

An International Journal of Analytical Chemistry

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talanta



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1963

VOLUME 10

JULY

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SUMMARIES FOR CARD INDEXES

The sorption of cations from complexan media—IV.: Separation of calcium and magnesium from solutions of ethyleneglycol-bis(β -amino-ethylether)-*N,N'*-tetra-acetic acid: PAVEL POVONDRA and RUDOLF PŘIBIL, *Talanta*, 1963, 10, 713. (Analytisches laboratorium, Polarographisches Institut der Tschechoslowakischen Akademie der Wissenschaften, Prag, Czechoslovakia.)

Summary—For the selective separation of calcium from magnesium, use has been made of the great difference in the logarithm of the stability constants of the two elements with EGTA. Over the pH range 7.5–8.5, calcium forms with this reagent a stable, negatively charged chelate, whereas the magnesium chelate is completely dissociated, and magnesium is quantitatively absorbed by a strongly acid cation exchanger. It is therefore possible to carry out the chromatographic separation of these elements with buffered solutions of EGTA. The procedure proposed has been applied to the determination of calcium in minerals rich in magnesium, and to the determination of calcium, manganese and magnesium in natural carbonates.

Improved method for error calculation of quantitative spectrophotometric measurements: G. SVEHLA, A. PÁLL and L. ERDEY, *Talanta*, 1963, 10, p. 719. [Institute for General Chemistry, Technical University, Budapest, XI, Gellért tér 4, Hungary.]

Summary—For the estimation of errors of spectrophotometric measurements it is not enough to determine only the error due to transmittance readings, but the errors due to uncertainties of intercept and slope of the calibration curves should also be taken into consideration. On this basis, separate error equations can be derived for “classical” and differential spectrophotometric determinations. General conclusions are drawn from the derived error equations and examples are given for the calculation.

Titrimetric determination of carbon in aqueous solutions and in organic compounds: D. C. WHITE, *Talanta*, 1963, 10, 727. [Research Department, The Distillers Company Ltd., Development Division, Great Burgh, Epsom, Surrey, England.]

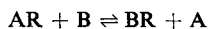
Summary—A method is described for the determination of submilligram amounts of organic carbon in aqueous solutions. A sample of up to 100 μ l is combusted in a Belcher-Ingram ‘empty tube’ furnace, and the carbon dioxide absorbed in acetone and continuously titrated with 0.005*M* sodium hydroxide in methanol/pyridine or methanol/methyl isobutyl ketone, using thymol blue as indicator. For amounts of carbon between 0 and 100 μ g the precision is within $\pm 2\mu$ g, so that the carbon content of a 100- μ l sample of aqueous solution may be determined to within $\pm 0.002\%$ absolute. The procedure is also applicable to solutions containing both organic carbon and carbonate carbon. In suitable cases it is possible to differentiate between organic carbon and carbonate carbon in the same sample. Amounts of carbon up to about 500 μ g may be determined using the same titrant, and larger amounts by using a stronger titrant. The same procedure is applicable to the determination of carbon in milligram samples of organic compounds. A procedure is described for internal coulometric generation of the titrant which has been used to determine amounts of carbon up to about 800 μ g.

Radiochemical separation of strontium by amalgam exchange: IQBAL H. QURESHI and W. WAYNE MEINKE, *Talanta*, 1963, 10, 737. [Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.]

Summary—The radiochemical separation of strontium by an amalgam-exchange technique has been critically evaluated with a saturated aqueous solution of potassium chloride as an exchange medium. With an optimised procedure strontium yields of about 34% were obtained, although mineral acids and alkalis above 0.1M decrease this yield considerably because of decomposition of the amalgam. In studies with tracers of 16 different elements, representative of the Periodic Table, this technique gave considerably better decontamination than does the fuming nitric acid procedure. The simple separation can be carried out in 8 min with no special equipment required, while application of the method to fall-out rain-water samples requires about 40 min. This procedure can also be easily adapted to the preparation of a ^{90}Y -free source of ^{90}Sr .

An analytical approach to chelating resins: G. SCHMUCKLER, *Talanta*, 1963, 10, 745. [Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel.]

Summary—Adsorption of lead and copper ions on the chelating resin Dowex A-1 is compared with that on the ordinary ion exchanger Dowex 50. The change in conditional capacity with the change in medium to which the metals are bound in solution is shown, as well as the additional information to be gained through chelating resins, which cannot be obtained with the ordinary type of exchanger. The exchange equilibria investigated show that a reaction of the type



may be readily controlled by binding the metals in solution to a suitable complexing agent. This widens the scope of metal separation facilities.

Selective determination of trace quantities of silver using sorption of $\text{Ag}(\text{NH}_3)_2^+$ on silica: F. VYDRA, *Talanta*, 1963, 10, 753. [Analytical Laboratory, Polarographic Institute of the Czechoslovak Academy of Science, Jilská 16, Prague, 1, Czechoslovakia.]

Summary—It is possible to adsorb silver, in the form of $\text{Ag}(\text{NH}_3)_2^+$, quantitatively on silica from solutions of pH higher than 8.5, even in the presence of EDTA. Conditions are described for the determination of trace amounts of silver in the presence of gram amounts of copper, mercury, cadmium, zinc, nickel, bismuth and iron.

8-Acetoxyquinaldine as an analytical reagent: Precipitation of thorium: E. J. BILLO, B. E. ROBERTSON and R. P. GRAHAM, *Talanta*, 1963, **10**, 757. [Burke Chemical Laboratories, McMaster University, Hamilton, Ontario, Canada.]

Summary—Thorium can be precipitated from homogeneous solution as the 1:4 chelate, $\text{Th}(\text{C}_{10}\text{H}_8\text{ON})_4$, by 8-hydroxyquinaldine generated by the hydrolysis of 8-acetoxyquinaldine. The use of this ester yields a precipitate with physical characteristics distinctly superior to those of the precipitate produced in a conventional way by 8-hydroxyquinaldine, but purity is attained under somewhat more restrictive conditions. Reasons for this are discussed.

Infrared determination of chlorate in the presence of other oxyhalogen anions: MICHAEL W. MILLER, ROBERT H. PHILP, JR. and A. L. UNDERWOOD, *Talanta*, 1963, **10**, 763. [Department of Chemistry, Emory University, Atlanta, Ga., U.S.A.]

Summary—Small quantities of chlorate may be determined in the presence of perchlorate, bromate, iodate, periodate, and many other substances by measurement of the $20.4\text{-}\mu$ chlorate absorption band. Quantities of potassium chlorate ranging from about 0.1 to 1.0 mg in 300-mg potassium bromide disks can be determined with errors of about 2%. The disk technique is applicable to aqueous solutions via the freeze-drying process. Cations affect the measured absorbance values, but this problem is easily circumvented by a simple ion-exchange step.

The complexometric analysis of pyro- and triphosphates—I: Stability constants of the proton and metal complexes of the acids: AXEL JOHANSSON and ERKKI WÄNNINEN, *Talanta*, 1963, **10**, 769. [Institute of Analytical Chemistry, The Royal Institute of Technology, Stockholm, Sweden.]

Summary—The stability constants of the proton and some metal complexes formed by pyro- and triphosphoric acids at 25° have been evaluated from potentiometric titration measurements.

Determination of rhodium-103, neodymium-143, samarium-149 and -151, and gadolinium-155 in irradiated uranium: M. WARD and J. K. FOREMAN, *Talanta*, 1963, **10**, 779. [United Kingdom Atomic Energy Authority, Production Group, Windscale Works, Sellafield, Seascale, Cumberland, England.]

Summary—Methods for the determination of rhodium-103, neodymium-143, samarium-149 and -151, and gadolinium-155 in irradiated uranium metal are described. The concentrations of these five isotopes have been determined in a rod of uranium, which had received an irradiation of approximately 850 MWday/ton in a Calder reactor. Rhodium-103 was determined colorimetrically following anion-exchange purification and the lanthanide isotopes by isotope dilution and mass spectrometry, again after ion-exchange purification.

