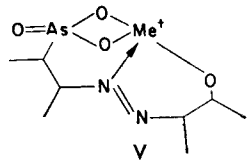
Influence of the pH

For arsenazo III and a number of elements (Th, Zr, Hf, U^{IV}, UO_2^{2+}, La, Sc, Cu) curves of isomolar series have been constructed at various values of pH. For triply and doubly charged cations, over the whole range of pH values, the composition corresponds to 1:1. For Th in $0{\cdot}1M$ HCl, without an excess of reagent there is a 1:1 composition. In $1M$ HCl and at other values of pH, with an excess of reagent the composition is ThR_2, *i.e.*, the more stable form is apparently the ThR_2 complex.

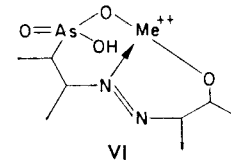
The same thing is found in the case of zirconium. In $0{\cdot}25M$ HCl and $0{\cdot}84M$ HCl the composition determined by the Ostromyslenskii—Job method is close to 1:1; but when the acidity is increased (in 2·0 and $5{\cdot}0M$ $HClO_4$) the composition is close to 1:2.

For Zr and Hf at comparable ratios of Me to R, as the acidity is increased a marked deepening of the coloration is found (violet → dark blue → green). This is apparently connected with a gradual conversion of the Zr ions from a partially hydrolysed to a purely ionic state, which leads to a marked enhancement of the positive auxochromic action of the cation. The same increase in the absorption intensity (at $\lambda = 665$ mμ), but considerably less marked, is found for Th, U^{IV}, and UO_2^{2+}—in the case of UO_2^{2+} right down to those values of the pH (~1) at which the complex begins to decompose.

On the basis of the determination of the compositions of the Me^{II}, Me^{III}, and Me^{IV} complexes and the literature data on the structure of complexes of the elements with reagents of the arsenazo group cited above, two possible structures of the complexes of arsenazo III with the elements may be assumed, fragments of which, for Me^{IV}, are illustrated in (V) and (VI):



V



VI

Structure of the complex in limits of the functional-analytical nucleus

M. P. Volynets and the author[35] have carried out experiments with Th and La to determine the number of protons liberated in the reaction with arsenazo III at various ratios of Me to R. The method of high-frequency titration was used, which permits inflections on the titration curves of the metal and addend to be determined more accurately.[19] The experiments were carried out on the VU-2A apparatus of GEOKhI AN SSSR[20] with a cell in the form of a thin-walled beaker (capacity 30 ml, diameter 23 mm), coated on the inside. The results of the titration were converted into graphs of microammeter reading versus ratio of the components in the solution (the curves are not given here). The use of this apparatus involved some limitations on the conditions of carrying out the experiment: the apparatus is sufficiently sensitive only for the titration of 10^{-2}–$10^{-4}M$ solutions. At such a concentration, and at high acidity, the separation of precipitates is possible; consequently, complex formation was studied at pH 3. Two preparations of arsenazo III were used—in the form of the Na salt and in the form of the acid. In the latter case the reagent, in the form of a mixture of the free acid and the salt, was passed through a column of KU-2 cation exchanger in the H-form. The concentration of the solution to be titrated was generally $0{\cdot}001M$, and the concentration of the titrating agent was 10 times greater.

The results obtained are given in Table I.

TABLE I.—DETERMINATION OF THE NUMBER OF PROTONS LIBERATED WHEN THORIUM AND LANTHANUM FORM COMPLEXES WITH ARSENAZO III

Ratio, *Me:R*, of components	KOH, *equivalents*			
	Th		La	
	Arsenazo III Acid	Arsenazo III Na salt	Arsenazo III Acid	Arsenazo III Na salt
1:1	3·1	2·95; 3·1	2·0	2·1; 1·9
1:2	3·85	4·2; 4·2	—	—

The results in Table I show that three protons are liberated in the formation of a 1:1 thorium complex and 4 protons in the case of a 1:2 complex. In the formation of a lanthanum complex, two protons are liberated.

Thus, the thorium complex of composition ThR has structure (V) (with one positive charge) and the ThR_2 complex has structure (VI), the remaining two valencies being compensated by a second molecule of arsenazo III. The complex of La with

arsenazo III has structure (VI). Elements forming doubly charged cations apparently also form complexes of type (VI).

Results for complexes extracted in the form of their diphenylguanidinium salt confirm the conclusions drawn. The ThR_2 (excess of reagent) and UO_2R complexes are extracted considerably more readily than the LaR and ThR complexes. In the latter case, to compensate for the positive charge of the complex, heavy hydrophobic anions must be added to the solution.[21]

Selectivity

It is possible to distinguish selectivity determined by the chemical properties of the element and selectivity determined by the nature of the reagent. In the first case, for reagents of the type R—OH the selectivity is based on the different tendencies of the ions of the elements to hydrolyse. In strongly acid media, a colour reaction is given by elements the ions of which have a considerable tendency to hydrolyse: Zr, Hf, U^{IV}, Th, Np^{IV}; in moderately acid media by UO_2^{2+}, rare earths, Bi, Fe^{III}; and in the weakly acid media by Pb, Cu, Ba, Ca, and NpO_2^+. Thus, in the determination of Me^{IV} a high selectivity is attained. The same case includes the possibility of increasing the selectivity by using masking complex-forming substances, extraction-photometric methods, and the like.[21]

The selectivity of a reagent, as is well known, is determined by the nature of the functional-analytical group. The more simple its structure, the higher its selectivity. To explain the different selectivities of reagents utilising one particular functional-analytical group, supplementary conceptions must be brought in.

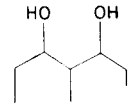
Arsenazo III gives colour reactions with a smaller number of elements than arsenazo I or arsenazo II. It is found that no colour reactions are observed for elements the cations of which have a radius less than 0·7–0·8 Å. In Table II the first column gives the element, the second the ionic radius[22] in Å, and the third the molar absorption coefficient at $\lambda = 665$ mμ.

TABLE II.—RELATION BETWEEN IONIC RADIUS AND MOLAR ABSORPTION COEFFICIENT

E^{II}	*r*, Å	K	E^{III}	*r*, Å	K	E^{IV}	*r*, Å	K
Be	0·314	~0	Al	0·55	~0	Ge	0·55	~0
Zn	0·566	~0	Ga	0·65	~0	Ti	0·60	~0
Pb	1·28	10×10^3	In	0·95	~0	Sn	0·65	~0
Ca	1·051	10×10^3	Sc	0·81	19×10^3	Hf	0·77	95×10^3
Sr	1·175	10×10^3	Y	0·93	55×10^3	Zr	0·80	120×10^3
Ba	1·395	10×10^3	Ce	1·18	47×10^3	U^{IV}	1·02	100×10^3
UO_2^{2+}	—	53×10^3	La	1·14	45×10^3	Th	1·10	130×20^3

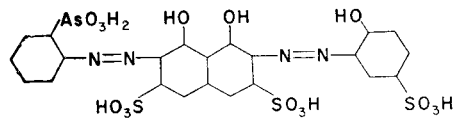
The figures suggest that apparently no ring-closure takes place when the radius of the metal ion forming the complex is relatively small. The values of K in Table II are approximate.

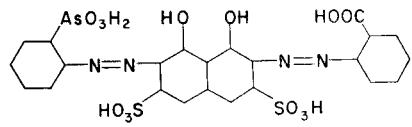
For some elements, complex formation may not take place through the functional-analytical group comprising the AsO_3H_2 group. For example, with Al and Ti the chromotropic acid grouping may form the complex:

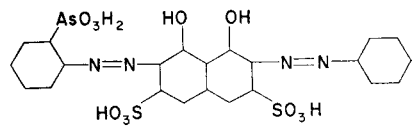


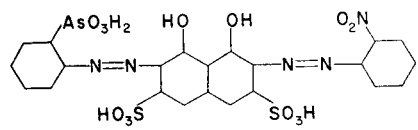
VII

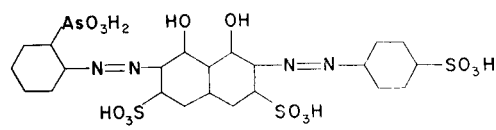
In the case of arsenazo I, arsenazo II, and unsymmetrical analogues of arsenazo III [reagents (VIII)–(XIV)], or even of reagents not containing salt-forming groups in the *o*-position to the azo group [(XV), (XVI)] this leads to the formation, within the framework of the conjugated system, of a molecule with some dipole character; and with this is associated a deepening of the colour. In the case of symmetrical reagents—arsenazo III and reagent (XVII)—no dipole is formed and no visible

VIII


IX


X


XI


XII


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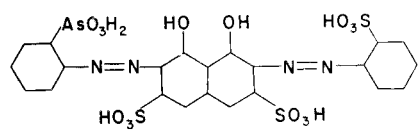
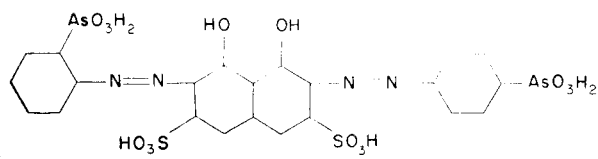
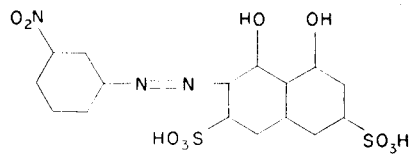
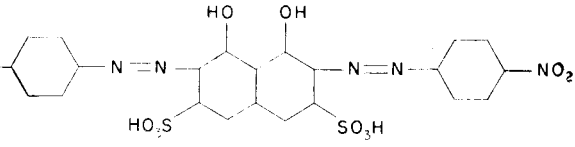


XIV


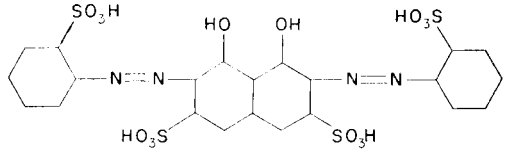
XV



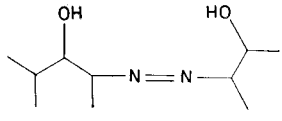
XVI



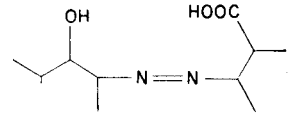
XVII



effects are found. With reagents (VIII) and (IX) complex formation may also take place through the second functional-analytical grouping:



XVIIIa

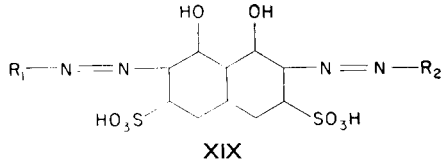


XVIIIb

which also leads to the appearance of a colour reaction.

Analogues of arsenazo III

In order to study the formation of complex formation by arsenazo III, more than 100 bis-azo derivatives of chromotropic acid and various amines of the type of



XIX

have been synthesized, no full list of them being given here. Many of the compounds obtained proved to be extremely interesting analytical reagents in themselves, and may be of interest in the determination of Nb, Zr, Hf, Th, Be, Pb, Cu, and some other elements.

Previously, results have been given (masking coefficients or specific instability indices[23]) showing that all the bis-azo derivatives of chromotropic acid containing even one *o,o'*-azo-hydroxyarsono group form considerably more stable complexes with elements than, for example, arsenazo I.[24,25] This is also found where the second benzene ring completely lacks a salt-forming group [reagents (X), (XI)]; or the group is not specific for thorium (XIII); or it is not located in the *o*-position to the azo group (XII, XIV). This shows that the marked rise in the stability of the

complexes observed with arsenazo III and other bis-azo derivatives of chromotropic acid cannot be caused by the simultaneous participation in complex formation of two functional-analytical groups and by the formation of closed rings, as is the case with EDTA.

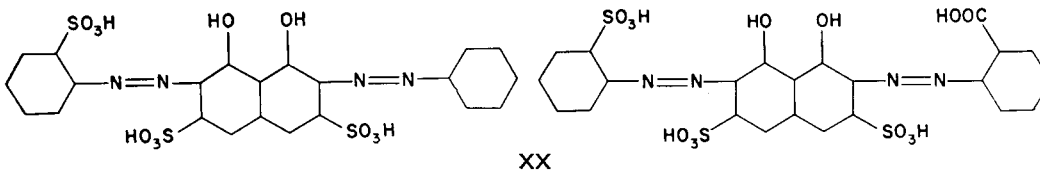
An indirect influence of the second substituent (possibly by enhancement of the tendency to protonisation of the azo group of the functional-analytical nucleus, and the marked stabilisation of the Me—N bond connected with this) is more probable. In addition, a definite effect is also attributed to the repeated occurrence in the reagent molecule of a grouping specific for a given element—if this does not lead to a marked deepening of the colour (through an enlargement of the system of conjugated bonds), to diminished solubility, and other undesirable features.

Somewhat unexpected is the extremely pronounced reduction in the reactivity of the second functional-analytical group when the first takes part in complex formation. It may be assumed that a certain mutual influence of the two conjugated systems leads, when the first group takes part in complex formation, to the transfer of some positive charge to the second azo group, thus lessening the possibility of the formation of a second Me^{n+}—N bond. The lengthening of the conjugated chain in arsenazo III as compared with arsenazo I, and the associated possibility of the distribution of a positive charge transferred to the first azo group, is possibly one of the causes of the increased tendency to protonisation of one of the azo groups and, in the end, leads to a stabilisation of the Me^{n+}—N bond and of the whole complex.

The other bifunctional reagents—arsenazo II and thoron II [reagents (III) and (IV)] have almost completely isolated conjugated systems. These reagents can form with Me^{II} a complex of the composition Me_2R having only one absorption band in the visible region, and having a considerably lower stability than the arsenazo III complexes, although higher than those of arsenazo I. The latter apparently indicates some slight interaction between the systems.

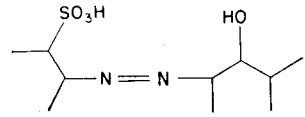
Marked stabilisation of the complexes is also found with the analogues of arsenazo III—bis-azo derivatives of chromotropic acid—containing other salt-forming substituents in place of AsO_3H_2: $-PO_3H_2$, $-SO_3H$, —COOH, —OH. The mechanism of complex formation for these compounds does not apparently differ in principle from the mechanism of the formation of arsenazo III complexes, with the essential limitation that the nature of the salt-forming substituent determines the selectivity of the action of the reagents.

A reagent[26] containing two—PO_3H_2 groups—chlorophosphonazo III—gives a colour reaction in acid solutions with U^{VI},[27] with Pa,[28,29] and with Th, Sc, Ti, and Zr.[30,31] Reagents containing —COOH and —OH groups are specific for Al, Ti, Cu, Nb, and Ta; reagents containing $-AsO_3H_2$, —COOH, and $-SO_3H$ groups have been proposed as metal indicators for the barium ion in the determination of sulphates.[32,33] Examples are reagents (IX) and (XIII). The following reagents are also promising as metal indicators:[33]



XX

They all contain as the complex-forming group of atoms:



XXI

Reagents with two of these groupings [(XVII), *etc.*[33]] form particularly stable complexes with Ba and Sr. The stability of the complex formed by reagent (XVII) with barium can be judged by the simple fact that an intensely coloured complex is formed even in acid media—down to pH 1—which is completely non-specific for barium and is not decomposed by sulphates. The sensitivity is 0·1–0·5 μg/ml of the element.[33]

SYNTHESIS OF ARSENAZO III

In the synthesis of arsenazo III, the method of increasing the activity of chromotropic acid, by treating it in the form of its cyclic salts,[4,34] is used.

Synthesis

Dissolve 60 g (0·276 mole) of *o*-aminophenylarsonic acid in 100–200 ml of water and 60 ml of concentrated hydrochloric acid. Treat the solution with 100–200 g of ice and add slowly, with vigorous stirring, a solution of 20 g of sodium nitrite (0·29 mole) in 50–100 ml of water. Destroy the excess if nitrous acid by the addition of *o*-aminophenylarsonic acid.

Dissolve 26 g (0·0717 mole) of chromotropic acid (mono- or disodium salt) in 200–300 ml of water, and add a mixture of 40 g of calcium oxide and 200–400 ml of water. Treat the mixture with 300–400 g of ice, and add the solution of diazotised *o*-aminophenylarsonic acid with stirring. Allow the mixture to stand for some hours at room temperature.