Separation of certain cations from mixtures of various cations on ion-exchange papers—II: Antimony and arsenic: JOSEPH SHERMA and CHARLES W. CLINE, *Talanta*, 1963, 10, 787. [Department of Chemistry, Lafayette College, Easton, Penna., U.S.A.]

Summary—Antimony and arsenic have been separated from multi-component mixtures by development with complexing solvents on filter paper impregnated with cation-exchange resin. Comparisons are made with the results of electrochromatographic migrations of the same ions with these solvents as background electrolyte.

The air-oxidation of vanadium^{IV} in alkaline solution: G. A. DEAN and J. F. HERRINGSHAW, *Talanta*, 1963, 10, 793. [Chemistry Department, Imperial College of Science and Technology, London, S.W.7, England.]

Summary—The air-oxidation of vanadium^{IV} in alkaline solution proceeds *via* the reduction of the aerial oxygen to peroxide. The initial rate of oxidation is proportional to the concentration of sodium hydroxide; iron^{III} catalyses the reaction and chromium^{III} inhibits it. At concentrations of vanadium not less than 0.002*N*, the rate of oxidation is controlled by the rate of diffusion of aerial oxygen. Under suitable conditions, quantitative recovery of vanadium as vanadium^V is obtained.

Communications on quantitative organic analysis—XXXIV: A study of the determination of oxygen in organic materials: M. VEČEŘA, J. LAKOMÝ and L. LEHAR, *Talanta*, 1963, 10, 801. Mikroanalytisches Laboratorium, Forschungsinstitut für Organische Synthesen, Pardubice-Rybitví, Czechoslovakia.

Summary—In the determination of oxygen in organic compounds, using an apparatus with a conductometric finish, the relationship between the temperature and the percentage conversion of oxygen to carbon dioxide has been examined.

Titration of weak acids with tetramethylguanidine as solvent: T. R. WILLIAMS and M. LAUTENSCHLEGER, *Talanta*, 1963, 10, 804. [Department of Chemistry, The College of Wooster, Wooster, Ohio, U.S.A.]

Summary—Indicators and electrode systems for the titration of weak acids in 1,1,3,3-tetramethylguanidine as solvent have been investigated. A glass electrode coupled with a silver-silver bromide reference is found to give the most reliable results. Alizarin yellow and azo violet give results in agreement with potentiometric end-point values. A large potassium ion effect is observed in this solvent. Attempts to differentiate several pairs of acids were unsuccessful, because the solvent showed a strong leveling effect.

Electrolytic generation of sulphate for precipitation studies: DAVID H. KLEIN and BERNARDO FONTAL, *Talanta*, 1963, **10**, 808. (Department of Chemistry, Los Angeles State College, Los Angeles 32, California, U.S.A.)

Summary—Electrolytic generation of sulphate from thiocyanate is found to proceed with 100% current efficiency over a wide range of pH in acid solution. Application of this coulometric technique to precipitation studies is discussed.

Spectrophotometric determination of decaborane via its β -naphthoquinoline complex: ROBERT S. BRAMAN and THOMAS N. JOHNSTON, *Talanta*, 1963, **10**, 810. [Callery Chemical Company, Callery, Pennsylvania, U.S.A.]

Summary—An improved spectrophotometric method has been developed for the determination of decaborane and its alkyl derivatives. Based upon the β -naphthoquinoline complex of these boranes in xylene, it has a sensitivity of 0.1 μg of decaborane/ml.

Analysis of aqueous mixtures of ϵ -aminocaproic and α,ϵ -diaminocaproic acid using ninhydrin: K. CZEREPKO and N. WOLOSOWICZ, *Talanta*, 1963, **10**, 813. [Department of Physiological Chemistry, Medical School, Bialystok, Poland.]

Summary—A simple method for the simultaneous determination of ϵ -aminocaproic acid and α,ϵ -diaminocaproic acid (lysine) in aqueous solution is based on the differential colorimetric reactions given with ninhydrin at pH 1 and pH 6.4.

Destructive chlorination of organic compounds—I: General observations: JIŘÍ KÖRBL and DAGMAR MANSFELDOVÁ, *Talanta*, 1963, **10**, 816. [Research Institute of Pharmacy and Biochemistry, Praha 3, Kofřimská 17, Czechoslovakia.]

Summary—Destructive chlorination at high temperature in the determination of some elements, particularly of hydrogen and oxygen, is discussed. Basic observations concerning the behaviour, in the course of the exhaustive chlorination, of some elements usually present in the organic compounds described.

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Because TALANTA is an international journal, contributions are expected to be of a very high standard. They should make a definite contribution to the subject. Papers submitted for publication should be new publications. The submission of a paper is held to imply that it has not previously been published in any major language (English, French, German, Russian), that it is not under consideration for publication elsewhere, and that, if accepted for publication, it will not be published elsewhere without the written consent of the Editor-in-Chief. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, **but should be critical**. The Editor-in-Chief will welcome correspondence on matters of interest to analytical chemists.

Original papers, short communications and reviews will be refereed (see *Talanta*, 1962, 9, 89). Referees will be encouraged to present critical and unbiased reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor-in-Chief, the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

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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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(Eingegangen am 10. September 1962. Angenommen am 20. Oktober 1962)

Zusammenfassung—Zur selektiven Abtrennung des Calciums vom Magnesium wurde die relativ grosse Differenz in den Logarithmen der Bildungskonstanten beider Elemente mit der Äthylenglykol-bis(β -aminoäthyläther)-*N,N'*-tetraessigsäure ausgenützt. Im pH-Bereich 7,5–8,5 bildet das Calcium mit dieser Säure ein stabiles, negativ geladenes Chelat, während das Chelat des Magnesiums völlig dissoziiert und das Magnesium quantitativ durch einen stark sauren Kationenaustauscher absorbiert wird. Es ist auch möglich, mit gepufferter Lösung dieses Chelons eine chromatographische Trennung beider Elemente durchzuführen. Die vorgeschlagene Trennung wurde für die Calciumbestimmung in magnesiumreichen Mineralien und für Calcium, Mangan und Magnesiumbestimmung in einigen natürlichen Carbonaten ausgenützt.

ZUR chromatographischen Trennung von an Ionenaustauschern sorbiertem Calcium und Magnesium bediente man sich meistens der fast 100%-igen Differenz der Atomgewichte der beiden Elemente, durch die die Unterschiede der Austauschgeschwindigkeiten bei der Elution mit einem Neutralsalz oder einer anorganischen Säure bedingt sind.¹ Zu dieser Art Trennung verwendete man meistens Chlorwasserstoffsäure,² Alkalichloride³ oder Ferrisalze.⁴ Weniger üblich ist die Anwendung komplexbildender Reagenzien, von denen hauptsächlich Milch- und Ameisensäure^{5,6} untersucht wurden. Obwohl Calcium und Magnesium mit Komplexanen verhältnismässig feste Chelate bilden, wurden die letzteren zur chromatographischen Trennung der beiden Metalle nur selten herangezogen. Ein Grund dafür war die geringe Differenz der thermodynamischen Stabilitätskonstanten der entstandenen Chelate mit den meisten Verbindungen des Komplexantyps. Die kleinen Differenzen der Konstanten beschränken die pH-Grenzen und die gegenseitigen Verhältnisse der zu trennenden Metalle, bei denen die Trennung quantitativ vor sich geht. Zur obigen Trennung wurde fast gleichzeitig von Taketatsu⁷ und Wunsch⁸ Äthylendiamin-*N,N,N',N'*-tetraessigsäure vorgeschlagen.

In der Tabelle I sind die Werte von thermodynamischen Stabilitätskonstanten des Calciums und Magnesiums mit einigen Komplexbildnern angeführt. Aus dieser Übersicht geht hervor, dass die grösste Differenz die Äthylenglykol-bis-(β -amino-

* III. Mitteilung: *Talanta*, 1962, 9, 647.

äthyläther)-*N,N'*-tetraessigsäure -ÄGTE- aufweist. Ihre Komplexbildungsfähigkeit mit Magnesium ist gegenüber derjenigen mit den übrigen Erdalkalimetallen besonders klein.

Die Eigenschaften dieser Säure wurden von Schwarzenbach und Mitarbeitern⁹ und von Holloway und Reilley¹⁰ untersucht. Sie wurde von Schmid und Reilley¹¹ zur selektiven Bestimmung von Calcium bei Gegenwart von Magnesium vorgeschlagen. Die Möglichkeit einer visuellen Indikation bei der obigen Titration studierten Ringbom und Mitarbeiter¹².

TAB. I.—LOGARITHMEN DER KOMPLEXBILDUNGSKONSTANTEN DES Ca UND Mg MIT EINIGEN CHELONEN

Chelon	log K_{Ca}	log K_{Mg}	log K_{Ca} — log K_{Mg}
Nitritotriessigsäure, NTE	6,4	5,4	1,0
Äthylendiamin-tetraessigsäure, ÄDTE	10,7	8,7	2,0
Diamincyclohexan-tetraessigsäure, DCTE	12,4	10,3	2,1
Äthylenglycol-bis(β -aminoäthyläther)-tetraessigsäure, ÄGTE	10,9	5,3	5,6
Diäthylentriamin-pentaessigsäure, DTPE	10,6	9,0	1,6
Äthylätherdiamin-tetraessigsäure, ÄEDTE	10,0	8,3	1,7
Hydroxyäthyläthylendiamintriessigsäure, HÄDTE	8,0	7,0	1,0

Die Eigenschaften von Äthylenglycol-bis-(β -aminoäthyläther)-*N,N'*-tetraessigsäure sind dem Grundglied der Chelonreihe, nämlich der Äthylendiamin-*N,N,N',N'*-tetraessigsäure sehr ähnlich; sehr nahe beieinander liegen die ersten Dissoziationskonstanten dieser Säuren, die grösste Differenz weisen die beiden Deprotonisierungen der Betainstrukturen auf. Aus der Ähnlichkeit der beiden Säuren geht hervor, dass sich bei der Gleichgewichtseinstellung zwischen einem stark sauren Kationenaustauscher und zwischen der das entsprechende Metall enthaltenden ÄGTE-Lösung ausser der analytischen Chelonkonzentration vor allem das pH betätigt, das den Dissoziationsgrad des Chelons und mithin auch die effektive Stabilitätskonstante des entstandenen Chelates bedingt. Wegen der hinreichend grossen Differenz der thermodynamischen Konstanten des Ca-ÄGTE und des Mg-ÄGTE-Chelates war zu erwarten, dass diese Verbindung die Trennung von Calcium und Magnesium auch bei derart gegenseitig unterschiedlichen Verhältnissen ermöglicht, bei denen sogar die direkte chelometrische Bestimmung mit dem untersuchten Reagenz versagt.

EXPERIMENTELLER TEIL

Reagenzien und Apparate: Die 0,05 m ÄGTE-Masslösung wurde durch Neutralisieren von 19,5 g der freien Säure (J. R. Geigy A. G., Basel, Schweiz*) mit 10%-iger Natronlauge (bzw. Ammoniak) zum pH-Wert von 7 und Auffüllen mit deionisiertem Wasser bereitet. Der Wert der Masslösung wurde durch Titration mit Calciumsalz in stark alkalischer Lösung gegen Fluorexon als Indikator ermittelt.

Die 0,05 m Calcium-, Magnesium- und Manganlösungen wurden aus "pro analysi"-Präparaten hergestellt. Ihre Werte wurden mittels bekannter chelometrischer Titrationen bestimmt. Als Ursubstanz zu diesen Bestimmungen diente metallisches Mangan.

Die pH-Werte wurden mittels eines aus den Entwicklungslaboratorien der Tschechoslowakischen Akademie der Wissenschaften stammenden Apparates, der eine genaue Ablesung der zweiten Dezimalstelle ermöglicht, gemessen. Als Messsystem diente die gasättigte Kalomelektrode mit einer Glaselektrode (Schott, Jena, DDR).

Der Ionenaustauscher (Amberlite IR-120) und die verwendeten Kolonnen wurden bereits in der I.

* Für die Überlassung der ÄGTE danken wir aufs herzlichste Herrn Dr. Krebsner.

Mitteilung dieser Reihe¹³ beschrieben. Die Füllungen wurden in dem entsprechenden Zyklus mittels 5%-igem Natrium- oder Ammoniumchlorids übergeführt. Die Sorption wurde an $15 \times 1 \text{ cm}^2$ Säulen, die praktische Trennung an $20 \times 1 \text{ cm}^2$ Säulen durchgeführt. In der vorangehenden Mitteilung¹³ sind auch die Konzentrationen und die pH-Bereiche der verwendeten Pufferlösungen angeführt.

Arbeitsmethodik

(a) Zu 10 ml der 0,05 m Metallsalzlösung setzt man 20 ml 0,05 m ÄGTE, 20 ml der entsprechenden Pufferlösung und verdünnt mit Wasser auf etwa 80 ml. Den erwünschten pH-Wert stellt man unter der potentiometrischen Kontrolle mit einer 10%-igen Lösung der zugehörigen schwachen Säure oder mit 10%-iger Natron Lauge ein, spült die Elektroden ab und verdünnt die Lösung auf 100 ml. Die Versuche wurden in einem pH-Bereich von 4–11 durchgeführt, und die Reihen wurden zu 0,3 pH abgestuft. Beim Studium der Sorption am Kationenaustauscher im Ammoniumzyklus wurde Natronlauge durch Ammoniak ersetzt und zum Herstellen von Pufferlösungen wurden Ammonsalze verwendet.

(b) Die Katexfüllung wurde mit 25 ml eines verdünnten (1:3) Puffers ausgewaschen. Die zu analysierende Lösung passierte die Füllung mit einer Geschwindigkeit von $3\text{--}5 \text{ ml} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$. Das Becherglas und die Säule wurden 3-mal mit je 5 ml des verdünnten Puffers ausgespült und die Füllung wurde zuletzt mit 50 ml deionisiertem Wasser ausgewaschen. Die vereinten Eluate wurden zur Bestimmung von Calcium oder Magnesium verwendet.

(c) Calcium wurde entweder durch Rücktitration von ÄGTE mit Calciumsalz in stark alkalischer Lösung gegen Fluorexon oder durch Rücktitration mit Mangan(II)-salz in ammoniakalischer Pufferlösung (pH 9) gegen Eriochromschwarz T bestimmt. Magnesium, dessen ÄGTE-Komplex schwächer als die entsprechenden Komplexe mit metallochromen Indikatoren ist, konnte durch Rücktitration nicht bestimmt werden. Bestimmt wurde daher das am Ionenaustauscher abgefangene Magnesium. Durch die Kolonne wurden bekannte Mengen ÄDTE, die mit der gleichen Menge des 0,1 m HBO_2 -NaOH-Puffers (pH 9) versetzt waren, durchgelassen und die freie ÄDTE wurde dann durch die bereits erwähnte Titration mit Mangan(II)-salz bestimmt.