Then add 4–5 litres of water and 0·5 litre of concentrated HCl, stir the mixture carefully, and set it aside. Then filter, wash the product on the filter with 1:5 hydrochloric acid, water, and ethyl alcohol, recrystallise 2–3 times. Check the purity of the product by the quantitative reaction with thorium salts. Yield of arsenazo III 53–56 g.

Zusammenfassung—Die zwei analytisch wesentlichen funktionellen Gruppen des Arsenazo-III-Moleküls liegen in zwei fast voneinander isolierten konjugierten Systemen. Die Komplexbildung findet nur an einem davon statt; dies führt zu zwei Banden im sichtbaren Spektralbereich. Die Zusammensetzung der Komplexe für Me(II) und Me(III) entspricht MeR, bei Me(IV) MeR oder MeR_2 (je nach Acidität und Konzentration der Komponenten). Elemente mit einem Ionenradius unter 0,7–0,8 Å geben keine Farbreaktion mit Arsenazo-III. Die Stabilität der mit Reagentien vom Typ des Arsenazo-III (Bisazoderivate der Chromotropsäure) gebildeten Komplexe hängt von der Natur der Me-N-Bindung ab und wird durch die Größe des konjugierten Systems im Reagens und der Natur des Substituenten bestimmt.

Résumé—Les groupes à deux fonctions analytiques de la molécule d'Arsenazo-III sont présents dans deux systèmes conjugués presque isolés. La formation de complexe avec les éléments n'intervient que dans le cas d'un d'entre eux. Ceci donne l'apparence de deux bandes d'absorption dans la région visible du spectre. La composition des complexes pour Me^{II} et Me^{III} correspond à MeR et pour Me^{IV} à MeR ou MeR_2 (selon l'acidité et les concentrations des composants). Les éléments à rayon ionique plus petit que 0,7–0,8 Å ne donnent pas de réaction colorée avec l'Arsenazo-III. La stabilité des complexes formés par les réactifs du type Arsenazo-III (dérivés bis-azo de l'acide chromotropique) avec des éléments dépend de la nature de la liaison Me-N et est déterminée pat la proportion de liaisons conjuguées dans la molécule du réactif et par la nature du substituant.

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A SYSTEMATIC SCHEME FOR THE IDENTIFICATION OF POLYATOMIC ANIONS BY INFRARED SPECTROSCOPY

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Summary—Using infrared absorption spectroscopy, a systematic scheme has been established for the identification of the following 16 anions: ferrocyanide, ferricyanide, thiocyanate, arsenite, periodate, salicylate, benzoate, bromate, iodate, silicate, oxalate, tartrate, phosphate, arsenate, chromate and sulphate.

INFRARED spectrophotometry has been established for some time as a popular—indeed well nigh indispensible—method for the identification and determination of organic compounds. Although it has also been used for the investigation of inorganic anions, only one application to systematic qualitative analysis has been attempted.[1]

In the present work infrared spectroscopy has been applied to the systematic identification of the following polyatomic anions: ferrocyanide, ferricyanide, thiocyanate, arsenite, periodate, bromate, silicate, iodate, salicylate, benzoate, oxalate, tartrate, phosphate, arsenate, chromate and sulphate. The above anions are separated into five groups according to the M.A.Q.A. Scheme of semi-micro qualitative inorganic analysis.[2–4] A few mg of each group of anions, after being separated by its selective group precipitant, are washed with a suitable reagent, and dried; the precipitate is mixed with KBr, and a suitable disc is made. The infrared spectrum obtained permits the identification of the anions present.

EXPERIMENTAL

Apparatus and reagents

The infrared spectra were recorded on a Perkin-Elmer "Infracord" spectrophotometer, model 137. The KBr discs were prepared with a Perkin-Elmer die using an "Apex" hydraulic press with a 10-ton capacity on a ram of 2⅛ inch diameter. Before use, the KBr, which was Analytical Reagent grade, was dried at 150° for at least 24 hr. All other chemicals used in the work were AnalaR.

Procedure

The procedure, technique, and equipment have already been described elsewhere.[1,2]

RESULTS

Characteristic absorption of the various anions

Slight differences were found when the characteristic frequencies of the various anions, determined using the KBr disc technique, were compared with those obtained as mulls. These shifts can, in general, be attributed to the short range crystal forces

operating on the anions when pressed into the KBr lattice, thus perturbing the vibrational levels. These effects do not occur in the mull, where the material under investigation preserves its own crystal structure and is merely dispersed in an inert medium.

Among the compounds studied here by the KBr disc technique, were some originally investigated by the mull technique,[5] such as silica gel, silver bromate, calcium orthoarsenate, calcium phosphate (dibasic), and barium chromate.

The characteristic absorptions observed were as follows:

(1) Silver ferrocyanide: very strong, sharp absorption at 4·9 μ with two other intense bands at 6·12 μ and 6·2 μ. A deep shoulder is noted at 4·95 μ on the 4·9 μ peak.

(2) Silver ferricyanide: a very strong, sharp band at 4·73 μ, (m. and sp. with sh.)* band at 4·90 μ, and two intense bands at 6·12 μ and 6·2 μ. The main and characteristic absorption band for ferricyanide is that at 4·73 μ; some of the others probably arise from ferrocyanide, produced on grinding the precipitate of silver ferricyanide with KBr. The fading of the orange colour of silver ferricyanide in the grinding process is evidence of this reduction.

(3) *Silver thiocyanate*: a very strong, sharp band at 4·77 μ, with a shoulder at 4·82 μ.

(4) *Silver arsenite*: strong bands at 6·92 μ and 13·5 μ, with two (s, b) bands at 12·5 μ and 14·5 μ. A deep shoulder is observed at 11·3 μ and a weak band at 6·1 μ.

(5) *Silver periodate*: a strong band at 6·92 μ, two (b, s) bands having maxima at 13·65 μ, 14·45 μ.

(6) *Benzoate* (as benzoic acid): (vs. sp) 14·05 μ, 5·92 μ; (s, sp) 7·55 μ, 7·75 μ; (m, sp) 6·9, 7·04 μ, 14·9 μ; (m) 10·66 μ; (w. sp) 14·55 μ, 9·74 μ, 9·32 μ, 8·86 μ, 6·34 μ; (w) 12·3 μ, 8·46 μ; (v, w) 10·0 μ, 9·1 μ, 6·7 μ, 6·18 μ, 6·25 μ, 6·12 μ, 5·6 μ, 5·22 μ, 4·8 μ, 3·9 μ, 3·74 μ, 3·54 μ, 3·35 μ, 3·1 μ.

(7) *Salicylate* (as salicylic acid): (vs, sp) 14·25 μ, 13·1 μ, 8·65 μ, 8·26 μ, 8·02 μ, 7·75 μ, 6·95 μ, 6·85 μ, 6·75 μ, 6·05 μ; (m) 11·15 μ; (m, sp) 12·68 μ, 11·68 μ, 9·7 μ, 8·42 μ, 7·58 μ, 6·22 μ; (w) 11·48 μ, 10·35 μ, 9·2 μ, 7·25 μ, 6·35 μ, 3·85 μ, 3·5 μ, 3·35 μ, 3·1 μ; (v, w) 12·35 μ, 10·05 μ, 7·15 μ, 6·58 μ, 5·72 μ, 5·48 μ, 5·22 μ, 5·15 μ, 5·06 μ, 4·82 μ, 4·62 μ.

(8) *Silicate* (as silica gel, $SiO_2 \cdot xH_2O$): a very strong band at 9·2 μ and a weak band at 10·4 μ.

(9) *Silver bromate*: a very strong band at 12·55 μ with a shoulder at 12·75 μ.

(10) *Silver iodate*: a very broad, strong band, having maxima at 13·0 μ, 13·75 μ and 13·3 μ. Medium shoulders at 12·5 μ, 14·0 μ and 14·2 μ are also observed.

(11) *Calcium oxalate*: (vs) 6·18 μ; (s, sp) 7·25 μ; (s, sp) 7·6 μ; (s, sp) 12·72 μ.

(12) *Calcium tartrate*: (m) 3·86 μ; (vs) 6·3; (vw) 6·75; (s, sp) 7·24, (sh) 7·0, (sh) 7·15, (m, sp) 7·52, (m, sp) 7·82; (w, sp) 8·1, (vs, sp) 8·72, (vs, sp) 9·42, (m, sp) 9·9, (m) 10·4, (vw) 10·82, (vw) 11·28, (vw) 11·76, (m, sp) 12·2, (m) 14·0.

(13) *Calcium orthoarsenate*: a (vs, vb) band at 11·9 μ with a shoulder at 11·3 μ.

(14) *Calcium phosphate (dibasic)*: a very broad, strong band, having maxima at 9·7 μ, 9·35 μ and 8·9 μ.

(15) *Barium chromate*: (s) 10·60 μ, (vs) 11·10 μ, (vs) 11·45 μ, (vs) 11·60 μ.

* m = medium sp = sharp sh = shoulder s = strong b = broad w = weak v = very.

(16) *Barium sulphate*: (vs) 8·48 μ, (vs) 8·95 μ, (vs) 9·25 μ, (m, sp) 10·15 μ.

Note: Absorption bands caused by reagents used in the course of analysis, such as the bands at 6·1 μ, 6·2 μ and 7·25 μ, are neglected.

Qualitative studies on mixtures of anions in groups

It would appear from the foregoing results that the infra-red absorption spectra of the anions under study could provide a useful method for their identification either alone or in mixtures:

Group 1: *Ferrocyanide, ferricyanide, thiocyanate, arsenite, periodate*: In a mixture containing all of these anions, identification of either arsenite or periodate was found impossible; however, if only one of these two is present alone [Fig. (1)] identification is possible. Ferrocyanide, characterised by its 4·9 μ absorption band, is always found wherever ferricyanide is present in the mixture. This band shows itself either as a shoulder on the thiocyanate peak, or separate, when present in higher ratio.

Ferricyanide, characterised by its 4·73 μ absorption band, may give a separate band or a shoulder on the thiocyanate peak, depending on the ratio of ferricyanide to thiocyanate.

Thiocyanate is identified either by its 4·77 μ absorption band; by the twin bands with ferrocyanide; or by the shoulder at 4·82 μ which at increased concentration develops into a new peak. This depends on the ratio of thiocyanate to the complex cyanide in the mixture and on the increase of the transmittancy of the disc.

Group 2: *Salicylate, benzoate*: For a mixture of salicylic and benzoic acids, the spectrum shows the characteristic absorption bands of the individual anions (Fig. 2), particularly at 7·04 μ, 10·66 μ, 12·3 μ, 14·55 μ, for benzoic acid; 13·1 μ, 12·68 μ, 11·68 μ, 11·15 μ, 8·65 μ, 8·26 μ, 8·02 μ, 6·75 μ for salicylic acid.

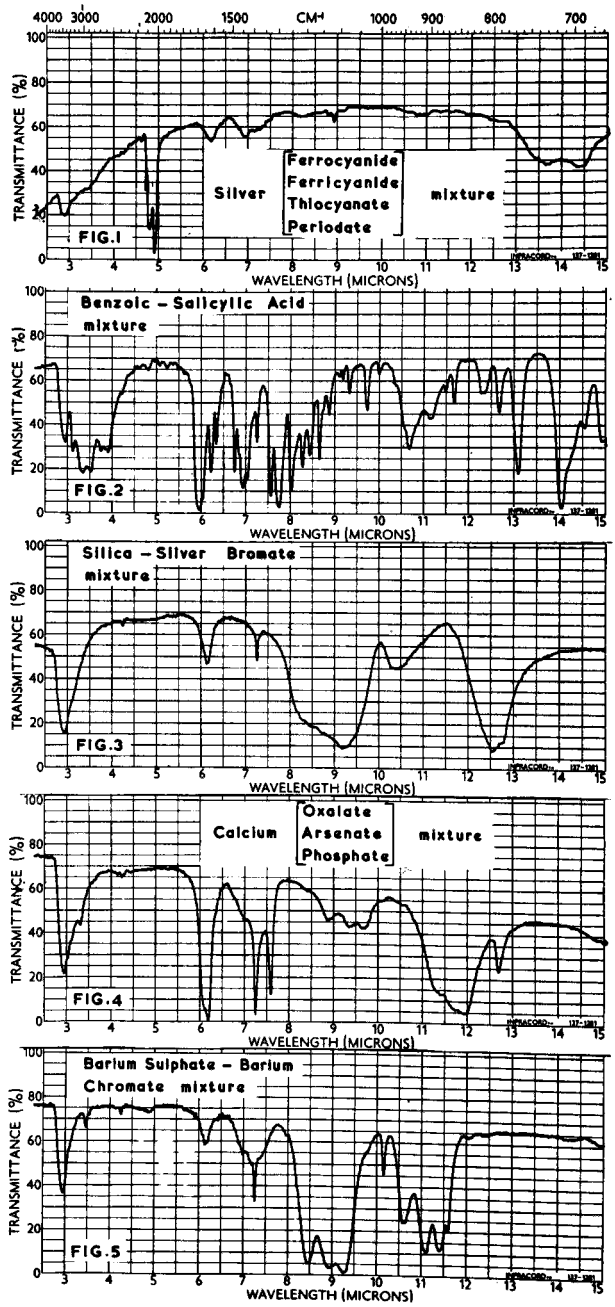
Group 3: *Bromate, silicate, iodate*: In a spectrum of a mixture of these three anions, only the presence of silicate and iodate can be detected, because the bromate peak is masked by the broad iodate band. When the bromate-iodate ratio in the mixture is increased, a change in the shape of the iodate band is observed which may be taken as evidence of the presence of bromate. Fig. 3 shows a spectrum of a mixture of silicate and bromate.

Group 4: *Oxalate, tartrate, phosphate, arsenate*: In a spectrum of a mixture of oxalate, phosphate and arsenate, the three anions can be identified (Fig. 4) from their characteristic absorption bands. Although a spectrum of all four anions of this group showed overlap of some bands, identification of the four individual anions is, however, possible by the following: oxalate by the 12·72 μ band; tartrate from the 14·0 μ band; phosphate and arsenate from their characteristic absorption bands (which may undergo slight modification in mixtures.)

Group 5: *Chromate, sulphate*: A spectrum of these two anions exhibits (Fig. 5) the characteristic absorption bands of the individual anions. No overlapping of the bands is observed.

DISCUSSION

Although attempts were made to use other existing schemes for the separation of anions[6–8] as the basis for this study, none of them proved satisfactory. This was caused by the accumulation of the spectral bands of many anions when precipitated in one


4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
TRANSMITTANCE (%)
Silver
Ferrocyanide
Ferricyanide
Thiocyanate
Periodate
mixture
FIG.1
WAVELENGTH (MICRONS)
Benzoic – Salicylic Acid mixture
FIG.2
WAVELENGTH (MICRONS)
Silica – Silver Bromate mixture
FIG.3
WAVELENGTH (MICRONS)
Calcium
Oxalate
Arsenate
Phosphate
mixture
FIG.4
WAVELENGTH (MICRONS)
Barium Sulphate – Barium Chromate mixture
FIG.5
WAVELENGTH (MICRONS)

FIGS. 1–5

group, and the impossibility of identifying the individual anions in the resulting spectrum. The effect of the reagents added during the course of analysis is very limited and the bands associated with them produce no interferences. Because of the decomposition at 100° of the silver salts (especially of Group 1) and the consequent accumulation of silver oxide, which tended to produce deformed spectra with poor transmittance, an alternative drying process, therefore performed in a vacuum desiccator, is recommended for this Group. Drying of Group 2 salts was done under a funnel attached to a water pump. Other groups may either be dried in an oven at 100°, or under vacuum. For oxalate and tartrate, vacuum drying is preferable. Under the above drying conditions, calcium dibasic phosphate, and calcium orthoarsenate are produced.

Washing is necessary for the elimination of strong absorptions by adsorbed reagent. Water is used for washing Group 1 precipitates; 0·04*M* HNO_3 for Group 3 precipitates; 0·04*M* ammonia for Group 4 and 5 precipitates. Washing is carried out by stirring the precipitate with the wash liquid, using a glass rod, discarding the washings after centrifuging.