ERGEBNISSE UND DISKUSSION

Die an Hand von Rücktitrationen ermittelten Metallmengen wurden auf % des am Ionenaustauscher sorbierten Metalls umgerechnet und in Abhängigkeit vom pH-Wert (Abb. 1) graphisch aufgetragen. Gleichzeitig wurde auch die Ausrechnung

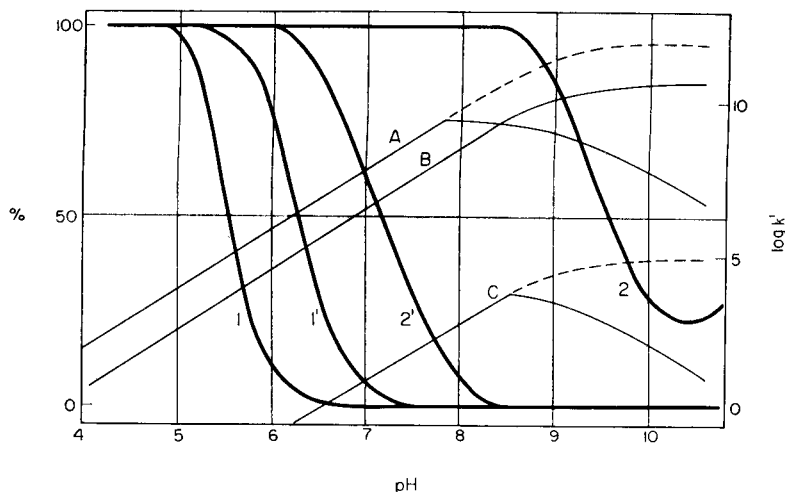


ABB. 1.—Sorption von Calcium und Magnesium am Kationenaustauscher Amberlite IR-120 aus ÄGTE—Medium und Verlauf der scheinbaren Bildungskonstanten ($\log K'$) einiger Metalle mit ÄGTE in Abhängigkeit von pH.

Konzentration der Metalle: $5 \times 10^{-3} \text{ m}$; Konzentration der ÄGTE: $1 \times 10^{-2} \text{ m}$. Ordinate: % der Sorption ($\log K'$). 1-Ca, 2-Mg, Na-Zyklus; (1', 2', NH_4 -Zyklus).

A = $\log K'_{\text{MnY}}$ B = $\log K'_{\text{CaY}}$ C = $\log K'_{\text{MgY}}$

der scheinbaren Stabilitätskonstanten ($\log K'$) der ÄGTE-Komplexe von Calcium, Magnesium und Mangan in Abhängigkeit vom pH-Wert durchgeführt. Die pK' -Werte von Mangan und Magnesium sind mit Rücksicht auf die Hydrolyse bei $pH > 7$ veranschaulicht. Die Abhängigkeit von $-pK' = f(pH)$ wurde mit dem pM -Wert korrigiert; dieser Wert wurde an Hand der von Reilley abgeleiteten Beziehung¹⁴ berechnet.

Aus dem Verlauf der im Na-Ionenmedium studierten Sorptionskurven des Paares Calcium-Magnesium geht hervor, dass die steigende Acidität den Zerfall des Chelates und mithin die Erhöhung der Metallsorption zur Folge hat. Dieser Zerfall steht im guten Einklang mit der pH-Abhängigkeit der Kurven der scheinbaren Komplexbildungskonstante $\log K'$. Bei solchen pH-Werten, bei denen das $\log K'$ auf den Wert von ~ 4 herabsinkt, erfolgt ein quantitativer Zerfall des Komplexes und die beiden Metalle werden am Ionenaustauscher quantitativ sorbiert. Die Bestimmung der Magnesiumsorption oberhalb pH 10 zeigte, dass die Bildung des Mg-ÄGTE-Komplexes infolge der steigenden Hydrolyse nicht quantitativ ist, so dass mit steigendem pH-Wert auch die Mengen des aufgefangenen Metalls zunehmen. Die gegenseitige Lage der pK' -Abhängigkeit des Mangans und Calciums zeigt, dass zur Rücktitration des Calciums Mangan(II)-salze ohne Gefahr der Calciumverdrängung aus dem Komplex verwendbar sind.

Sehr interessant ist die Verschiebung der beiden Sorptionskurven bei der Metalltrennung aus ammoniumionenhaltigem Medium. Besonders deutlich ist die Verschiebung der Sorptionskurve des Magnesiums zu niedrigeren pH-Werten, die auf die Bildung eines festen Komplexes, wahrscheinlich des $MgY \cdot NH_3^{2-}$ -Derivates hinweist.

Aus der Lage der Sorptionskurven von Calcium und Magnesium im Medium von Na-Ionen ist ersichtlich, dass zwischen der 100%-igen Magnesiumsorption und der 0%-igen Calciumsorption ein breiter pH-Bereich vorliegt, der eine quantitative Abtrennung des Calciums auch von einem grossen Überschuss des Magnesiums ermöglicht. Dies wurde an einer Reihe von Lösungen, die 3–10 mg Calcium neben 50 mg Magnesium enthielten, bewiesen. Zur Metallsalzlösung in 100 ml Volumen wurden 10 ml 0,5 m Borsäure zugesetzt, der pH-Wert der Lösung wurde mit 10% iger Natronlauge unter potentiometrischer Kontrolle auf den Wert von $8,0 \pm 0,1$ eingestellt und die so bereitete Lösung wurde durch die Ionenaustauschersäule durchgegossen. Das Auswaschen der Säule und die Calciumbestimmung wurden bereits im experimentellen Teil unter (b) und (c) beschrieben. Aus den erzielten Ergebnissen geht hervor, dass die vorgeschlagene Trennung zufriedenstellende Resultate liefert; die Bestimmung ist mit einem praktisch konstanten, positiven Fehler behaftet. Der Fehler von 0,2 mg Ca ist auf Spuren von Verunreinigungen in den verwendeten Laugen und Salzen und auf den Titrationsfehler bei der visuellen Indikation zurückzuführen. Der überschuss des Komplexbildners ist auf die Bestimmung ohne Einfluss.

PRAKTISCHE ANWENDUNGEN

Die vorgeschlagene Trennung des Calciums von überschüssigem Magnesium und die eigentliche Bestimmung wurden bei den Analysen von Magnesit praktisch erprobt. Da Eisen(III) und Aluminium(III), die im Material vorkommen, mit ÄGTE bei pH 8 einen verhältnismässig stabilen Hydroxokomplex bilden, muss man sie vor der eigentlichen Trennung durch Fällung mit Urotropin entfernen. Mangan, das gleichfalls einen festen Komplex bildet, wird bei der Rücktitration maskiert.

Arbeitsvorschrift: Etwa 1g fein verriebene Probe zerlegt man in einem geräumigen Becherglas mit 10 ml verdünnter (1:1) Chlorwasserstoffsäure und oxydiert sie in der Wärme mit 0,5 g $NaClO_3$. Nach beendetem Aufschluss verdünnt man die Lösung mit warmem Wasser auf 400 ml, setzt einige

Tropfen von 1%-igem Wasserstoffperoxyd zu und neutralisiert mit 10%-iger Natronlauge zum pH-Wert von 3. Die dreiwertigen Elemente werden als Hydroxyde mit einer frisch hergestellten Urotropinlösung gefällt. Die Lösung samt Niederschlag kocht man kurz auf, überführt sie in einen 500 ml Messkolben, kühlt sie auf Raumtemperatur ab, füllt zur Marke auf und mischt gründlich durch. Aus der klaren Lösung entnimmt man einen 100 ml Anteil, versetzt ihn mit einem hinreichenden Überschuss von ÄGTE-Masslösung, setzt 10 ml 0,5 m Borsäure zu und stellt das pH auf $8,0 \pm 0,1$ ein. Aus dieser Lösung wird am Ionenaustauscher das Magnesium in der bereits beschriebenen Weise adsorbiert. Zu den vereinigten Eluaten aus der Säule setzt man 5–7 g festes Kaliumhydroxyde, 5 ml 10%-iges Triäthanolamin zu und bestimmt unter intensivem Rühren die überschüssige ÄGTE mit Calciumsalz-Masslösung gegen Fluorexon.

Die Ergebnisse von zwei Magnesianalysen, durchgeführt in der vorgeschlagenen Weise, zeigt Tab. II. Die Kontrollbestimmung ist ein Durchschnittswert von wiederholter gewichtsanalytischer Bestimmung des Calciums als Sulfat.

TAB. II.—DIE CALCIUMBESTIMMUNG IN ANORGANISCHEN ROHSTOFFEN

Probe	CaO % gefunden	CaO %	CaO % durch Kontrollmethoden	
Magnesit I.	7,39:7,36:7,33:	7,36 ₄	7,37 ^a	7,36 ^b
	7,33:7,39:	$\sigma = \pm 0,02$		
Magnesit II.	4,02:4,09:3,95:	4,00 ₅	4,00 ^a	4,01 ^b
	4,01:4,00:3,96:	$\sigma = \pm 0,05$		
Schweissmittel VUS-34 B	MnO 37,31	MnO 37,10 ^c		
	CaO 7,00	CaO 7,15 ^c		
	MgO 11,20	MgO 11,23 ^c		
		Al ₂ O ₃ 14,00 ^c		

a—gravimetrisch

b—flammenphotometrisch

c—synthetisches Gemisch

Die gepufferten Masslösungen der ÄGTE kann man auch für die selektive chromatographische Trennung des Calciums und des Magnesiums, die am stark sauren Kationenaustauscher adsorbiert sind, verwenden. Dieses Prinzip benutzen wir bei der Analyse von magnesiumreichen Manganerzen und synthetischen Schweissmitteln, bei der gleichzeitigen Abtrennung aller Bestandteile des Materials.

Arbeitsvorschrift: 0,2 g der Einwaage zersetzt man in der Platinschale durch Abrauchen mit Flussäure und einigen Tropfen Perchlorsäure; den Rückstand löst man in Chlorwasserstoffsäure und wiederholt das Abrauchen auf dem Wasserbade. Den feuchten Rückstand versetzt man mit 2g Zitronensäure und nimmt mit 80 ml Wasser auf. Den pH-Wert dieser Lösung stellt man mit Natronlauge unter potentiometrischer Kontrolle auf 3,3–4,0 ein und bringt das Volumen auf c. 100 ml. Die so bereitete Lösung schickt man durch eine Kolonne des Kationenaustauschers mit der Geschwindigkeit 2–3 ml. min⁻¹. cm⁻² und wäscht die Säule nach dem Durchgang der erwähnten Lösung mit 50 ml Wasser. Die abgetrennten Zitate des Eisens und Aluminiums werden verworfen.

Elution des Mangans: Man wäscht die Säule mit den sorbierten Metallen mit 30 ml 0,25 m Azetatpuffer (pH 4,8); Mangan wird dann selektiv mit einer 0,05 m Lösung von ÄDTE, die vorher mit dem gleichen Volumen eines 0,5 m Azetatpuffers (pH 4,8) versetzt wurde, abgetrennt.

Elution des Calciums: Nach Durchwaschen der Kolonne mit 30 ml 0,25 m Borsäurepuffers (pH 8,0) eluiert man das Calcium selektiv mit einer 0,05 m Lösung der ÄGTE (pH 8,0, gleiche Menge des Borsäurepuffers).

Elution des Magnesiums: Das Magnesium wird ähnlich mit der ÄDTE-Lösung (pH 9,5) im Boratpuffer quantitativ ausgewaschen. (Nach jeder Stufe der Trennung wäscht man die Kolonne mit 3 × 10 ml und dann mit 50 ml Wasser aus.

Bestimmung der einzelnen Metalle: Die mangan- und magnesiumhaltigen Anteile bringt man mit ammonikalischem Puffer zum pH 9 und bestimmt den Komplexanüberschuss mit 0,05m Zinksalzlösung gegen Eriochromschwarz T. Die Fraktion mit dem Calcium versetzt man mit einem Boratpuffer (pH 10) und titriert ähnlich mit Zinkmasslösung gegen Zincon¹².

Aus den Ergebnissen (zusammengefasst in Tabelle II) geht hervor, dass sich auf diese Weise alle drei Metalle verhältnismässig einfach und schnell (auch bei grossem Überschuss der dreiwertigen Elemente) abtrennen und bestimmen lassen.

Summary—For the selective separation of calcium from magnesium, use has been made of the great difference in the logarithmic of the stability constants of the two elements with EGTA. Over the pH range 7.5–8.5, calcium forms with this reagent a stable, negatively charged chelate, whereas the magnesium chelate is completely dissociated, and magnesium is quantitatively absorbed by a strongly acid cation exchanger. It is therefore possible to carry out the chromatographic separation of these elements with buffered solutions of EGTA. The procedure proposed has been applied to the determination of calcium in minerals rich in magnesium, and to the determination of calcium, manganese and magnesium in natural carbonates.

Résumé—Les logarithmes des constantes de stabilité du calcium et du magnésium en présence de l'EDTA montre une différence de 100%. Cette différence de stabilité est utilisée pour la séparation sélective du calcium en milieu magnésien; dans un domaine de pH compris entre 7,5 et 8,5 les formes calciques sont stables, le chélate étant chargé négativement, tandis que le chélate du magnésium est complètement dissocié et le magnésium absorbé par un échangeur de cation fortement acide. Il est alors possible d'effectuer une séparation chromatographique de ces deux éléments en employant des solutions tamponnées d'EDTA. Le procédé envisagé a été appliqué au dosage du calcium dans les minéraux riches en magnésium et au dosage du calcium, du manganèse, et du magnésium dans les carbonates naturels.

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IMPROVED METHOD FOR ERROR CALCULATION OF QUANTITATIVE SPECTROPHOTOMETRIC MEASUREMENTS

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(Received 1 October 1962. Accepted 26 February 1963)

Summary—For the estimation of errors of spectrophotometric measurements it is not enough to determine only the error due to transmittance readings, but the errors due to uncertainties of intercept and slope of the calibration curves should also be taken into consideration. On this basis, separate error equations can be derived for “classical” and differential spectrophotometric determinations. General conclusions are drawn from the derived error equations and examples are given for the calculation.

THE accuracy of spectrophotometric analyses has been improved by the widespread use of high-performance spectrophotometers. The full accuracy of spectrophotometric results is, however, seldom established. Most authors determine only the differences between theoretical and experimental results and characterise the accuracy of their method with these data.

The error calculation of photometric analyses has been excellently summarised by Ayres.¹ He emphasised—following Kolthoff and Sandell² and Sandell³—the importance of the equation for error

$$\frac{dc}{c} = \frac{dI}{I} \cdot \frac{0.4343}{E}$$

which shows a minimum at the transmittance $\frac{I}{I_0} = 0.368$. Thus, spectrophotometric measurements are most accurate if the transmittance of the solution is 0.368 (optical density 0.4343). The error calculation of differential spectrophotometric methods—yielding highly accurate results—has been described by Hiskey.⁴ His equation for error, together with the former one, valid for “classical” spectrophotometric determinations, are, however, only first approximations to solving the problem. In the following paper an attempt is made to deal with it in more detail and to present a uniform method for the error calculation.

Presentation of experimental results

The results of quantitative spectrophotometric measurements are gained mostly from calibration curves. If the concentration of the solution is c (g/litre), the optical path (cell length) is l (cm) and the optical density of the solution is E , then the usual

way is to plot values of $\frac{E}{l}$ as a function of c . If Beer's Law is valid for the measurement, a linear curve is obtained. The relationship can be expressed in general by the equation:

$$\frac{E}{l} = ac + b \quad (1)$$

where a is the slope of the curve and b is the intercept with the $\frac{E}{l}$ -axis. In the case of classical (*i.e.*, non-differential) spectrophotometric measurements, b is equal to zero, but it has a certain uncertainty which should be taken into consideration in error calculation.

The first task is to obtain the "best linear curve" from the experimental results obtained in a preliminary standardisation or calibration. From this the "best" values of " a " and " b " and their respective standard deviations are evaluated. Using the method of "least squares" (for details see references 5, 6 and 7), the following calculations must be made:

(a) the constants a and b must be calculated (see reference 6, p. 539);

(b) the standard deviations of these constants, s_a and s_b , must be computed (see reference 6, p. 535, equations 18.3.30 and 18.3.31).

These data will be used in the error calculation later.