The transmittances of the KBr discs of the compounds studied, were better than 80%, except for those made from silver arsenite and periodate; reasonable transmittance for these is only obtained when they are present in lower concentration in KBr. The decomposition of these two compounds, with the production of silver oxide, was also observed when their discs were subjected to infrared radiation, the discs being blackened at the end of each experiment. It is unlikely that the decomposition is brought about either by the grinding of the material with potassium bromide, or in the actual disc preparation, because clear discs could be made and stored successfully. The blackening of the disc during the duration of the experiment might be ascribed to either or both of thermal decomposition because of temperature rise of the disc, or photochemical decomposition of the material, since the disc is exposed to a wide range of wavelengths of light. The minimum wavelength given out by the source is of the order of 1000 Å, and these wavelengths could result in the partial decomposition observed.

Halides and sulphides are, of course, unsatisfactory for spectroscopic investigation, being transparent to infrared radiation. One possible further application, however, is the identification of those anions which, when treated with acid, evolve gases: a multiple-path cell could be used to achieve enhanced sensitivity. Such anions include sulphite, carbonate, hypochlorite, hypobromite.

Zusammenfassung—Mit Hilfe der IR-Absorptionsspektroskopie wurde ein systematisches Schema zur Identifizierung folgender 16 Anionen aufgestellt: Hexacyanoferrat(II) und -(III), SCN^-, AsO_3^{3-}, IO_4^-, Salicylat, Benzoat, BrO_3^-, IO_3^-, Silicat, Oxalat, Tartrat, PO_4^{3-}, AsO_4^{3-}, CrO_4^{2-} und SO_4^{2-}. Die Methode ist einfacher, schneller und empfindlicher als die orthodoxen Identifizierungsmethoden.

Résumé—L'emploi de la spectroscopie d'absorption infra-rouge permet d'établir un tableau systématique d'identification des 16 anions suivants: ferrocyanure – ferricyanure – thiocyanate – arsenite – périodate – salicylate – benzoate – bromate – iodate – silicate – oxalate – tartrate – phosphate – arseniate – chromate et sulfate. Cette méthode est supérieure aux méthodes d'identification habituelles car elle est simple, rapide et sensible.

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RE-ACTIVATION ANALYSIS OF VANADIUM

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Summary—Re-activation analysis is applied to the determination of vanadium. After the addition of vanadium carrier to the irradiated sample, vanadium-52 is separated radiochemically pure by extraction with benzene as vanadium oxinate. The γ-ray spectrum of the vanadium-52 is recorded; the height of the photopeak at 1·44 MeV is measured and compared with that of a vanadium standard. The chemical yield of the purification step is decided by re-irradiation of the separated vanadium oxinate solution and comparing the activity of the vanadium-52 with that of a further vanadium standard. The vanadium content of the sample is determined from the activity of the vanadium-52 induced by the first irradiation and corrected for the chemical yield from the second irradiation.

IN previous papers[1,2] the authors reported on the method of re-activation analysis and its application to the determination of aluminium. This method has the advantage of determining precisely the chemical yield after counting without loss of the sample.

In a normal destructive activation analysis using short life nuclides, the chemical yield is determined by weighing a suitable precipitate of the element being analysed after counting its activity. For the precise determination of chemical yield it is not desirable to treat the irradiated sample after being counted.

On the other hand, when the element to be determined does not have a suitable precipitate for weighing, the chemical yield is determined using a radio-isotope tracer. This method has the disadvantage of producing an error from the difference of chemical yield in each separation.

In re-activation analysis, the chemical yield is easily corrected by re-activation of the counted sample and thus the source of error mentioned above can be eliminated.

The re-activation technique consists of several typical steps, *viz.* the first irradiation of the sample, addition of a carrier, radiochemical separation, counting of the induced activity from the first irradiation, sealing the counted sample in a polyethylene tube, cooling, a second irradiation and counting the induced activity from the second irradiation. The element is determined by measuring the induced activity from the first irradiation, which is corrected for the chemical yield calculated from the induced activity from the second irradiation.

In other words, the technique of non-destructive activation analysis is applied to determine the yield of radiochemical separation in normal destructive activation analysis. This method has now been satisfactorily applied to the determination of vanadium.

THEORETICAL

Solvent extraction was adopted for the radiochemical separation of vanadium because of its rapidity. In this method, the carrier to be added is limited to a rather small amount. Therefore, the amount of the element to be determined in the sample

cannot be neglected in the calculation of the chemical yield. From these considerations an equation for determining an element in the sample from the induced activities from the first and second irradiations has been derived:[2]

$$W = \frac{A_{sam} \cdot W_c \cdot W_{st}}{\dfrac{A_{st} \cdot A'_{sam} \cdot W'_{st}}{A'_{st}} - A_{sam} \cdot W_{st}} \tag{1}$$

where W = weight of vanadium in the unknown sample (g),

A_{st} = induced activity of vanadium-52 in the standard sample from the first irradiation,

W_{st} = weight of the standard sample for the first irradiation (g),

A_{sam} = induced activity of vanadium-52 isolated from the unknown sample after the first irradiation,

W_c = weight of vanadium carrier added to the irradiated unknown sample (g),

A'_{sam} = induced activity of vanadium-52 from the unknown sample after the second irradiation,

A'_{st} = induced activity of vanadium-52 in the standard sample from the second irradiation,

and W'_{st} = weight of the standard sample for the second irradiation (g).

The calibration curves of vanadium for the first and second irradiations (Figs. 2 and 3) were not linear and therefore the amount of vanadium could not be determined from equation (1).[2] However, if the calibration curves are used to find the weights of vanadium corresponding to A_{sam} and A'_{sam}, then A_{sam} and A'_{sam} become equal to A_{st} and A'_{st}, respectively, and equation (1) can be simplified to:

$$W = \frac{W_c(W_{st})_{obs}}{(W'_{st})_{obs} - (W_{st})_{obs}} \tag{2}$$

where $(W_{st})_{obs}$ = weight of vanadium corresponding to A_{sam} as observed from the calibration curve for the first irradiation (Fig. 2),

and $(W'_{st})_{obs}$ = weight of vanadium corresponding to A'_{sam} as observed from the calibration curve for the second irradiation (Fig. 3).

EXPERIMENTAL

Standard samples

224·5 mg of ammonium vanadate (G.R.) were dissolved in 100 ml of water. This solution was further diluted to give vanadium solutions of several different concentrations. 1 ml of each standard solution was sealed in a polyethylene tube and placed in the centre of a capsule by packing with soft paper.

Samples

Samples containing different amounts of vanadium, manganese, sodium and potassium were prepared in the same way as the vanadium standard samples.

Apparatus

The JRR-1 reactor was used as a neutron source and the RCL-256 channel pulse height analyser with a 1·75 × 2 inch NaI (Tl) crystal (well-type) used as a counter.

Neutron irradiation

All irradiations were made in the No. 16 experimental hole (pneumatic tube) at a neutron flux of about 3×10^{11} neutrons.cm^{-2}.sec^{-1}. The first irradiation was continued for 3 min and the second irradiation for 10 sec.

Procedure

After irradiation in the reactor for 3 min, the unknown sample solution was transferred to a separating funnel. 1 ml of vanadium carrier solution (48·889 μg of vanadium) was added, followed by 50 ml of 0·1*M* ammonium tartrate solution (pH 4·6). Vanadium was then extracted with 5 ml of a 1% w/v solution of oxine in benzene. The benzene phase was transferred to a polyethylene tube, which was mounted in the NaI (Tl) crystal 5 min after the end of irradiation, counted for 2 min and the resultant γ-ray spectrum plotted. The polyethylene tube containing the benzene phase was sealed and allowed to cool sufficiently for the vanadium-52 activity to decay to a negligible amount. It was then irradiated for 10 sec, cooled for 110 sec, counted for 1 min and the resultant γ-ray spectrum plotted. The γ-ray spectra of the irradiated standard samples for the first and second irradiations were recorded under the same conditions as for the unknown sample. Vanadium carrier solution was not added to either standard sample nor was the solvent extraction carried out. In each of the resultant γ-ray spectra, the height of the photopeak at 1·44 MeV from the vanadium-52 was measured.

Calibration curves were prepared for the first and second irradiations using the data of standard samples. $(W_{st})_{obs}$ and $(W'_{st})_{obs}$ were determined from these curves as the weights of vanadium producing the same activities as A_{sam} and A'_{sam}, respectively. The amount of vanadium in the unknown sample was then calculated by equation (2).

RESULTS AND DISCUSSION

γ-Ray spectrum

An example of the γ-ray spectrum of vanadium-52 measured after the extraction with oxine-benzene solution is shown in Fig. 1.

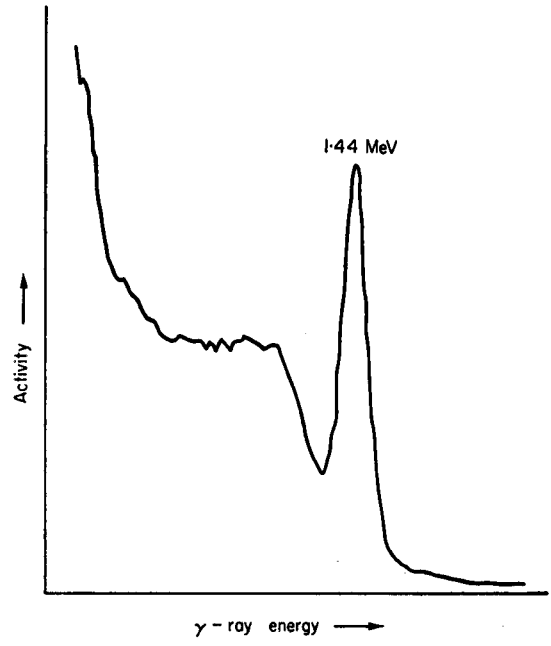

FIG. 1.—γ-Ray spectrum of vanadium.

Calibration curves

The calibration curves of vanadium for the first and second irradiations are shown in Figs. 2 and 3, respectively

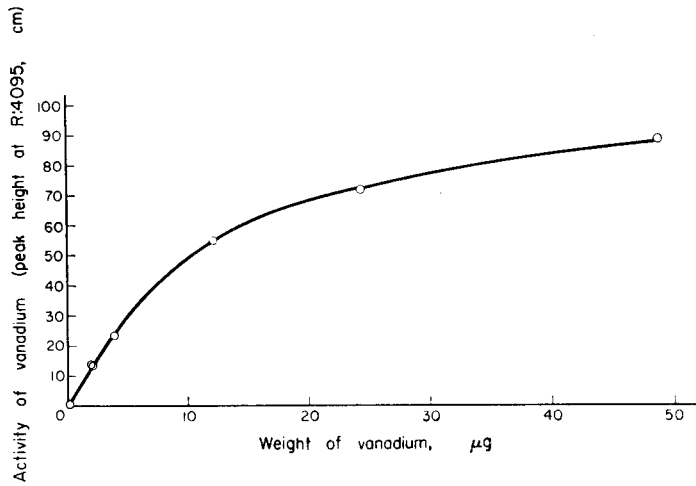

FIG. 2.—Calibration curve of vanadium for the first irradiation.

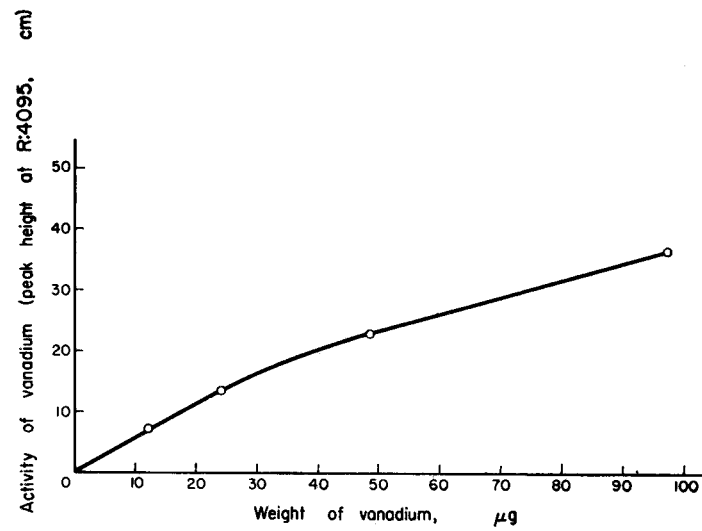

FIG. 3.—Calibration curve of vanadium for the second irradiation.

Results

Some results of analyses by this method are shown in Table I. The upper and lower limits of determination of vanadium are 25 μg and about 0·05 μg, respectively. The coefficient of variation of analysis for 3·91 μg of vanadium is 3·81% (6 results).

Interferences

γ-Rays which may be confused with the 1·44 MeV γ-ray of vanadium-52 are the 1·368 MeV of sodium-24, 1·37 MeV of holmium-166, 1·479 MeV of molybdenum-93m, 1·49 MeV of nickel-65 and 1·53 MeV of potassium-42. Also, the 1·81 MeV γ-ray of manganese-56 would affect measurement of the height of the 1·44 MeV vanadium-52

TABLE I.—ANALYSES OF VANADIUM BY RE-ACTIVATION ANALYSIS

Sample no.	Sample		V found, μg
	V taken, μg	Other elements taken, mg	
1	0·20	0	0·20
2	0·39	0	0·29
3	1·96	0	2·07
4	3·91	0	3·68
5	3·91	0	4·00
6	3·91	0	4·01
7	3·91	0	4·12
8	3·91	0	3·78
9	3·91	0	3·90
10	12·22	0	11·8
11	24·44	0	27·2
12	3·91	Na 0·1	3·78
13	3·91	Na 1	3·90
14	3·91	K 0·1	3·90
15	3·91	K 1	3·91
16	3·91	Mn 0·1	4·61

peak. The interference from manganese-56, sodium-24 and holmium-166 must be taken into account because of their high activation cross sections and saturation factors.[3]

Because sodium and potassium are not extracted with oxine-benzene solution, these elements do not affect the determination of vanadium by the present method. Manganese should not affect it either, because of its non-extractability with oxine-benzene solution, but some interference was found. Some precipitation of manganese hydroxide takes place at the pH of the sample solution at the extraction stage and part of this precipitate is presumably carried into the benzene phase. No method of overcoming the interference from manganese was found.

Zusammenfassung—Die zweistufige Aktivierungsanalyse wird auf die Bestimmung von Vanadin angewandt. Nach Zugabe von Vanadinträger zur bestrahlten Probe wird ^{52}V radiochemisch rein als Oxinat durch Extraktion mit Benzol abgetrennt. Das Gammastrahlenspektrum des ^{52}V wird registriert; die Höhe der Linie bei 1,44 MeV wird gemessen und mit der eines Vanadiumstandards verglichen. Die chemische Ausbeute des Abtrennungsschrittes wird durch erneute Bestrahlung der Vanadiumoxinatlösung bestimmt; deren ^{52}V-Aktivität wird mit der eines weiteren Vanadiumstandards verglichen. Der Vanadingehalt der Probe wird aus der durch die erste Bestrahlung hervorgerufenen ^{52}V-Aktivität berechnet und für die auf Grund der zweiten Bestrahlung bestimmte chemische Ausbeute korrigiert.

Résumé—L'analyse par réactivation est appliquée à la détermination du vanadium. Après addition d'un porteur de vanadium à l'échantillon irradié, le vanadium-52 est séparé sans impureté radiochimique par extraction au benzène sous forme d'oxinate de vanadium. On enregistre le spectre de rayon γ du vanadium-52; la hauteur du pic à 1,44 MeV est mesurée et comparée à celle d'un spectre étalon de vanadium. On détermine le rendement chimique de la purification en irradiant à nouveau la solution séparée d'oxinate de vanadium et en comparant l'activité du vanadium-52 à celle d'un autre étalon de vanadium. On détermine la quantité de vanadium contenue dans l'échantillon à partir de l'activité de vanadium-52 provenant de la première irradiation et la correction due au rendement chimique est calculée à partir de la deuxième irradiation.

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SEPARATION OF THE OLIGOPHOSPHATES

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Summary—Mixtures consisting of orthophosphate, its linear polymers up to and including tridecaphosphate, and three cyclic polymers have been separated by ion-exchange chromatography. One of the cyclic polymers (found in polyphosphate glasses of $\bar{n} \simeq 10$) is probably pentametaphosphate. Its cyclic nature has been demonstrated by end-group titrations and by paper chromatography, but attempts to determine the number of phosphorus atoms in the ring failed because of the very small amount of the compound available. Evidence is presented in support of the common assumption that the linear phosphates above the tetramer are eluted in the sequence of their increasing degree of polymerisation.

INTRODUCTION

THE oligophosphates consist of two homologous series of reasonably stable compounds. The linear polymers can be represented by the general formula $Na_{n+2}P_nO_{3n+1}$, while the cyclic polymers have the general formula $Na_nP_nO_{3n}$.[1] In the latter case, the trimer and tetramer are commercially available. Evidence for the existence of the higher cyclic phosphates in partially degraded Graham salt (long-chain linear polymers) has been obtained by paper chromatography,[2] but these compounds have been isolated only in trace quantities.

In dilute aqueous solution, all of the oligomers undergo slow degradation to orthophosphate. However, at room temperature and at pH levels near 7, the degradation is slow enough to permit the analysis and the study of the properties of the individual polymeric species.

The properties of adjacent members of the polymeric series are so similar that the analysis of mixtures of these polymers is a difficult task. Classical, wet chemical methods are not able to distinguish between oligomers greater than the trimer.[3] Two-dimensional paper chromatography has isolated "spots" for both the linear and cyclic polymers through the tetramers and has partially resolved spots for higher compounds of both types.[4] Quantitative applications of this technique are subject to relative errors of several per cent because of the small samples and the relatively harsh elution conditions. Ion-exchange chromatography has been utilised for the separation and determination of each constituent in mixtures of phosphates.[5–9] The fundamental theory of this approach, applied to the phosphates, was published in 1954,[6] and succeeding papers have extended the original separation to higher oligomeric species. A description of a device for the automatic recording of the elution graph in the analysis of phosphate mixtures has been published.[10]

Matsuhashi[8] extended the range of the ion-exchange method as far as the dodecaphosphate. However, his separation of the linear polymers above the trimer was not quantitative and the cyclic polymers would have overlapped the linear in any

single elution. Jameson[9] achieved a quantitative separation of the linear polymers through the dodecaphosphate by gradient elution, but he did not separate the cyclic polymers from the linears.

RESULTS AND DISCUSSION

Anion-exchange chromatography

Previous work in this laboratory[5,7] had indicated that moderately crosslinked polystyrene resins with the ionic group $-CH_2N^+(CH_3)_3$ are best for the separation of the condensed phosphates. Amberlite XE–119 (analogous to IRA–400 but with a mesh range of 400 to 600) was selected.

In the previous work,[5] the pH of the eluent had been chosen with the aid of equations (19) and (20) of reference 6 (or similar equations) so as to give maximum separations between neighbouring members of the polymeric series.

A difficulty was experienced in the present work in applying these equations because the values of the ionisation constants and the selectivity coefficients are not known for the polymers above the tetramers. Therefore, the following semi-empirical method was used to predict the elution behaviour of the higher linear polymers at pH 5.[11]

From the data of Irani and Callis,[12] it seems likely that for any oligophosphoric acid, $H_{n+2}P_nO_{3n+1}$, the last three ionisation constants will have the values: $K_{Z-2} \cong 10^{-2}$, $K_{Z-1} \cong 10^{-6}$, $K_Z \cong 10^{-8}$ ($Z = n + 2$). It can then be calculated that at pH 5·0, almost 91% of the polymer is present as H_2A^{-Z+2}, 9% as HA^{-Z+1} and negligible amounts as other species. By neglect of all species except the predominant H_2A^{-Z+2} it can be proved[6,11] that at pH 5·0

$$C = \frac{WQ}{V} \cdot \frac{E_{Z-2}}{[Cl^-]^{Z-2}} \tag{1}$$

W is the dry weight of the resin in the column (g); Q is the exchange capacity of the resin (mequiv/g); V is the interstitial volume of the column (ml); E_{Z-2}, the selectivity coefficient, is the classical equilibrium constant of the exchange reaction between the ions $H_2A^{-(Z+2)}$ and Cl^-. For any given ion-exchange column, WQ/V is constant over a range of eluent concentrations. Then equation (1) indicates that each linear phosphate in Fig. 1 should have a slope of $-(Z - 2) = -n$. The actual slopes from $n = 1$ to $n = 3$ are about 10% steeper than the predicted values. The data for these species were taken from the work of Lindenbaum and coworkers.[5,6] Furthermore, E_{Z-2} for these linear phosphates did not vary much over the range of eluent concentrations used nor from one polymer to another.[11] Therefore the graphs for the species larger than the trimer were drawn with slopes of $-1{\cdot}10\,n$ and with $E_{Z-2} = 6 \times 10^{-2}$ in all cases.

Because all ionisation constants of the cyclic phosphates are very large, their elution behaviour is not affected by the pH of the eluent. Their C values vary with the concentration of the eluent[6] approximately according to the equation

$$C = \frac{WQ}{V} \cdot \frac{E_Z}{[Cl^-]^n} \tag{2}$$

For cyclic phosphates, $Z = n$.

The position of any peak in an elution graph with only one concentration of eluent is given by the equation

$$U^* = CV + V \tag{3}$$

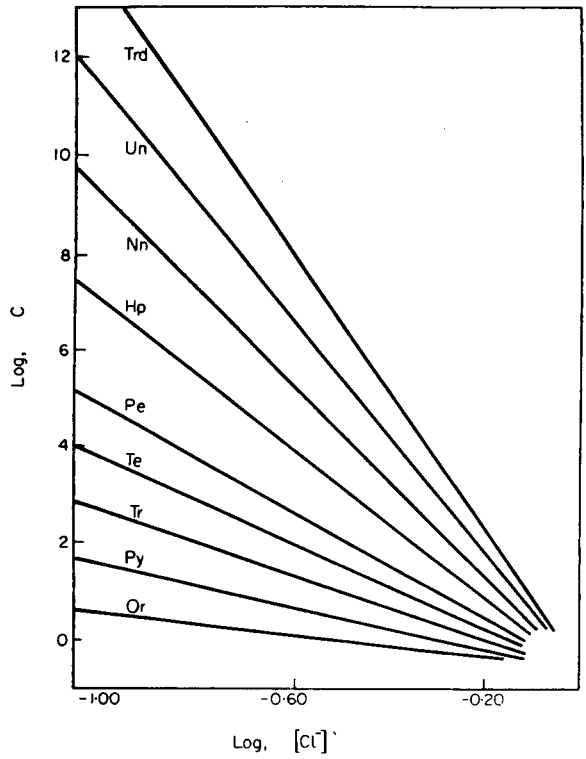

FIG. 1.—Values of log C for various linear phosphates eluted by potassium chloride at pH 5·0:

Trd—tridecaphosphate, Pe—pentaphosphate,
Un—undecaphosphate, Te—tetraphosphate,
Nn—nonaphosphate, Tr—triphosphate,
Hp—heptaphosphate, Py—pyrophosphate,
Or—orthophosphate.

Log C is plotted against the logarithm of the eluent concentration. The curves for ortho- through triphosphate were determined experimentally,[5,6] while those for tetra- through tridecaphosphate were determined as described in the text.

where U^* is the volume of effluent at the peak. The separation factor for any two adjacent polymers is the ratio of their C values, C_2/C_1. Thus the facility with which any two phosphates may be separated is given by $\Delta \log C = \log C_2 - \log C_1$, *i.e.*, the vertical distance between the appropriate graphs in Fig. 1. Obviously, the separation is very difficult (requiring very long columns) at large concentrations of eluent and much easier at small concentrations. On the other hand, small concentrations of chloride cause large values of C and U^* and hence lengthy elutions. In order to obtain a satisfactory elution, it is necessary to use an eluent less than 0·30M until several of the lower polymers are eluted, then to increase the concentration in several steps (or gradiently) to about 0·40M.

Several preliminary elutions were performed in which unsatisfactory separations were obtained. In each elution, the concentration or the volume of one or more of the eluents was changed to improve the separation according to the principles discussed above. Minor changes in pH of some of the eluents were also made in order to improve the separation of overlapping pairs consisting of one cyclic and one linear

polymer. The elution shown in Fig. 2 was finally obtained. This shows a nearly perfect separation of the linear polymers as far as trideca and three cyclic compounds. The peaks of the compounds with four or less phosphorus atoms per molecule were identified by running elutions with known compounds under the same conditions. The identity of the other peaks, especially the "unknown cyclic phosphate" is discussed in the next section.

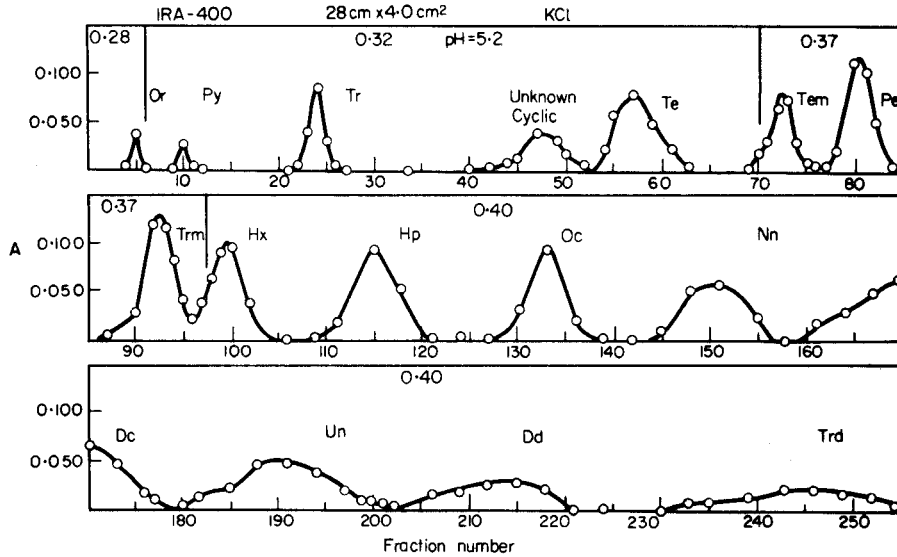

FIG. 2.—Separation of the oligophosphates by anion-exchange chromatography. Absorbance, A, at 400 mμ plotted against fraction number. Each fraction equals 26 ml. A flow rate of 0·42 cm/min was maintained. The sample contained 62 mg of a polyphosphate glass with $\bar{n} \cong 8$. Trm and Tem denote trimetaphosphate and tetrametaphosphate, respectively.

"Unknown cyclic phosphate"

In several preliminary elutions, a "shoulder" appeared on the left side of the peak of tetraphosphate, indicating that another compound was being eluted at this point. As indicated in Fig. 2, conditions were found that gave a very good separation of these two compounds.

In attempting to identify the compound causing the new peak, the fraction of eluate containing it was collected and freed of the acetate buffer used in the eluent to control the pH. The solution of the unknown compound was then adjusted to a pH of about 4 and subjected to a potentiometric micro titration with sodium hydroxide solution. Under these conditions, linear phosphates above the tetramer give two jumps at pH values about 5 and 8; the base used between the jumps corresponds to the two weakly ionised hydrogens on the end groups. This titration in conjunction with a determination of total phosphorus furnishes the data needed to calculate the degree of polymerisation of the linear compound[1]

$$n = \frac{2G}{\theta} \tag{4}$$

where θ is the number of mequiv of weakly ionised hydrogen and G is the number of mg atoms of phosphorus present as linear polymer. The titration graph of the

unknown compound showed only one jump[11] (Table I), indicating that it has no weakly ionised hydrogens and is therefore cyclic.

Further confirmation of the cyclic nature of the unknown compound was obtained by two-dimensional paper chromatography. Because the ratio of potassium chloride to phosphate in the eluate was too great for satisfactory paper chromatography, the major part of the potassium chloride was removed as described subsequently.

TABLE 1.—END-GROUP TITRATION OF THE UNKNOWN CYCLIC PHOSPHATE

Burette reading, *ml*	pH	ΔpH
0·0300	4·09	
		0·10
0·0340	4·19	
		0·16
0·0380	4·35	
		0·22
0·0420	4·57	
		0·42
0·0460	4·99	
		2·10
0·0500	7·09	
		1·44
0·0540	8·53	
		0·38
0·0580	8·91	
		0·27
0·0620	9·18	
		0·14
0·0660	9·32	

Total phosphorus = 14·8 μmole

Under conditions very similar to those recommended by Karl-Kroupa,[4] the unknown cyclic gave a spot in the region where pentametaphosphate would be expected. It was moved very little by the acidic solvent; in the basic solvent, its R_f value was 0·35 compared with 0·39 for tetrametaphosphate. These facts indicate that the unknown compound was probably pentametaphosphate. However, positive identification by chromatography, either on paper or through ion-exchange columns, requires the use of known cyclic polymers above the tetramer, which are not available.

Hydrolysis of cyclic phosphates by base results in large quantities of the corresponding linear phosphates.[13] Several attempts were made to apply this technique to determinations of the unknown cyclic phosphate.

Reasonably large quantities of this compound were isolated by successive elutions and subsequent removal of acetate ion. The samples were hydrolysed with various concentrations of sodium hydroxide solution. The temperature and time for the hydrolysis were also varied. After hydrolysis, cations were removed by the technique for the removal of potassium chloride. The neutralised solution was then subjected to anion-exchange chromatography under conditions similar to those of Fig. 2 in order to identify and determine the products of degradation. Large quantities of tetraphosphate were isolated along with smaller quantities of ortho-, pyro-, tri- and the unknown cyclic phosphate. Although pentaphosphate was not found in the hydrolysate, it is possible that this compound was formed during the hydrolysis, then

was itself degraded. The small amounts of unknown cyclic compound present in these samples did not allow a detailed investigation of its properties. Because this sort of hydrolysis data is generally indicative rather than conclusive, this approach was not pursued further.

The compound is certainly cyclic as is evidenced by both its titration behaviour and its behaviour in paper chromatography. It is impossible to state, at the present time, the number of phosphorus atoms per ion. For this reason the compound has been designated "unknown cyclic phosphate".

Identification of peaks in the elution graph

The oligophosphates through the tetramer are easily prepared or obtained commercially. The peaks corresponding to these compounds have been identified by eluting the known compounds. Higher oligomers through the octamer have been identified by paper-chromatographic analysis of their degradation products.[14] In this laboratory, peaks corresponding to linear oligomers were identified by end-group titration, on the micro scale, of the appropriate fraction of eluate.

A titration of the phosphate contained in fractions 78 to 85, obtained from two successive elutions similar to that in Fig. 2, is summarised in Table II. Several of these micro end-group titrations are summarised in Table III. The phosphate had been degraded somewhat between the time of elution and the titration. The procedure for

TABLE II.—END-GROUP TITRATION OF FRACTIONS 78 TO 85

Burette reading, *ml*	pH	ΔpH	Δ²pH
0·0600	4·99		
		0·33	
0·0640	5·32		+0·12
		0·45	
0·0680	5·77		−0·09
		0·36	
0·0720	6·13		
0·0800	6·90		
		0·44	
0·0840	7·34		+0·19
		0·63	
0·0880	7·97		−0·10
		0·53	
0·0920	8·50		

0·0866 − 0·0663 = 0·0203 ml = 2·40 μmole of end group

Volume = 26 ml (after acetate removal); NaOH = 0·118*M*; total phosphorus = 5·7 μmole

TABLE III

Fraction numbers	Titrant, μmole	Total P, μmole	Cyclic P, μmole	*n*, Experimental	Compound
78–85	2·4	5·7	0	4·8	penta
78–85	10·8	33·1	4·9	5·2	penta
103–113	8·2	34·2	6·6	6·7	hepta

acetate removal also removes oligomers smaller than the trimer; thus a major source of error in the titration was the presence of trimetaphosphate which resulted from the degradation.[14] This was corrected by precipitation of the linear phosphates by barium ion and the quantitative determination of the soluble trimetaphosphate.[15] The procedure differed in that the volume of the solution before precipitation was adjusted to 40 ml and 10 ml of 1·5*M* barium chloride were added. The solution volumes were about one-fifth of those used in the other study.[15]

EXPERIMENTAL

Reagents

Reagent-grade chemicals and de-ionised water were used throughout this work.