General expression for the maximal error

To obtain the error of concentration determination, first the concentration must be expressed from equation (1) as

$$c = \frac{\frac{E}{l} - b}{a} \quad (2)$$

Now the total differential of c can be expressed

$$dc = \frac{\partial c}{\partial E} dE + \frac{\partial c}{\partial l} dl + \frac{\partial c}{\partial b} db + \frac{\partial c}{\partial a} da \quad (3)$$

The partial differential quotients can be expressed as follows:

$$dc = \frac{1}{al} dE - \frac{E}{al^2} dl - \frac{1}{a} db - \frac{\frac{E}{l} - b}{a^2} da \quad (4)$$

Instead of dE , dl , db and da , the standard deviations $\pm s_E$, $\pm s_l$, $\pm s_b$ and $\pm s_a$ can be inserted. In the worst case the sign of these fractional errors are summed. It is advisable, therefore, to change all of the signs in equation (4) to + and to calculate only with the absolute value of standard deviations:

$$s_c = \frac{1}{al} s_E + \frac{E}{al^2} s_l + \frac{1}{a} s_b + \frac{\frac{E}{l} - b}{a^2} s_a \quad (5)$$

The percentage relative error (coefficient of variation) $\frac{s_c}{c} \cdot 100$ can be gained from equations (2) and (5):

$$\frac{s_c}{c} \cdot 100 = \left(\frac{1}{E - bl} s_E + \frac{1}{l \frac{bl^2}{E}} s_l + \frac{l}{E - bl} s_b + \frac{1}{a} s_a \right) 100 \quad (6)$$

This is the general expression of error. It is interesting to see that the error depends on the measured optical density (E), *i.e.*, it depends on the concentration. Therefore, for each spectrophotometric calibration curve an equation for total error can be derived. This function does not contain errors due to weighing, volume measurement, *etc.*, which can be decreased to negligible values by adequate technique.

Maximal error of "classical" spectrophotometric determinations

In classical spectrophotometric measurements $b = 0$ (but $s_b \neq 0!$), so equation (7) can be written as:

$$\frac{s_c}{c} \cdot 100 = \left(\frac{s_E}{E} + \frac{s_l}{l} + \frac{s_a}{a} + \frac{s_b l}{E} \right) 100 \quad (7)$$

The fractional errors in (7) are calculated separately:

(a) The error $\frac{s_E}{E}$ can be expressed¹ as

$$\frac{s_E}{E} = \frac{0.4343}{\frac{I}{I_0} \cdot \log \frac{I}{I_0}} s \left(\frac{I}{I_0} \right) \quad (8)$$

where I/I_0 is the transmittance of the solution, while $s(I/I_0)$ is the standard deviation of the transmittance determination. This can be determined by 6–10 parallel transmittance readings (including refilling and replacement of the cells). The values of the other part of the product,

$$\frac{0.4343}{\frac{I}{I_0} \cdot \log \frac{I}{I_0}}$$

can be calculated for each 0.1 increment of I/I_0 and expressed as a function of I/I_0 (see Table I and Fig. 1). The function shows a minimum at $I/I_0 = 0.386$. Thus the

TABLE I.—VALUES OF $\frac{0.4343}{\frac{I}{I_0} \log \frac{I}{I_0}}$ AT VARIOUS TRANSMITTANCIES

$\frac{I}{I_0}$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$\frac{0.4343}{\frac{I}{I_0} \log \frac{I}{I_0}}$	4.300	3.106	2.768	2.728	2.885	3.252	4.0	5.595	10.534	

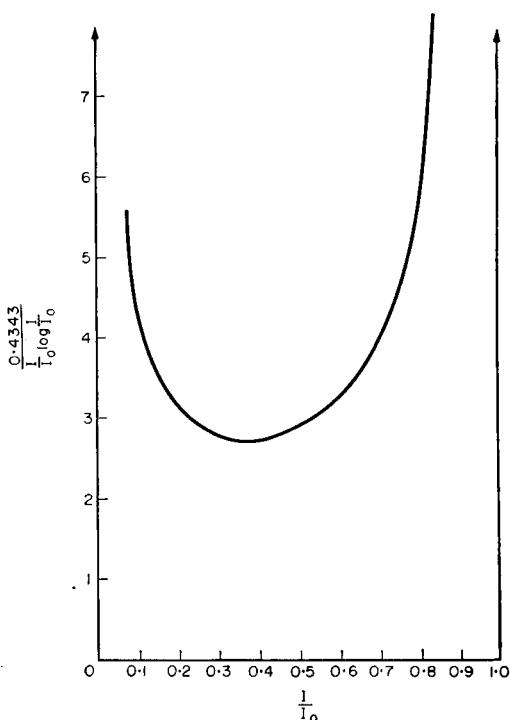


FIG. 1

value of this function (perhaps gained by linear interpolation from Table I), must be multiplied with the standard deviation $s(I/I_0)$ and inserted into equation (7).

(b) The relative error s_l/I can be calculated from the deviation of cell lengths s_l . For an experimental determination of s_l Hiskey⁴ presents a good method. However, if optical density is measured in all cases systematically in the same cells, the error s_l can be neglected. (In this case the values a and b will contain the error due to the incongruency of cell lengths; the results of analyses, however, will not contain this error.) It is essential that the position of the cells in the instrument should be the same in all cases.

(c) The error s_a/a contains the standard deviation of a .

(d) The error s_b/ac depends on the concentration of the solution. Here s_b is the standard deviation of b .

From equation (7) the following general conclusions can be drawn for the accuracy of spectrophotometric measurements. The error is smaller:

- (i) the nearer is the transmittancy of the solution to 0.386 (optical density 0.4343);
- (ii) the lower is the standard deviation of the transmission measurements;
- (iii) the smaller is the deviation between cell lengths used;
- (iv) the longer the cells used;
- (v) the smaller is the standard deviation of the slope of the calibration curve;
- (vi) the bigger is the value of the slope (*i.e.*, the greater is the extinction coefficient);
- (vii) the smaller is the standard deviation of the intercept;
- (viii) the higher is the concentration of the solution.

Some of these requirements [like (i), (iv) and (viii)] seem to contradict each other.

The following may serve as an example for calculation. Cobalt^{II} was determined as cobalt^{II} perchlorate with water as the reference solution. The optical density was measured at 511 μ in 1-cm silica cells, using a Hilger Uvispek spectrophotometer. The corresponding concentration c_i and optical density E_i/l data, as well as results of the calculations are shown in Table II.

TABLE II.—ERRORS IN THE DETERMINATION OF COBALT^{II} AS ITS PERCHLORATE BY THE CLASSICAL SPECTROPHOTOMETRIC METHOD

c_i g of cobalt ^{II} /litre	$\frac{E}{l}$	$\frac{0.4343}{I_0} \frac{1}{\log \frac{I}{I_0}} \cdot s \left(\frac{I}{I_0} \right)$	$\frac{s_a}{a} \cdot 100$	$\frac{s_b}{ac} \cdot 100$	$\frac{s_c}{c} \cdot 100$
		%	%	%	(total error), %
2	0.168	13.57×10^{-1}	1.0532	6.5353	8.95
4	0.334	2.225×10^{-1}		3.2676	4.54
6	0.506	1.497×10^{-1}		2.1784	3.38
8	0.674	0		1.6338	2.68
10	0.816	1.068×10^{-1}		1.3070	2.65
12	1.045	1.424×10^{-1}		1.0892	2.28
14	1.194	2.51×10^{-1}		0.93362	2.23

* Further data: $a = 0.0874$; $s_a = \pm 0.0092$; $b = 0.0206$; $s_b = 0.0114$

From these data it is seen that it is not enough to regard simply $(s_E/E) \cdot 100$ (column 1) as the error of concentration determination, because errors due to uncertainty of a and b are high, especially at lower concentrations.