Preparation of phosphate glasses: Samples of glassy sodium polyphosphate were prepared by mixing sodium pyrophosphate decahydrate with sodium dihydrogen phosphate monohydrate. The quantities of the two compounds were adjusted so that phosphorus was present in a 15% excess of the desired sodium to phosphorus ratio in order to compensate for the hydrogen that is not expelled by the fusion.[16] The mixture was placed in a platinum boat and inserted in an electric oven where it was kept at 600° for 17 hr. The mixture was removed and cooled rapidly between steel plates. The glassy buttons were broken and dissolved in water. The solution was filtered into a 100-ml volumetric flask, diluted to the mark and stored in a refrigerator at about 5°. A new sample of glass was prepared every month because of the degradation of the polymer.

Eluents: Preparation of the buffered eluents has been described previously.[7]

Procedure for ion-exchange chromatography

Preliminary treatment of resin. The resin was slurried with an excess of water and allowed to settle. The fines were removed by decantation. This process was repeated until the resin settled homogeneously. Supernatant water was poured off and the resin was slurried with 0·1*M* hydrochloric acid. The slurry was then poured into a Pyrex tube with a fritted-glass plug at the bottom. A short piece of Tygon tubing was attached to the bottom of this tube and a Hoffman screw clamp was used to regulate the flow of liquid through the tubing. The resin was allowed to settle and was then washed with 1 litre of 0·1*M* hydrochloric acid. This was followed by a washing with water until the acid was completely removed from the column.

The resin, in the chloride form, was converted to the hydroxide form by elution with 0·1*M* sodium hydroxide solution until the eluate gave a negative test for chloride. Interstitial base was removed by washing with water and the resin was reconverted to the chloride form by the addition of 3*M* hydrochloric acid. After 12 hr the exchanger was washed with 1 more litre of acid.

The resin was then equilibrated with the first eluent. Experience in this field has shown that the first elution with a "prepared resin" is seldom satisfactory. In order to avoid this, a "pseudo elution" was performed, *i.e.*, an elution was carried out with a sample of phosphate glass, but the fractions, instead of being analysed, were discarded. The column was washed with 3*M* hydrochloric acid, allowed to stand overnight, and again eluted with the acid.

The purpose of these washings is to remove impurities which are trapped by the resin during the synthetic process. The forgoing eluents should remove iron^{III} ion, soaps, any phosphates originally present as well as most other materials.

Chromatography. The eluent was drained to within 1 mm of the resin bed. A 1- to 5-ml sample, was delivered to the top of the bed by means of a pipette. The solution was once again drained to the bed. Collection of fractions was started after this step. The wall of the tube was washed twice with 5-ml portions of the first eluent and drained to the bed between washings. Delivery of eluent was started at this point. The flow rate was maintained at 0·42 cm/min by means of a chromatographic "Minipump"(Milton Roy Company, Chestnut Hill, Pennsylvania, U.S.A.). The pump was connected to Tygon delivery tubes by means of "Vari-grip" fittings made of Teflon (Beckman Instruments, Inc., Mountainside, New Jersey, U.S.A.). The fraction-collecting assembly has been previously[6] described.

Upon completion of an elution, the pump was disconnected and the resin was equilibrated with 3*M* hydrochloric acid delivered with the aid of hydrostatic pressure. The resin was allowed to stand overnight in contact with the acid, then eluted with 1 litre of the 3*M* acid. High polymeric phosphates are removed by this procedure.

End-group titrations

Removal of acetate buffer. Fractions containing the desired phosphates were obtained by elutions similar to that in Fig. 2. The fractions were combined and diluted with water to give a solution

0·25*M* in potassium chloride. This was adjusted to pH 7·0 ± 0·3 by the addition of 0·1*M* sodium hydroxide solution. The entire solution was passed through a column of the resin in the chloride form which measured 6·0 cm × 3·8 cm². Potassium chloride (0·25*M*, pH 7·0 ± 0·3) which was free from acetate was passed through the column at a flow rate of 0·6 cm/min until the effluent gave a negative test for acetate. After removal of the acetate, the elution was continued with 0·70*M* potassium chloride which was at pH 7·0 ± 0·3. The desired phosphate was contained in the first one or two 26-ml fractions of this eluent.

These elutions condensed the volume of phosphate-containing solution from about 170 to 26 ml. The amount of potassium chloride present was decreased from about 42 to 18 mmoles.

Test for acetate. A 2·0-ml sample of $1{\cdot}0 \times 10^{-3}M$ hydrochloric acid was added to a 26-ml fraction of effluent and the pH was compared to that of a solution prepared from 26 ml of eluent and the acid. Identity of pH after the removal of carbon dioxide with nitrogen indicated the absence of acetate.

Titration procedure. After removal of the acetate buffer, the phosphate-containing samples were titrated with the aid of a Gilmont micro burette (Manostat Corporation, New York, U.S.A.) The sample was contained in a polyethylene bottle. A glass electrode and a fibre-type calomel electrode were inserted through a hole in the shoulder of the vessel. They were connected to a Beckman pH meter, model G. A thin Pyrex tube which was connected to a tank of nitrogen was introduced, through the plastic wall, into the solution. The microburette was similarly introduced into the liquid. The pH of the solution was adjusted to less than 4·0 by addition of 1*M* hydrochloric acid. The bottle was stoppered with a one-hole rubber stopper through which a short piece of glass tubing was inserted for the escape of gas. Nitrogen was bubbled through the solution for 15 min, expelling any dissolved carbon dioxide. The bubbling was maintained throughout the titration to afford mixing.

Sodium hydroxide titrant. The base was prepared from an aliquot of 18*M* reagent-grade sodium hydroxide and was diluted with freshly prepared de-ionised water. The solution was stored in a polyethylene bottle and protected against carbon dioxide by Ascarite. The solution was standardised against potassium hydrogen phthalate and potassium dihydrogen phosphate.

Determination of total phosphate in a fraction. Standard solutions of the phosphate were used to prepare a "Beer's-Law curve." Total phosphorus was determined after titration and separation by the use of this spectrophotometric technique.[5,6]

Paper chromatography

Elimination of potassium chloride eluent. A 26-ml sample of 0·70*M* potassium chloride, which contained a particular phosphate, was prepared by the procedure for the removal of acetate. A column of Dowex 50-X4, 200–400 mesh, which measured 6 cm × 3·8 cm² was converted to the hydrogen form with 3*M* hydrochloric acid. It was washed with water to remove the interstitial acid. The solution was passed through the column, the wall was washed with cold water and additional water was used as an eluent. The first 50-ml portion contained the desired oligophosphoric acid, some hydrochloric acid and no cations other than hydrogen ion. This procedure was carried out in the refrigerator to minimise degradation of the polymer.

The 50 ml of effluent were evaporated to about 2 ml *in vacuo*. A trap with a Dry Ice-acetone mixture was placed in the line. The rapid evaporation maintained the temperature of the solution at 5 to 10° and prevented serious degradation. The small aqueous residue in the flask was treated with a slight excess of 0·1*M* sodium hydroxide solution so that the resultant solution was basic.

The procedure was performed as soon as possible after the isolation of the phosphate by anion-exchange chromatography. As a result, only small amounts of its degradation products along with sodium chloride and hydroxide were also present. The quantities of these contaminants are probably not great enough to interfere seriously in the later experiments.

Paper-chromatographic procedure. This technique has been previously described.[2,4] Twenty μl of the phosphate solution, from which the potassium chloride had been removed, were applied to the paper in increments of 3 μl or less. Samples of tetraphosphate and tetrametaphosphate were similarly applied to the paper at some distance from the origin to serve as standards.

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Zusammenfassung—Mischungen aus Orthophosphat, seinen linearen Polymeren bis einschließlich Tridekaphosphat und drei cyclischen Polymeren wurden durch Ionenaustauschchromatographie getrennt. Eines der cyclischen Polymeren (das sich in Polyphosphatgläsern mit $\bar{n} \simeq 10$ findet), ist wahrscheinlich Pentametaphosphat. Seine cyclische

Natur wurde durch Endgruppentitrationen und durch Papierchromatographie bewiesen, aber Versuche zur Bestimmung der Anzahl der Phosphoratome im Ring schlugen fehl, da nur eine sehr geringe Menge der Verbindung zugänglich war. Es wird über Ergebnisse berichtet, die die übliche Annahme stützen, daß die linearen Phosphate oberhalb dem Tetrameren in der Reihenfolge ihres Polymerisationsgrades eluiert werden.

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DETERMINATION OF TRIMETAPHOSPHATE ION IN THE PRESENCE OF LINEAR PHOSPHATES

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Summary—A method for the determination of trimetaphosphate in the presence of linear oligophosphates above the trimer has been developed. It has been demonstrated that ortho-, pyro- and triphosphate are incompletely precipitated by barium ion, while higher oligomeric linear phosphates are precipitated quantitatively. The latter species have been isolated from phosphate mixtures by anion-exchange chromatography, mixed with known quantities of cyclic phosphate, and precipitated with barium ion. A mean error of +0·8 and a standard deviation of ±3 μmole of phosphorus as the cyclic ion have been found for mixtures containing from 0 to 203 μmole of phosphorus as trimetaphosphate in the presence of 0 to 81 μmole of phosphorus as the linear polymers.

A NUMBER of cases has been found in which there was a need for a rapid method for the determination of trimetaphosphate in the presence of linear phosphates.[1,2]

It is well known that the barium salts of linear phosphates are sparingly soluble while those of the cyclics are much more soluble. There was doubt, however, that a quantitative separation of these species was possible by precipitation. Jones[3] attempted to precipitate the degradation products of trimetaphosphate at pH 9 using barium chloride, while Healey and Kilpatrick[4] reported that the precipitation of orthophosphate was incomplete under these conditions. The determination of trimetaphosphate, by this technique, in the presence of ortho-, pyro- and triphosphate has been shown to be erratic.[5]

The following study was made to find out whether trimetaphosphate can be determined in phosphate mixtures by precipitation of the linear polymers by barium ion.

RESULTS AND DISCUSSION

All attempts to precipitate quantitatively the phosphates from solutions of phosphate glasses failed when the average degree of polymerisation ($\bar{n}$) was about 4. In these cases, the method described in the next section left 10 to 15 μmole of phosphorus in solution. Varying the pH from 5 to 9, precipitating from the solutions at 5° and "gathering" with sulphate did not improve the results appreciably.

On the other hand, the precipitation was nearly quantitative with samples of phosphate glasses with $\bar{n} \cong 6$. The slightly low results were probably because of the presence of small amounts of cyclic compounds in these glasses.[6] It was, therefore, postulated that the method of precipitation is not quantitative with linear phosphates of $\bar{n} \leqq 3$. In order to test this hypothesis, two samples of sodium triphosphate were treated with barium chloride, one in the presence and one in the absence of a phosphate glass of $\bar{n} \cong 8$. In both cases, the same amount of phosphorus remained in solution.

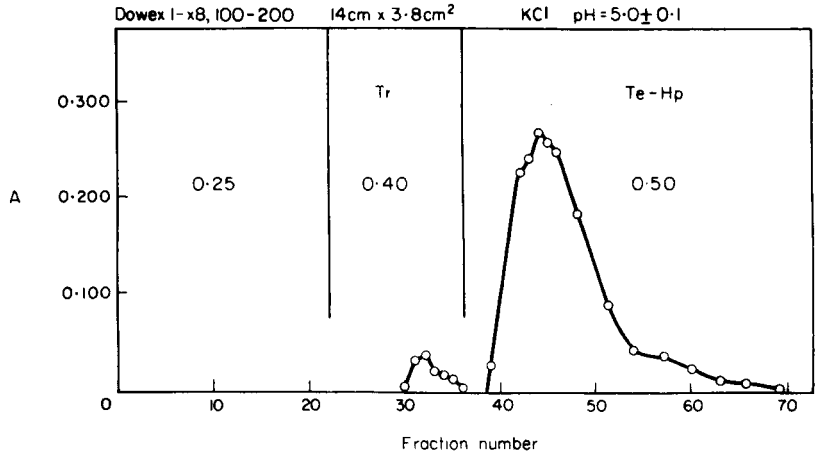

FIG. 1.—Elution of a phosphate glass by potassium chloride eluents at pH 5·0:
Tr—triphosphate,
Te—tetraphosphate,
Hp—heptaphosphate.

Absorbance, A, at 400 mμ plotted versus fraction number. The total number of μ mole of phosphorus in a fraction is equal to 39·0 A. Each fraction equals 10·8 ml. The concentrations of the potassium chloride eluents are indicated on the graph. Fourteen mg of a phosphate glass, with an $\bar{n}$ of about 4, were utilised.

TABLE I.—SUMMARY OF PRECIPITATIONS OF LINEAR PHOSPHATES BY BARIUM ION

Sample no.	P taken, *μmole*		P found, *μmole*		Error, *μmole*	
	Linear	Cyclic	Linear	Cyclic	Linear	Cyclic
1	65	0	61	4	−4	+4
2	66	26	61	31	−5	+5
3	68	71	67	72	−1	+1
4[a]	70	117	54	133	−16	+16
5	73	180	70	183	−3	+3
6	72	0	72	0	0	0
7	73	34	72	35	−1	+1
8	75	68	74	69	−1	+1
9	78	136	84	130	+6	−6
10	81	203	85	200	+4	−3
11	0	0	0	0	0	0
12	0·5	13	0	14	−1	+1
13	3·3	75	4·8	73	+2	−2
14	4·9	112	6·0	111	+1	−1
15	8·2	188	0	196	−8	+8
16	29	0	28	0	−1	0
17	29	0	30	0	+1	0
18	60	0	60	1	0	+1
			Mean		−0·7	+0·8
			Standard deviation		±3	±3

[a] Omitted in the calculation of the mean and the standard deviation.

As a further test of this hypothesis, linear phosphates below the tetramer were removed from phosphate glasses by anion-exchange chromatography. A typical elution is shown in Fig. 1. The fraction containing the polymers from the tetramer to about the heptamer was isolated and immediately used as a source of linear polymers. A known amount of trimetaphosphate was added to this fraction or an aliquot thereof. The resultant mixture was subjected to the precipitation procedure described below.

The results are given in Table I. The second column is the quantity of phosphorus in the glass plus the small amount of non-cyclic phosphorus present as an impurity in the recrystallised sodium trimetaphosphate (see next section). The third column is the corrected quantity of trimetaphosphate present. The fifth column is the quantity of phosphorus found in the filtrate after the precipitation. The fourth column is the total quantity of phosphorus less that in the fifth column. Except for one sample, the results are satisfactory.

EXPERIMENTAL

Reagents

De-ionised water and reagent-grade chemicals, except for sodium trimetaphosphate, were used. Commercial sodium trimetaphosphate (Victor Chemical Works) was recrystallised[7] and analysed by the method of Peters.[8] The analysis indicated that 96·0, 1·2, 1·4 and 1·6% of the total phosphorus were present as trimeta-, ortho-, pyro- and triphosphate, respectively.

Preparation of phosphate glasses. This has been described in a previous paper.[1]

Apparatus

All pH measurements were made with a Beckman pH meter, model G, to which a glass electrode and a fibre-type calomel electrode were attached.

Precipitation procedure

Low linear polymers were removed from solutions of fresh phosphate glasses by anion-exchange chromatography. The phosphate glasses had degrees of polymerisation of about 4. The fraction containing the linear phosphates from the tetramer to about the heptamer was isolated and diluted with water so that the resulting concentration of potassium chloride was 0·4*M*. Two-hundred ml of the solution were delivered into a 250-ml volumetric flask. A known quantity of a solution of sodium trimetaphosphate was added. The solution was diluted to the mark and a 25-ml aliquot was taken. Total phosphorus in the solution was determined from this aliquot. A 200-ml aliquot was removed, its pH was adjusted to 7·0 ± 0·1 with 0·1*M* sodium hydroxide solution, and the solution was transferred to another 250-ml volumetric flask. The phosphates were precipitated by a slow addition of 40 ml of 1·5*M* barium chloride which was at a pH of 7·0 ± 0·1. The solution was diluted to the mark and allowed to digest for 15 min. It was filtered through a fritted-glass funnel of fine porosity, and a 25-ml aliquot was taken for the determination of unprecipitated (cyclic) phosphate.