Error function of differential spectrophotometric measurements

The method of differential spectrophotometry as well as its error calculation has been described by Hiskey.⁴ A more precise method for error calculation can, however, be derived in a manner similar to that already adopted in the present paper. The following symbols are used: c_X is the concentration of the unknown solution, c_r is the concentration of the reference solution (c_r being in all cases $\leq c_X$), I_X/I_r is the transmittance of the unknown solution measured against the reference solution, E_X is the corresponding optical density, I_r/I_0 is the transmittance of the reference solution measured against the solvent and $s(I_X/I_r)$ is the standard deviation of transmittance measurements of the unknown solution against the reference solution. Other symbols are the same as mentioned above. If the E_X/l values are expressed as a function of c_X :

$$\frac{E_X}{l} = a \cdot c_X + b$$

(the values of a and b and of the standard deviations s_a and s_b are determined by the method of least squares, as described above, but with b finite), the equation for total error can be similarly derived and expressed in the following way:

$$\frac{s_{c_X}}{c_X} \cdot 100 = \left[\frac{0.4343}{\frac{I_X}{I_r} \left(\log \frac{I_X}{I_r} + \log \frac{I_r}{I_0} \right)} \cdot s \left(\frac{I_X}{I_r} \right) + \frac{c_X - c_r}{c_X} \cdot \frac{s_l}{l} + \frac{s_b}{ac_X} + \frac{s_a}{a} \right] 100 \quad (9)$$

The first term of the right-hand side of equation (9) contains the expression

$$\frac{0.4343}{\frac{I_x}{I_r} \left(\log \frac{I_x}{I_r} + \log \frac{I_r}{I_0} \right)}$$

This is not a uniform function as in the case of "classical" spectrophotometric measurements, but depends on the transmittance of the reference solution measured against the solvent. Thus, for each reference solution a special equation can be derived. Relationships corresponding to some I_r/I_0 transmittancies are shown in Fig. 2. Values

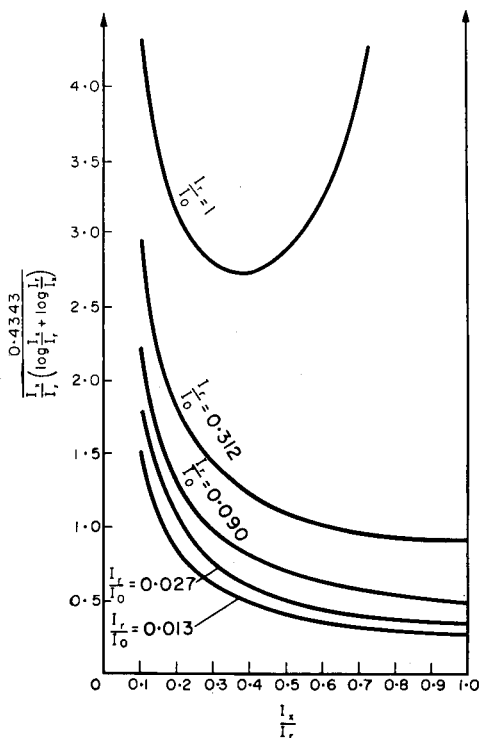


FIG. 2

for other reference solutions can be gained by interpolation. It is interesting to mention that if the transmittance of the reference solution against solvent I_r/I_0 is lower than 0.386 (optical density > 0.4343), the minimum disappears and the function becomes a monotone. It is advantageous to choose experimental circumstances where the values of functions are lower than 1, which means that the standard deviation of transmittance readings is not magnified, but lessened on multiplication.

The term in equation (9) containing the error of cell lengths is multiplied by the factor $(c_x - c_r)/c_x$. The nearer the values of c_x and c_r are to each other, the smaller is the error caused by cell length incongruities. If the cells are used systematically, the error s_l/l becomes negligible and need not be taken into consideration. The other terms in equation (9) are analogous of those of equation (7), detailed above.

From equation (9) the following general conclusion can be drawn for the accuracy of differential spectrophotometric measurements. The error is smaller:

- (i) the more concentrated is the reference solution (its optical density measured against the solvent, should be higher in any case than 0.4343);
- (ii) the higher is the transmittance of the unknown solution measured against the reference solution, being most favourable if I_x/I_r is equal to 1, *i.e.*, the concentrations of unknown and reference solutions are identical;
- (iii) the smaller is the standard deviation of the transmittance readings;
- (iv) the smaller is the uncertainty of cell lengths;
- (v) the longer are the cells used;
- (vi) the higher is the concentration of the unknown solution;
- (vii) the smaller is the standard deviation of the intercept;
- (viii) the greater is the slope of the calibration curve, *i.e.*, the higher is the absorption coefficient of the coloured compound, and
- (ix) the smaller is the standard deviation of the slope.

Some of these requirements seem to contradict each other. Thus, according to (i) the reference solution should be as concentrated as possible. With increase of concentration, however, light signals measured by the photocell become weaker and weaker and therefore the standard deviation of transmittance readings will increase, which contradicts (iii). Thus, for a differential spectrophotometric method an optimal concentration of reference solution can be established on the basis of the error function. This is described in a separate paper.⁸

Calculated total error as well as the separate fractional errors of the differential spectrophotometric measurement of 14–26 mg of cobalt^{II}/litre in the form of its perchlorate (measured against a solution containing 12 mg of cobalt^{II}/litre) are shown in Table III. Details of the method are described in a separate paper.⁸

TABLE III.—ERRORS IN THE DETERMINATION OF COBALT^{II} AS ITS PERCHLORATE BY THE DIFFERENTIAL SPECTROPHOTOMETRIC METHOD

c_x , g of cobalt ^{II} /litre	$0.4343 \cdot s \left(\frac{I_x}{I_r} \right) \cdot 100$, $\frac{I_x}{I_r} \left(\log \frac{I_x}{I_r} + \log \frac{I_r}{I_0} \right) \cdot 100$, %	$\frac{s_a}{a} \cdot 100$, %	$\frac{s_b}{ac_x} \cdot 100$, %	$\frac{s_c}{c} \cdot 100$, (total error) %
14	0.0432	} 0.4327	0.6725	1.15
16	0.0273		0.5885	1.05
18	0.0200		0.5231	0.98
20	0.0159		0.4708	0.92
22	0.0837		0.4279	0.94
24	0.0704		0.3923	0.90
26	0.0448		0.3621	0.84

$c_r = 12$ g of cobalt^{II}/litre

It is interesting to mention that although the error due to transmittance readings (column 1) is essentially decreased by differential spectrophotometric methods, the total error of concentration determination is much higher. Thus, the extremely high precision of differential spectrophotometric methods reported by a number of authors (on the basis of error-type shown in column 2) must be treated critically. An essential

decrease of the experimental errors, as could be proved by calculations, can be expected only if the number of points determined on the calibration curve is increased considerably; thus, within a similar concentration range about 20 points should be determined.

Zusammenfassung—Zur Berechnung des Fehlers bei spektralphotometrischen Bestimmungen ist es nicht genug den durch Durchlässigkeitsablesungen bedingten Fehler allein zu berücksichtigen; es ist vielmehr nötig auch die Unsicherheiten der Schnittpunkte und der Neigung der Eichkurve in Rechnung zu stellen. Auf dieser Grundlage können Fehlergleichungen sowohl für klassische als auch differentielle Spektralphotometrie abgeleitet werden. Allgemeine Schlussfolgerungen werden von den abgeleiteten gezogen; Fehlergleichungen und Rechenbeispiele werden mitgeteilt.

Résumé—La détermination de l'erreur due aux lectures de la transmission n'est pas suffisante pour apprécier les erreurs dans les mesures de spectrophotométrie. On doit aussi tenir compte des erreurs provenant des intersections et de la pente des courbes d'étalonnage. D'après ceci, les équations d'erreurs séparées peuvent en être déduite pour les dosages spectrophotométriques "classiques" et différentiels. Des considérations générales en sont déduites et des exemples sont donnés pour le calcul.