Phosphate determination

Total and unprecipitated phosphorus were determined by a spectrophotometric method.[7] Ten ml of 0·4*M* potassium chloride were added to the unprecipitated fractions before they were heated. The inside surface of the vessels, which are heated during the colour-development, should be extremely clean and smooth, otherwise a precipitate is noted during this step.

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Zusammenfassung—Eine Methode zur Bestimmung von Trimetaphosphat in Gegenwart linearer Oligophosphate oberhalb des Trimeren wurde entwickelt. Es wird gezeigt, daß Ortho-, Pyro- und Triphosphat durch Barium unvollständig gelfällt werden, wogegen höhere oligomere lineare Phosphate quantitativ gelfällt werden. Diese wurden aus Phosphatmischungen durch Anionenaustauschchromatographie isoliert, mit bekannten Mengen cyclischem Phosphate gemischt und mit

Barium gefällt. Ein mittlerer Fehler von +0,8 und eine Standardabweichung von ±3 Mikromol Phosphor als cyclisches Ion wurden für Mischungen mit 0 bis 203 Mikromol Phosphor als Trimetaphosphat neben 0 bis 81 Mikromol Phosphor als lineare Polymere gefunden.

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TITRIMETRIC DETERMINATION OF QUINOL

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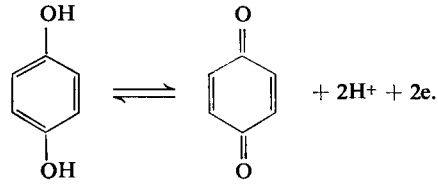
Summary—A critical review is presented of the literature on the titrimetric determination of quinol. For the standardisation of pure quinol solutions the cerimetric titration procedure can be recommended, but in the presence of various organic contaminants vanadate, hexacyanoferrate(III) plus zinc and dichromate are the best titrants.

INTRODUCTION

IN the literature many publications have appeared concerning the titrimetric determination of quinol (hydroquinone). The principle of these methods lies in the possibility to oxidise quinol quantitatively to quinone according to the equation:



The reason for the many different oxidimetric determinations is undoubtedly the fact that many of the impurities which can be present in quinol, *e.g.*, phenolic compounds, are oxidised partly or quantitatively by most of the common oxidimetric titrants. Accurate results for the analysis of low purity mixtures of quinol are therefore *a priori* impossible. It must be stated, moreover, that many of the titration procedures recorded in the literature are not very easy to carry out.

The use of quinol as a reductimetric titrant has increased of late, especially since the work of Zýka and coworkers[1,2]. Advantages connected with the use of quinol are that it can easily be obtained analytically pure, it is relatively inexpensive and, especially, its solutions in a weakly acidic medium (*ca.* 0·01 *N* sulphuric acid) show a constant titre for periods of up to 8 weeks; in contrast with the solutions of nearly all other reductimetric titrants, solutions of quinol are hardly subject to air oxidation.[3]

In view of these facts it seems useful to present a critical literature survey of the titrimetric determination of quinol. The survey has been arranged according to the various titrants which have been used.

Iodine[4,5]

The oldest known titrimetric determination of quinol originates from Valeur[6] and has been adopted in a sometimes more or less altered form by many authors;[4,5,7–9] independently, Gardner and Hodgson[10] reported an analogous method.

The great difficulty of the iodometric determination lies in correctly adjusting the pH of the solution to be titrated. In order to obtain quantitative reaction the pH must be at least 6;[4] at pH 8–9 (bicarbonate), however, one must take into account the

air oxidation of quinol, the velocity of this oxidation being proportional to the square of the hydroxyl ion concentration in the solution.[11,12] Moreover, quinone may undergo disproportionation reactions in an alkaline medium, giving rise to the formation of coloured products and therefore a less sharp end-point; an extra consumption of iodine may also occur.[12,13]

The procedure which involves back-titration of excess iodine has the disadvantage of possible oxidation of thiosulphate to sulphate because of the excess iodine present in the alkaline solution:

$$I_2 + 2OH^- \rightleftharpoons OI^- + I^- + H_2O.$$

It is therefore recommended to use only a small excess of iodine and to use arsenite instead of the more usual thiosulphate.

When carrying out a direct titration it is not possible to use carbon tetrachloride or chloroform as indicator, because the quinone formed during the titration dissolves in the organic layer and forms a compound with iodine. According to Kolthoff[4] a direct titration is possible using a potentiometric end-point.

A serious drawback of the iodometric determination of quinol lies in the fact that many organic compounds are partly or wholly oxidised under the same conditions.

Potassium dichromate

The use of potassium dichromate for quinol determination has been recommended by Kolthoff,[4] who employed a redox indicator (diphenylamine) as well as potentiometric end-point detection. According to Kolthoff it is not possible to carry out the titration at room temperature. The solution must be warmed to 40–60° and even then the titration must be carried out slowly towards the end or over-titration will occur. This statement of Kolthoff has been corroborated by other investigators,[14] but it does not correspond with the conclusions of Casolari,[9] who carried out the titration at room temperature long before Kolthoff. In this connection it is remarkable that the Czech investigators,[3] who use quinol as a reductimetric titrant, standardise it according to Kolthoff, although it must be concluded from the procedures given that they work at room temperature! From experiments carried out by Brinkman and Snelders,[15] it follows that warming the solution has not much influence on the velocity with which the titration can be carried out and that, moreover, the results are practically the same.

According to Kolthoff the quinone formed during the titration poisons the platinum electrode in the potentiometric determination. In more recent investigations on cerimetric titrations in non-aqueous solvents (see below) Prabhakar Rao and Murthy[16] have had somewhat analogous experiences, but on the other hand, Furman and Wallace[8] contradict Kolthoff's statements for cerimetric titrations. In our potentiometric determinations[15] no indication of quinone poisoning was ever found. Instead of diphenylamine, *N*-phenylanthranilic acid has been recommended as an indicator for the direct titration with dichromate,[17] as well as the chemiluminescence indicator siloxene.[18]

Although the titration mentioned above is time-consuming and tedious (50°, slow titration), the use of dichromate is advantageous because it is an easily obtainable high-quality primary standard. A recent investigator[14] has, therefore, proposed an indirect titration in which an excess of ammonium iron^{III} sulphate is added to the solution in a weakly acidic medium; after reduction of iron^{III} to iron^{II} the equivalent

amount of iron^{II} formed is titrated with dichromate using barium diphenylamines sulphonate as indicator. In this titration, of course, iron^{III} is the real oxidant, but for the sake of simplicity the method has been included under the heading of potassium dichromate.

As regards the dichromate titrations it can be stated that phenol and cresols do not interfere, whereas they do interfere in the iodometric titrations. Compounds like oxalic acid, citric acid, lactic acid and glycerol, which are normally not attacked by dichromate are, however, partly oxidised in the presence of quinol as inductor.[17]

Bromine water

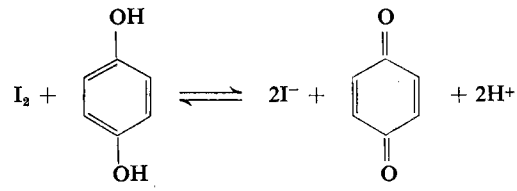
Rosenthaler[19,20] has recommended the use of an aqueous bromine solution for quinol titration; the hydrobromic acid liberated in the reaction can be titrated with a base using methyl red as indicator. The oxidation of quinol occurs immediately: the excess bromine can be blown out of the solution after some minutes, then the hydrobromic acid can be titrated. In the presence of much quinol, which consequently means the presence of much quinone in the neighbourhood of the end-point, the colour change in the acid-base titration is not very sharp.

Freshly prepared solutions of bromine water do not contain any free hydrobromic acid; nevertheless, it is necessary to correct the values found by the amount of alkali consumed by an equivalent amount of bromine water freed from bromine by blowing air through it. This corresponds with *ca.* 0·2 ml of 0·1*M* hydroxyl ion/100 ml of bromine water. For titration procedures in non-aqueous solvents, see reference 21.

Potassium bromate

Bromination with bromate-bromide mixtures in an acid medium yields titration procedures for many derivatives of benzene. Depending on the *o*- *p*- or *m*-directing influence of the substituents, in many instances di- or tribromo-substitution products are formed. In some instances, however, the reaction proceeds in a different way. With dihydroxy- and diaminobenzenes the *m*-compounds are brominated in the normal way yielding a tribromo product, but the *o*- and *p*-isomers do not take up any bromine. The two strongly *o*-*p*-directing groups present in the quinol molecule do not allow *m*-substitution.

Using the procedure given by Francis and Hill,[22] in which an excess of bromate-bromide is added to the acidified solution, after which potassium iodide is added, whereupon the iodine liberated is titrated with thiosulphate, no difficulties arise because of the temporary oxidation of quinol to quinone. Although this oxidation occurs initially, after the addition of potassium iodide the reaction:



proceeds quantitatively to the left.

Kolthoff,[4] who titrated quinol with bromate-bromide using a direct potentiometric procedure so that quinol was really oxidised to quinone, found in contradiction with the authors mentioned above, that at the equivalence-point free bromine

reacts with the quinone present to form an addition or substitution product, so that sharp end-points were not possible.

Brinkman and Snelders[15] have found that in a titration of quinol with bromate-bromide at room temperature some bromination does indeed occur. This not only means a direct titration is difficult to carry out, but also that a titration of other benzene derivatives in the presence of quinol is subject to significant errors. When the titration is carried out, however, at about 0° there is very little bromination; although the results are not very accurate, they give a good indication of the ratio quinol/impurity, especially when this ratio is not too extreme.

Cerium^{IV} sulphate

Extensive investigations concerning the cerimetric titration of quinol have been carried out by Furman and Wallace.[8] According to these authors, the rapid and direct cerimetric titration that can be carried out in about 1*N* sulphuric acid is in many respects superior to the titrations with iodine or dichromate. In potentiometric determinations there is not the slightest indication of quinone poisoning of the platinum electrodes. Methyl red is not a very suitable indicator, but the use of ferroïn, diphenylamine or diphenylamine sulphonic acid is completely satisfactory. Recently, the iron^{II}-2,2′-dipyridyl complex[23] has been used as an indicator in a cerimetric titration. Other indicators mentioned in the literature are *e.g.*, brucine,[24,25] siloxene,[18] copper phthalocyanine tetrasulphonic acid[26] and such triphenylmethane dyes as erioglaucine A, eriogreen B and xylene cyanol FF.[27] Resorcinol and catechol are oxidised by cerium^{IV} farther than the quinone stage, although oxalic acid is not oxidised at all. Attention is called to the fact that both Gopala Rao and coworkers[28] and Brinkman and Snelders[15] have found results 0·3–0·5% too low in cerimetric determinations of pure quinol solutions.

Cerimetric titrations have also been carried out in non-aqueous solvents,[16] using ammonium nitratocerate(IV) as oxidant and acetonitrile as solvent. To obtain a reproducible and fast adjustment of the potential it is necessary to add glacial acetic acid to the solvent. The potentiometric determinations[8,29] can only be carried out when cerium^{IV} is titrated with quinol. In the reverse case quinol exhibits a curious behaviour in contact with the platinum indicator electrode; the results are much too low and, moreover, not reproducible. There is no satisfactory explanation of this fact.

The titrations in non-aqueous solvents can also be carried out with visual end-point determination, using ferroïn, diphenylamine, Janus Green or methyl red as indicator. Ferroïn and diphenylamine are reversible redox indicators under the conditions; with diphenylamine and methyl red the results are about 0·7% high.

An indirect titration of quinol with cerium^{IV} sulphate has been described by Singh and Singh,[30,31] who back-titrate the excess cerium^{IV} sulphate with the iron^{II}-EDTA complex using ferroïn as indicator.

Potassium permanganate

As far as has been investigated, potassium permanganate is the only oxidant that oxidises quinol further than quinone, the end-products in this case being carbon dioxide and water. Under the most favourable circumstances, *viz.* an alkaline medium and excess of permanganate, the time-consuming oxidation takes place almost quantitatively,[32] but many phenolic and other organic compounds are over 90%

oxidised under the same conditions. This very unselective titration can therefore hardly be recommended.

Hypobromite

Generally speaking, titrations with hypobromite are not very suitable because this titrant is not very stable for any length of time; moreover, the results are nearly always high because of the conversion of hypobromite into bromate. A procedure recommended by Kolthoff and Stenger[33] consists in the use of a calcium hypochlorite solution in a weakly alkaline medium, which is added to the solution to be titrated after the addition of potassium bromide. The oxidant hypobromite is generated *in situ*. In most instances, however, not only oxidation but also bromination occurs, *e.g.*, with phenol, oxine and aniline. This hypobromite titration is therefore only suitable in isolated cases, one of these being with quinol.[34] Under favourable conditions (passing of carbon dioxide) the results are not more than 0·2% high. Without carbon dioxide the error increases to about 1%. Most probably this oxidation is brought about by a partial bromination of quinone. It has been proved that the error is not caused by air oxidation.

Sodium metavanadate

Cerium^{IV} sulphate oxidises phenol, cresols and analogous compounds to coloured substances insoluble in concentrated sulphuric acid. Therefore Gopala Rao and coworkers[28] have investigated the use of vanadate as an oxidant for quinol. It appears that vanadate does not oxidise the above-mentioned phenols nor catechol, although it does attack resorcinol.

According to Gopala Rao the quinol concentration of the solution to be titrated must be below 0·01 *M* (0·02*N*) and the total acid concentration must be at least 1·0*N* in order to ensure a sharp end-point. A large quantity of oxalic acid is necessary as a catalyst. The results of the titration are 0·2–0·3% low. Diphenylbenzidine and *N*-phenylanthranilic acid are used as indicators.[28,35]

Hexacyanoferrate(III)

In the literature a potentiometric titration of hexacyanoferrate(III) with quinol in 50% sulphuric acid has been described, which can also be carried out with visual end-point detection.[36] Brinkman and Snelders[15] found that this titration can be carried out in the reverse direction, giving good results for quinol itself and for quinol in mixtures with oxalic acid. In the presence of, for example, phenol, catechol or resorcinol, the colour of the acid solution darkens considerably, however, thereby making titration impossible. Good results are obtained according to these authors,[15,37] when a large excess of hexacyanoferrate(III) is added to an acid quinol solution, whereupon the hexacyanoferrate(II) formed is titrated with a standard solution of zinc using diphenylamine as indicator. The titration can also be carried out potentiometrically, giving results that are about 0·5% high, but it can be used in the presence of oxalic acid, phenol, citric acid and tartaric acid; resorcinol and catechol must be absent, however.

Miscellaneous

In the literature titration procedures are also recorded for quinol with chloramine-B in a weakly acid medium,[38–40] chloramine-T,[41] *N*-bromosuccinimide,[42] manganese^{III}

pyrophosphate,[43] potassium copper^{III} periodate,[44] iron^{III} chloride,[45] potassium periodate[46–48] and iodine monochloride.[49,50] Beranová and Hudeček[51] describe a titration of quinol with barytes using a differential potentiometric titration technique. Tomiček and coworkers[21,52] have carried out titrations with various oxidants, *e.g.*, bromine, chromic acid, sodium permanganate and lead tetra-acetate in glacial acetic acid. They all give good results and the titration with lead tetra-acetate is even used for the standardisation of this substance.

Zusammenfassung—Es wird einen kritischen Überblick gegeben von den in der Literatur beschriebenen Methoden für Quinol Bestimmung. Für die Bestimmung von reinen Quinol Lösungen wird die cerimetrische Titration empfohlen, aber bei Anwesenheit von organischen Verunreinigungen sind Vanadat, Ferrizyanid mit Zink und Dichromat am besten geeignet.

Résumé—On présente un résumé critique de la littérature concernant les méthodes titrimétriques pour détermination d'hydroquinone. Pour le dosage des solutions pures d'hydroquinone, le titrage cérimétrique est recommandé; en cas de présence d'impuretés organiques au contraire, vanadate, ferricyanure avec zinc et dichromate sont les meilleurs titrants.

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SHORT COMMUNICATIONS

The determination of thiourea using chloramine-T

(*Received* 18 *August* 1963. *Accepted* 14 *October* 1963)

METHODS are available for the determination of thiourea by oxidation with hypoiodite[1] and hypobromite[2] reagents. Eight equivalents of the oxidant are utilised for each mole of thiourea. In the present study, chloramine-T and sodium hypochlorite were examined as oxidants and a procedure evolved for the determination of thiourea using chloramine-T, which takes less time than the other hypohalite methods. Earlier work on the oxidation of thiourea with chloramine-T relates to acid media, in which the authors[3–5] have claimed quantitative results. However, our results indicate that the oxidation in acid medium is unreliable and unsuited for quantitative work.

EXPERIMENTAL

Reagents

Thiourea solutions of desired molarity ($M/50$–$M/80$) were prepared from dried, recrystallised solid and the strengths were checked by the hypoiodite method.

Chloramine-T was purified, dissolved in water (approx. $0{\cdot}1N$ solution) and the solution was standardised by the method of Bishop and Jennings.[6]

Sodium hypochlorite solution (approx. $0{\cdot}1N$) was prepared from chlorine and sodium hydroxide,[7] and its strength was determined iodometrically.

The other chemicals used were of standard purity.

The extent of reaction between thiourea and chloramine-T, thiourea and sodium hypochlorite, ammonia and chloramine-T, and urea and chloramine-T was studied under different conditions and order of addition of reagents. The mixtures of known amounts of reagents were set aside for the

TABLE I.—OXIDATION OF THIOUREA(T) BY CHLORAMINE-T(CAT)
Total volume = 100 ml

Order of mixing reagents	T taken, *mM* (I)	CAT taken, *mequiv*	Duration of keeping reagent mixt., *min*	CAT used up, *mequiv* (III)	III/I
T–CAT	0·1250	2.520	2	0·9987	7·989
	0·1250	2·520	15	0·9994	7·997
	0·1875	2·520	2	1·504	8·021
	0·2750	2·520	2	2·201	8·005
	0·2750	2·520	15	2·204	8·015
T–NaOH–CAT*	0·1250	2·520	2	1·002	8·015
	0·1250	2·520	15	0·9984	7·987
	0·2750	2·520	2	2·198	7·993
T–HCl–CAT**	0·1250	3·124	15	0·8634	6·906
	0·1250	3·124	60	1·063	8·504
	0·2500	2·520	15	1·557	6·229
	0·2500	2·520	30	1·706	6·824
	0·2500	2·520	60	1·872	7·488
T–HCl–CAT–NaOH***	0·2500	2·520	15	1·943	7·772
	0·2500	2·520	30	1·940	7·760
	0·2500	2·520	60	1·941	7·764

* NaOH = 10 ml of $1M$ soln.
** HCl = 10 ml of $1M$ soln.
*** HCl = 10 ml of $1M$ soln., and 20 ml of $1M$ NaOH were added immediately after addition of CAT.

requisite periods of time, potassium iodide was added (and only then was added sufficient excess of acid if the main reaction was being carried out in neutral or alkaline medium) and the liberated iodine was determined with thiosulphate. The difference between the amount of chloramine-T or hypochlorite taken and the remaining excess, found iodometrically, gave the amount of oxidant used up in the main reaction.

In Table I are recorded typical results obtained for the thiourea-chloramine-T (T-CAT) system. The results indicate that exactly 8 equivalents of oxidant are consumed by 1 mole of thiourea when neutral or alkaline conditions prevail during the addition of chloramine-T to thiourea. The reaction is completed, in contrast with the other hypohalite methods, almost immediately after the reagents are mixed. The presence of free acid during the reaction, however, causes erratic results, the number of equivalents of chloramine-T used up being less than 8 when it is taken in small excess and more than 8 when it is taken in considerable excess over the thiourea. The titre of chloramine-T becomes less with time in acid medium, and corrections were made accordingly, using blank experiments run under identical conditions. Later addition of excess alkali to a T-HCl-CAT system does not yield good results. Invariably, a slight amount of the oxidant seems to be lost by side reactions in acid medium.

The oxidation of thiourea by chloramine-T in neutral or alkaline medium may proceed as follows:

$$NH_2CSNH_2 + 6H_2O \rightarrow 2NH_4^+ + CO_2 + SO_4^{2-} + 8H^+ + 8e \quad (1)$$

(NH_3, HCO_3, CO_3^{2-} may also be present depending on the pH of solution); *or*

$$NH_2CSNH_2 + 10OH^- \rightarrow NH_2CONH_2 + SO_4^{2-} + 5H_2O + 8e \quad (2)$$

The oxidation of ammonium chloride and of urea with chloramine-T was studied in order to ascertain the particular course of oxidation of thiourea. The results are recorded in Table II. This indicates that oxidation of NH_4^+ occurs rapidly in neutral medium and sluggishly in acid medium. At pH 10 and above, the ammonia (and NH_4^+) is not oxidised by chloramine-T. Urea is not oxidised in either alkaline or neutral medium; the NH_4^+ produced on very slow hydrolysis of urea in acid

TABLE II.—EXTENT OF REACTION OF CHLORAMINE-T(CAT) WITH UREA(U) AND NH_4Cl(A)
Total volume = 100 ml

Order of mixing reagents	U taken, *mM*	A taken, *mM*	CAT taken, *mequiv*	Duration of keeping the mixt., *min*	Unreacted excess of CAT found, *mequiv*
U–CAT	0·5000		2·520	30	2·520
	20·00		2·520	30	2·518
U–NaOH–CAT*	0·5000		2·520	30	2·518
	20·00		2·520	30	2·523
U–HCl–CAT†	0·5000		2·520	30	2·504
	20·00		2·520	30	2·507
A–CAT		0·5000	2·520	1	2·498
		0·5000	2·520	60	0·463
		20·00	3·870	60	0·686
A–$NaHCO_3$–CAT (1 g.)		0·5000	2·520	60	2·514
A–NaOH–CAT*		0·5000	2·520	60	2·517
		20·00	2·520	1	2·519
		20·00	2·520	60	2·517
A–HCl–CAT†		0·5000	2·520	60	2·423
		20·00	2·520	2	2·442
		20·00	2·520	60	1·802

* NaOH added = 30 ml of 1*M* soln.
† HCl added = 10 ml of 1*M* soln.

medium during 30 min consumes a low amount of chloramine-T. However, it was observed that hydrolysis of urea under similar conditions, for a keeping period of 10 min or less, was negligible, and no loss in the titre of chloramine-T occurred. The results indicate that thiourea is oxidised by chloramine-T according to the reaction (2), and that for the quantitative evaluation of thiourea in the presence of ammonium salts it is imperative that the oxidation be carried out in alkaline medium.

Attempts to utilise the reaction between ammonium ion and chorlamine-T for the determination of ammonium did not yield promising results.

The oxidation of thiourea by hypochlorite was found to be very rapid and to proceed even beyond the stage of 8 equivalents in neutral and alkaline media. The presence of excess of potassium bromide slowed down the reaction appreciably, as expected, since the hypochlorite is converted to the hypobromite, but the reaction was of little analytical interest.

Procedure for determination of thiourea

To a solution containing 0·1–0·3 mmole of thiourea, add sufficient alkali to raise the pH to about 10. Add a known excess (a ml) of chloramine-T solution. After about 2 min, add 15 ml of 20% potassium iodide solution, acidify the solution with dilute hydrochloric acid, and titrate the liberated iodine with zN thiosulphate (V ml.) Carry out a blank with a ml of chloramine-T ($\equiv V_1$ ml of thiosulphate). The amount of thiourea in the sample is equal to $(V_1 - V).z/8$ mmole. Urea does not interfere, and large amounts of ammonium salts are tolerated.

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Summary—Chloramine-T oxidises thiourea quantitatively to urea and sulphate ion in neutral and alkaline media. The oxidation is completed within 2 min, even with a very small excess of the oxidant. Urea and ammonium ion do not interfere if the oxidation is carried out in an alkaline medium.

Zusammenfassung—Chloramin-T oxydiert Thioharnstoff in neutralen und alkalischen Medien quantitative zu Harnstoff und Sulfat. Die Oxydation ist in 2 Minuten beendet, selbst bei sehr geringem Überschuß von Oxydationsmittel. Harnstoff und Ammoniumionen stören nicht, wenn die Oxydation in alkalischem Medium ausgeführt wird.

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Titration of anthranilic acid with electrolytically generated bromine: Application to coulometric determination of copper

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Although the coulometric titration of inorganic substances has been rather extensively investigated in recent years,[1,2] the application of coulometric titrimetry to the determination of organic substances has been somewhat limited. A discussion of the application of coulometric titrimetry to organic substances has been given by Lingane,[3] DeFord[4] and Bard.[5] The use of electrolytically generated bromine to oxidise thiodiglycol to thiodiglycol sulphoxide[6] and isonicotinic acid hydrazide to isonicotinic acid[7] are illustrations of oxididative reactions involving this reagent. Substitution bromination reactions for olefins[8] and 8-quinolinol[9] have been investigated. Aniline has been brominated by a back-titration technique in which the excess electrolytically generated bromine was titrated with electrolytically generated copper^{I}.[10] A study of the feasibility of titrating fifteen organic compounds of possible analytical significance by electrolytically generated bromine was undertaken

in order to delineate the stoichiometry involved in colorimetric methods for bromine, and also to circumvent gravimetric methods in the determination of small amounts of metal ions when organic precipitants are employed. This paper reports the results of the investigation involving anthranilic acid (*o*-aminobenzoic acid).[11]

EXPERIMENTAL

Reagents

Double-distilled water was used throughout the investigation.

Electrolyte solution. Dissolve 11·9 g of reagent-grade potassium bromide in 370 ml of distilled water and dilute to 500 ml with 95% ethanol. This solution is 0·2*M* in potassium bromide and 25% by volume ethanol.

Anthranilic acid. Anthranilic acid (Eastman, technical grade) was recrystallised three times from ethanol-water solutions. Only the first crop of crystals was used in each successive recrystallisation. The melting point was 145–145·5° (uncorrected).

Standard anthranilic acid solution. Dissolve 10 mg of the recrystallised material in 27 ml of 95% ethanol and dilute with distilled water to 100 ml in a volumetric flask. One ml of this solution contains 0·1 mg of anthranilic acid.

Precipitant solution. Dissolve 1·0 g of recrystallised anthranilic acid in 50 ml of water containing 0·3 g of sodium hydroxide. Adjust the pH of this solution to 5–6 with dilute hydrochloric acid and dilute to 100 ml with distilled water.

Standard copper^{II} solution. Dissolve 0·5 g of reagent-grade copper sulphate pentahydrate in 1 litre of distilled water. Standardise gravimetrically by precipitating copper anthranilate.

Apparatus

A Leeds and Northrup coulometric analyser was used as the constant current source and timing mechanism. Constant current outputs of 64·3, 6·43 or 0·643 mA are available with this apparatus. The cell contained a platinum generating anode and a platinum counter electrode which was protected from the solution by a glass sleeve which made electrical contact through a fritted disc. A Beckman micro calomel electrode served as the reference electrode while a rotating platinum electrode was used as the indicator electrode. The micro electrode was driven at 1800 rpm by a Sargent synchronous stirrer. A Sargent Ampot was used for the amperometric measurements.

General procedures

The platinum micro electrode and generator electrodes were pretreated by the procedure described by Kolthoff and Tanaka.[12] The electrodes were immersed in concentrated nitric acid for 10–15 sec, washed with distilled water, immersed in a solution of 0·01*M* iron^{II} sulphate and 0·05*M* sulphuric acid for 5 min, then again rinsed with distilled water. The sleeve containing the cathode was filled with 0·2*M* potassium bromide solution.

The desired volume of sample or standard solution was pipetted into the cell and the electrolyte solution, which had been adjusted to the desired pH, added. The electrodes were inserted and the magnetic stirrer and synchronous stirrer motor for rotating the platinum micro electrode was started. A potential of 250 mV *vs.* S.C.E. was applied to the micro electrode. After 10–15 min the indicator current reached a constant value and the titration was started using a generating current of 6·43 mA. The generating current was interrupted periodically in order to obtain current readings of the indicator electrode. Several readings were taken before and after the equivalence point, the exact equivalence point being determined graphically.

In determining copper the following procedure was followed: Transfer the desired volume of copper^{II} solution to a 100-ml beaker and adjust to pH 4. Heat the solution to boiling and add 1% anthranilic acid reagent until a ten-fold excess is present. Maintain the solution just below boiling point for 5 min, then allow to cool for 5–10 min. Collect the precipitate on a filter stick, rinse repeatedly with small volumes of 0·005% anthranilic acid solution and finally twice with a few ml of distilled water. Dissolve the precipitate in 4 ml of 2*M* hydrochloric acid, drain through the filter stick into the suction flask and transfer to a 25-ml volumetric flask. Dilute to volume with distilled water and mix thoroughly. Transfer 5 ml of this solution to the coulometric cell for bromination and follow the previously described procedure.

RESULTS

Preliminary investigation showed that anthranilic acid reacted fairly rapidly with bromine to give tribromoaniline.[13] Ultraviolet absorption spectra confirmed the absence of a carboxylic group in the product. The effect of acidity on the rate and extent of bromination was investigated. The rate becomes slow in both very acidic and basic solutions. Quantitative bromination takes place in the pH range 1 to 6 with the optimum rate occurring at a pH of about 4.

When titrations were performed in strictly aqueous solution the results were found to be about 1% low, possibly because of some incompletely brominated product precipitating. When a 25–40% ethanolic solution was used, however, the stoichiometry was in accord with the calculated values.

When a generator current of 64·3 mA was used, the bromine was generated much faster than it was consumed by the anthranilic acid. A lower rate of 0·643 mA was also tried and found to be acceptable although a much longer time was required for the titration. Using the 6·43-mA current output, 0·1–2·0 mg of anthranilic acid can be titrated within 25 min. The coulometric method is sensitive to about 0·1 mg of anthranilic acid.

Some results of determining copper by precipitating copper anthranilate, dissolving the precipitate and titrating the liberated anthranilic acid with electrolytically generated bromine are given in Table I.

TABLE I. ESTIMATE OF ACCURACY AND PRECISION IN DETERMINATION OF COPPER

Copper taken, *mg*	No. of determinations	Copper found, *mg*	Relative standard dev., %	Relative error, %
0·099	3	0·019	11	−81
0·494	4	0·487	1·9	−1·4
0·988	3	0·994	0·26	+0·6
1·976	12	1·998	0·65	+1·1

When less than 0·5 mg of copper^{II} is present in about 50 ml of solution the solubility losses are too significant for quantitative results. The determination of larger amounts of copper (>2 mg) is not practical because of the time required for the bromination process. Other metals whose ions form precipitates with anthranilic acid should be determinable by this proposed coulometric titration method.[14]

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Summary—Anthranilic acid when brominated by electrolytically generated bromine requires 3 moles of bromine per mole. Amperometric detection of the equivalence point is utilised. Small amounts of copper (0·5–2 mg) can be determined by precipitating copper anthranilate, dissolving the precipitate and titrating the liberated anthranilic acid with electrolytically generated bromine.

Zusammenfassung—Bromiert man Anthranilsäure mit elektrolytisch erzeugtem Brom, so verbraucht sie 3 Mole Brom pro Mol, was durch amperometrische Äquivalenzpunktsbestimmung festgestellt wurde. Kleine Mengen Kupfer (0,5–2 mg) können durch Fällung als Kupferanthranilat, Lösen des Niederschlags und Titration der Anthranilsäure mit elektrolytisch erzeugtem Brom bestimmt werden.

Résumé—La bromuration de l'acide anthranilique par le brome généré électrolytiquement nécessite 3 moles de brome par mole. On a utilisé la détection ampérométrique du point d'équivalence. De petites quantités de cuivre (0,5–2 mg) peuvent être dosées par précipitation à l'état d'anthranilate de cuivre, dissolution du précipité, et titrage de l'équivalent d'acide anthranilique au moyen de brome généré électrolytiquement.

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A simple separation of large quantities of 8-hydroxyquinoline from trace gallium

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DURING an investigation of the precipitation of gallium with 8-acetoxyquinoline, a method was required for the determination of the unprecipitated gallium (<0·2 mg) in each filtrate (*ca.* 300 ml). The presence of the very large excess of 8-hydroxyquinoline (*ca.* 0·9 g) seriously interfered with the three methods attempted, *viz.* polarography, or extraction of the gallium 8-hydroxyquinolate followed by a spectrophotometric or fluorimetric measurement.

It was therefore necessary to remove almost completely the 8-hydroxyquinoline without loss of gallium. Because of the volatility of gallium compounds, evaporation to dryness and subsequent ignition of the residue was considered unsuitable. Wet ashing of 8-hydroxyquinoline with a perchloric-nitric acid mixture[1] resulted in "... rapid clearing at end of period; beaker caught fire with hissing noise." Berg[2] has sublimed ammonium 8-hydroxyquinolate.

The simplest procedure seemed to be steam volatilisation.[3] Although Wegner[4] has used this technique to separate 8-hydroxyquinoline from other organic materials, it has not previously been used to separate the compound from aqueous metal-ion solutions.

When a filtrate (pH *ca.* 4·0) was slowly evaporated in a 400-ml beaker on a steam bath, most of the 8-hydroxyquinoline was removed, except occasionally some colourless needles crystallised on the upper parts of the vessel. Two repetitions with 30–50 ml of water completely eliminated the compound, as was evidenced by the absence of its characteristic spectral peak[5] at 3,180 Å in a chloroform extract of the residue in the beaker.

Furthermore, in four experiments with 0·1–0·8 mg of gallium in the presence of 0·9 g of 8-hydroxyquinoline, a gallium recovery of >97% was experienced. It was also established that most of the gallium in the residue was in the form of its water-insoluble 8-hydroxyquinolate.

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Summary—A simple method for the removal of large amounts of 8-hydroxyquinoline from aqueous solutions containing traces of gallium has been devised. It involves steam volatilisation of the organic compound, and gives >97% recovery of gallium as a non-volatile residue.

Zusammenfassung—Eine einfache Methode zur Entfernung großer Mengen 8-Hydroxychinolin aus wäßrigen Lösungen mit Spuren Gallium wurde entwickelt. Es handelt sich um Dampfdestillation der organischen Verbindung, wobei mehr als 97% Gallium als nicht-flüchtiger Rückstand gewonnen werden.

Résumé—On a trouvé une méthode simple pour éliminer de grandes quantités de 8-hydroxyquinoléine de solutions aqueuses contenant des traces de gallium. Elle comprend un entraînement à la vapeur du composé organique, et permet de récupérer plus de 97% du gallium à l'état de résidu non volatil.

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LETTER TO THE EDITOR

The reaction of copper^{II} and copper^{I} with 8-mercaptoquinoline

SIR,

Mercapto compounds are usually considered sufficiently strong reductants to reduce Cu^{II} to Cu^{I}. The assumption that this is true with all mercapto compounds can lead to erroneous conclusions. For example, Bankovskis and coworkers[1,2] found that the reaction of both Cu^{II} and Cu^{I} with 8-mercapto-quinoline led to the formation of the same dark brown complex having a ligand:metal ratio of 2:1. They proposed the following reaction scheme:

$$6C_9H_6N\text{—}SH + 2Cu^{II} \rightarrow C_9H_6NS\text{—}SNH_6C_9 + 2Cu^{I}(C_9H_6NS)(C_9H_7NS) + 4H^+ \quad (1)$$

and concluded that the complex involves 4-co-ordinate Cu^{I} in which one ligand is bonded in the anionic form and the other ligand as the neutral thione tautomer. This reaction scheme correctly describes the stoichiometry of the copper complex as well as the number of protons released per metal ion on complex formation.

In the course of an investigation of the metal chelate stabilities of 8-mercaptoquinoline[3] we have carried out potentiometric titrations of 8-mercaptoquinoline both in the absence and presence of Cu^{II} and have found that the amount of base consumed at the end-point corresponding to the neutralisation of the mercapto group is unchanged by the presence of Cu^{II}. Because equation (1) predicts that only $\frac{2}{3}$ of a mole of protons is released for every mole of reagent involved in the reaction, the amount of base consumed in the titration must vary with the amount of Cu^{II} present. Thus, unless the postulated copper complex loses protons in exactly the same pH region as the free reagent, the above reaction scheme is incorrect.

In order to investigate the alternative possibility that the complex obtained from the reactions of Cu^{II} and Cu^{I} with 8-mercaptoquinoline is $Cu^{II}(C_9H_6NS)_2$, the electron spin resonance spectrum of a chloroform solution of the complex was examined. The signal obtained was characteristic of a Cu^{II} complex, and it was possible to account quantitatively for the copper content of the complex as Cu^{II}.

Therefore a mercapto containing ligand is capable of reacting with a metal in a higher oxidation state without reducing it. This probably results from the greater stability of the complex of the metal in the higher oxidation state.

Acknowledgment—The authors are grateful to the U.S. Atomic Energy Commission for financial assistance, and to Gordon Tollin for assistance with the E.S.R. measurements.

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NOTICES

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

CZECHOSLOVAKIA

At the **National Meeting on Activation Analysis** at Modrá from 4 to 7 November, 1963, 20 papers were presented. The subjects included instrumental activation analysis, neutron sources, methods of counting and gamma spectrometry. Substoichiometry, especially its use for determination of traces of elements by activation analysis, was discussed. The meeting was sponsored by the Scientific and Technical Society in collaboration with the Department of Radiochemistry and Radiation Chemistry, Faculty of Chemistry Bratislava Kollárovo nám. 2. Abstracts of the papers are available from the above address.

III. Internationaler Polarographischer Kursus

In der Zeit vom 31.8. bis 12.9.1964 veranstaltet das Institut für Physikalische Chemie der Karls Universität und das Polarographische Institut der Tschechoslowakischen Akademie der Wissenschaften einen Lehrgang in Polarographie. Dieser Kursus besteht aus Vorlesungen über die Grundlagen der Polarographie, die in deutscher Sprache abgehalten werden, und einen entsprechenden Praktikum. Der Lehrgang ist für Hochschulabsolventen gedacht, spezielle Vorkenntnisse der Polarographie sind jedoch nicht Bedingung. Die Zahl der Teilnehmer wird auf 20 begrenzt. Dieser Lehrgang wird vorbereitet unter Schirmherrschaft von Professor Dr. J. HEYROVSKÝ, die Vorlesungen und das Praktikum liegen in den Händen von Fachkräften der Karls-Universität und des Polarographischen Instituts. Die Teilnahmegebühr beträgt Kčs 300.-einschliesslich eines Ausfluges in die Umgebung Prags und eines gemeinsamen Abendessens am Abschlusstage des Lehrganges. Eine Unterbringung in Studentenheimen zu mässigen Preisen bzw. auf besonderen Wunsch im Hotel, wird gewährleistet.

Vorläufige Anmeldungen mit Angabe von Titel, Name und Adresse sind an das Institut für Physikalische Chemie der Karls-Universität, Prag 2, Albertov 2030, bis spätestens 15. Mai 1964 zu richten.

UNITED KINGDOM

Wednesday 5 *February* 1964: Brains Trust Evening entitled **High Purity Chemicals:** E. F. HERSANT, B. ILLINGWORTH and F. H. LEVER: *Society for Analytical Chemistry, Midlands Section:* University, Edgbaston, Birmingham 15: 6.30 p.m.

Friday 14 *February* 1964: **Hydrolytic Studies of Phosphorus Compounds using Chromatographic Methods:** F. H. POLLARD: *Society for Analytical Chemistry, North of England Section* and *Leeds University Chemical Society:* University, Leeds: 6.00 p.m.

Friday 21 *February* 1964: **Annual General Meeting** followed by **Ordinary Meeting:** *Society for Analytical Chemistry, Microchemistry Group:* Burlington House, London W.1.

Tuesday 25 *February* 1964: Meeting on **Atomic Absorption Spectroscopy: Chemistry of Flames,** T. M. SUGDEN: **Review of Progress in Field of Atomic Absorption Spectroscopy:** J. B. DAWSON: *Society for Analytical Chemistry, Midlands Section* and *Physical Methods Group* with *Royal Institute of Chemistry, East Midlands Section* and *Leicester University Chemical Society:* University, Leicester: 7.00 p.m.

Friday 28 *February* 1964: Meeting on **Qualitative Analysis:** W. MOSER and E. H. REID: *Society for Analytical Chemistry, Scottish Section:* Paisley College of Technology: 7.15 p.m.

A **Conference of the Society for Analytical Chemistry** will be held at Nottingham University between 19 and 23 July, 1965.

The scientific programme, which will consist of original papers on all aspects of analytical chemistry, is to be organised by the Programmes Committee of the Society, and the responsibility for refereeing of papers will be in the hands of *The Analyst* Editorial Committee. A Trade Exhibition (Secretary,

Mr. N. Mix, Standards Department, Boots Pure Drug Co. Ltd., Nottingham) and a programme of social functions will also be arranged.

Preliminary enquiries should be addressed to Mr. C. A. Johnson, Honorary Secretary, SAC Conference 1965, 14 Belgrave Square, London S.W.1.

At the **Nineteenth Annual General Meeting** of the *Physical Methods Group* of the *Society for Analytical Chemistry* held on Tuesday, 26 November, 1963, the following Officers were elected for the forthcoming year:

Chairman: L. BREALEY
Vice-Chairman: G. F. REYNOLDS
Secretary and Treasurer: T. L. PARKINSON, Product Research Department, Beecham Food and Drink Division Ltd., Harpenden Rise, Harpenden, Herts.

At the **Nineteenth Annual General Meeting** of the *Biological Methods Group* of the *Society for Analytical Chemistry* held on Thursday, 12 December, 1963, the following Officers were elected for the forthcoming year:

Chairman: W. A. BROOM
Vice-Chairman: M. W. PARKES
Secretary and Treasurer: K. L. SMITH, Standards Department, Boots Pure Drug Co. Ltd., Pennyfoot Street, Nottingham.

UNITED STATES OF AMERICA

Monday–Tuesday 3–4 *February* 1964: Research Conference on **Progress in Gas Chromatography:** University of California, Los Angeles, Calif.

The programme is as follows:

Monday, February, 3

Preparative Gas Chromatography	J. HOWARD
Mixed Bed Columns	C. N. REILLEY

Tuesday, February 4

Improvements in Detectors and Readout	J. C. STERNBERG
Gas Chromatography of Steroids and Related Substances	E. C. HORNING

The Conference will be followed by an intensive basic **Three-Day Chromatography Course** (5–7 February) of lectures and laboratory work for those with a limited amount of experience in gas chromatography, as well as those who are new to the field.

Monday–Thursday 3–6 *February* 1964: **International Conference on Materials:** *American Society for Testing and Materials:* Sheraton Hotel, Philadelphia, Pa.

The following items from the programme may be of interest to analytical chemists:

Monday, 3 *February: Application of Advanced and Nuclear Physics to Testing Materials*

Application of Microwave Spectroscopy in Non-destructive Testing	A. WATSON
X-Ray Fluorescence Analysis of Materials	B. L. BEAN and W. MULLIGAN
Use of Neutron Diffraction in Study of Properties of Matter	E. LIGRAND
Non-destructive Estimation of Cement Content of Finished Concrete	E. YALTKAYA, S. URKAN, S. SENTÜRK, K. KÖKSAL and B. V. ENÜSTÜN.
Impact of Nuclear Technology on Highway Engineering	P. L. BLACKWELL
Measurement of Moisture Content in Brick Walls by a Neutron-Scattering Technique	B. ROSSINSKI, T. PRZEDECKI and Z. STACMONWICZ

Tuesday, 4 *February*

Influences of Modern Physics on Properties of Wood and their Evaluation	R. L. YOUNGS
Applications of Centimetric Radio Waves in Non-destructive Testing	R. W. NURSE
Microwave and X-Ray Diffraction Studies of Swelling of Baked Clays by Radioisotope Techniques	J. BROCARD, C. DAWANCE, R. LACHAUD and J. PAQUET

Wednesday, 5 February: Impact of Physics on Analysis and Testing of Materials

Electron Beam Microprobe as a Tool in Materials Engineering	F. P. LANDIS, R. W. MERCHANT and P. D. ZEMANY
Progress in Field Ion Microscopy	E. W. MUELLER
Nuclear Magnetic Resonance in Materials Analysis and Testing	C. M. HUGGINS
Modern Solid-State Mass Spectroscopy as a Tool for Standardisation in Analysis of Nuclear Materials	T. L. COLLINS, JR.

Thursday, 6 February: Modern Physics and New Materials

Lasers and Laser Materials	K. NASSAU

Monday–Friday 3–7 *February* 1964: **Winter Gordon Research Conference on Electrochemistry: Electrode Reactions:** Miramar Hotel, Santa Barbara, California [see *Talanta*, 1963, **10** (December), Notices p. ii].

Tuesday 4 *February* 1964: Panel Discussion on **Emission Spectroscopy Techniques:** E. JAYCOX, T. SHEEHY and C. ALBRIGHT: *Society for Applied Spectroscopy, New York Section:* Hotel Manhattan, 8th Avenue and 44th Street, New York: 8.00 p.m.

Thursday–Saturday 27–29 *February* 1964: **Fifth Omnibus Conference on Experimental Aspects of Nuclear Magnetic Resonance Spectroscopy:** Mellon Institute, Pittsburgh, Pa.

National Bureau of Standards has announced the availability of a new nitrogen-bearing and two new precipitation-hardening stainless steel standards. NBS Standard Sample No. 343 is intended for calibrating procedures for determining nitrogen and the precipitation-hardening standards, Nos. 344 and 345, for controlling the composition of these stainless steels.

In addition, nine other standard materials, previously available but recently out of stock, have been renewed. Of these, No. 158a is a standard copper alloy (silicon bronze), No. 3a is a standard white iron in chip form, Nos. 83c and 84g are standards of purity (arsenious oxide and acid potassium phthalate, respectively) and the remaining five are rubber or rubber-compounding standards (sulphur: 371d; stearic acid: 372e; benzothiazyl disulphide: 373e; oil furnace black: 378a; styrene-butadiene, type 1500: 386d).

Talanta, 1964, Vol. 11, p. iv. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

The electrolytic determination of rhodium and its separation from iridium: W. A. E. McBryde and N. A. Graham. (1 *November* 1963)

The determination of tetraethylthiuram disulphide and elemental sulphur in organic extracts using the cathode-ray polarogram: A. F. Taylor. (1 *November* 1963)

Substoichiometric determination of traces of metals: J. Starý and J. Růžička. (4 *November* 1963)

Ultrasonic study of the complex formed by chrome azurol S with tervalent aluminium: Satya Prakash, Alakh Dhari Pandey and Jata Dhari Pandey. (12 *November* 1963)

A new oxidimetric reagent: Potassium dichromate in a strong phosphoric acid medium: II—Titrimetric determination of vanadium^{IV}: G. Gopala Rao and P. Kanta Rao. (12 *November* 1963)

Microtitrimetric estimation of plutonium^{III} and hydrogen peroxide present with plutonium^{IV} in hydrochloric acid solutions: P. V. Balakrishnan, A. S. Ghosh Mazumdar and B. N. Singh. (12 *November* 1963)

Zur Kenntnis der Gibbs'schen Farbreaktion auf Phenole: F. Feigl, V. Anger and H. Mittermann. (13 *November* 1963)

Spectrophotometric determination of microamounts of nitrogen with organic solvent extraction: Michiko Namiki, Yachiyo Kakita and Hidehiro Goto. (15 *November* 1963)

Spot tests for chlorate, bromate and iodate: Ervin Jungreis and Lina Ben-Dor. (18 *November* 1963)

Nachweis und quantitative Bestimmung von chlorierten Cyclopentadienderivaten durch Gaschromatographie und UV-Spektrophotometrie: L. Lechner and A. Somogyi. (22 *November* 1963)

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