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TITRIMETRIC DETERMINATION OF CARBON IN AQUEOUS SOLUTIONS AND IN ORGANIC COMPOUNDS

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

Summary—A method is described for the determination of submilligram amounts of organic carbon in aqueous solutions. A sample of up to 100 μ l is combusted in a Belcher-Ingram 'empty tube' furnace, and the carbon dioxide absorbed in acetone and continuously titrated with 0.005*M* sodium hydroxide in methanol/pyridine or methanol/methyl isobutyl ketone, using thymol blue as indicator. For amounts of carbon between 0 and 100 μ g the precision is within $\pm 2\mu$ g, so that the carbon content of a 100- μ l sample of aqueous solution may be determined to within $\pm 0.002\%$ absolute. The procedure is also applicable to solutions containing both organic carbon and carbonate carbon. In suitable cases it is possible to differentiate between organic carbon and carbonate carbon in the same sample. Amounts of carbon up to about 500 μ g may be determined using the same titrant, and larger amounts by using a stronger titrant. The same procedure is applicable to the determination of carbon in milligram samples of organic compounds. A procedure is described for internal coulometric generation of the titrant which has been used to determine amounts of carbon up to about 800 μ g.

INTRODUCTION

IN 1955 Blom and Edelhausen¹ described a procedure for the continuous titration of carbon dioxide in acetone or pyridine solution using sodium methoxide in methanol/pyridine as titrant and thymol blue as indicator. The end-point occurs at the formation of bicarbonate.

When initially tried the method proved to be insufficiently precise and unsuitable for the determination of small amounts of carbon dioxide, mainly because of a very marked end-point drift. Investigation revealed the causes of this drift and enabled the sharpness of the end-point to be improved and the method to be applied to the precise determination of very small amounts of carbon dioxide.

DISCUSSION

Experiments were carried out using the combustion and absorption apparatus as described later. The titrant, 0.02*M* sodium methoxide, was made by diluting 0.1*M* sodium methoxide in methanol to 0.02*M* with AnalaR pyridine. The indicator was 0.1 ml of 0.1% thymol blue in methanol, and the absorbent 25 ml of undried reagent grade acetone. The absorption cell was attached directly to the end of the combustion train and about 2 mg of carbon as benzoic acid were combusted with an oxygen flow of 50 ml/min. The absorption of carbon dioxide and the titration were quite satisfactory but, after all of the carbon dioxide had been titrated, the end-point continued to drift on at about 0.32 ml/10 min.

It was established that the excessive end-point drift was caused by the presence of

* That part of the paper dealing with solutions containing both organic carbon and carbonate carbon was received on 21 December 1962.

water and too much methanol in the titration system. The adverse effects of water and methanol were examined more closely and conditions found for minimum drift and maximum sharpness of the end-point. Alternatives to acetone as absorbent and sodium methoxide as titrant were also examined.

Effect of water and methanol on end-point drift

The following examples show to what extent water causes the end-point to drift. With dry reagents (0.02M titrant and 25 ml of acetone as absorbent), the drift, after titration of the carbon dioxide derived from 2 mg of carbon, was 0.02 ml/10 min. The addition of 10 mg of water increased this to 0.03 ml/10 min, 30 mg to 0.05 ml/10 min and 100 mg to 0.15 ml/10 min. This effect is enhanced when a weaker titrant is used. Thus, when employing a 0.005M titrant, the addition of 50 mg of water at the end-point caused the drift to increase from 0.02 ml/10 min to 0.10 ml/10 min and 100 mg to 0.20 ml/10 min.

Methanol causes blurring of the end-point and also promotes end-point drift although to a lesser extent than water. Blurring of the end-point is very pronounced if a 0.02M solution of sodium hydroxide in dry methanol is used as titrant. In this case the end-point is extremely vague and drawn out, and the subsequent addition of pyridine does not improve the situation. When 0.01M sodium hydroxide in methanol/pyridine (1:9) is used (*ca.* an 8-ml titre), the end-point is sharper than with a similar titre of 0.02M solution (1:4). This is apparently because of the reduction in the amount of methanol introduced with the titrant. The effect of methanol was shown by the following experiment. Approximately 0.3 mg of carbon as sucrose was combusted and titrated with 0.005M titrant (0.1M sodium hydroxide in methanol diluted 1:19 with pyridine), giving a titre of about 8 ml. The end-point was sharp to 0.01 ml and the drift at the end-point 0.02 ml/10 min. At this point 1.2 ml of methanol were added. The end-point became much less distinct and the drift increased to 0.08 ml in 10 min.

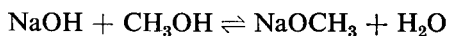
The conditions for maximum sharpness of and minimum drift at the end-point are, therefore, to exclude water from the titration system and to keep the amount of methanol introduced with the titrant to a minimum.

Choice of solvent for absorption of carbon dioxide

Consideration of available data suggested that acetone or pyridine are probably the only practicable solvents, as was found by Blom and Edelhausen.¹ Acetone is the better absorbent of the two and also to be preferred by reason of cost and odour.

Titrant

Lithium hydroxide in methanol/methyl isobutyl ketone, and trimethylbenzylammonium hydroxide in methanol/pyridine were examined as titrants but found to be unsuitable. Sodium hydroxide dissolved in anhydrous methanol (0.1M), to which some Drierite was also added, and then diluted with dry pyridine, was found to provide a titrant indistinguishable from one prepared from sodium methoxide made by dissolving sodium in dry methanol. These two are in fact identical because in the presence of only small amounts of water the reaction



moves largely to the right. For instance, in 99.8% methanol the percentage of base present as methoxide is 98.5%.²

It was found possible to replace pyridine as a diluent in the titrant by methyl isobutyl ketone (MIBK). Titrants made up with these two solvents are equally good, except that the one made up with pyridine keeps better. Dioxan can also be used, but it is insidiously toxic and liable to peroxidise. An entirely methanolic titrant cannot be used.

When anhydrous pyridine was used to make up a 0.005*M* titrant, the rate of decrease of strength was 10% in the first 24 hr. After the pyridine was redistilled and the main fraction used, the rate of decrease was reduced to 3% in the first 24 hr.

A solution made up with MIBK showed a decrease in strength of 6% per day.

The need for continuous titration

Towards the end of this investigation a paper by Patchornik and Shalitin³ appeared describing a titrimetric determination of carbon dioxide in which benzylamine is used in the absorbing solution. This is stated to form a stable salt with carbon dioxide which may be subsequently titrated, after absorption has taken place, with sodium methoxide. It is claimed that this avoids the need to titrate continuously. The absorbing solution recommended by these workers was tried, *i.e.*, absolute alcohol, dry dioxan and benzylamine in the ratio 3:3:1 v/v, of which 25 ml were taken. The end-point using 0.005*M* titrant was so drawn out and indistinct as to be quite useless. A 10% solution of benzylamine in acetone was tried as absorbent: 0.3 mg of carbon was combusted and the carbon dioxide titrated with 0.005*M* titrant, 10 min after commencing the combustion when all of the carbon dioxide had been swept over. The end-point was less distinct than with acetone alone, and only about 90% of the carbon dioxide was retained. This was not investigated further, and continuous titration has been used throughout this work.

EXPERIMENTAL

Apparatus

Combustion train: A Belcher-Ingram 'empty tube' combustion train,⁴ as employed for carbon-hydrogen determinations, complete with preheater and silver furnace, is used. The silver furnace is kept switched on, even in the absence of halogens and sulphur, to prevent condensation of water in that part of the combustion tube. Manganese dioxide is used as an external absorbent for oxides of nitrogen when nitrogen is present in the sample. A plug of silica wool is placed in the part of the combustion tube normally occupied by the sample boat. The aqueous solution is injected on to this absorbent plug from an Agla micrometer syringe.

Absorption cell: This is illustrated in Fig. 1. The burette tap may be sealed into the cell via a rubber closure, or alternatively a current of nitrogen may be passed from outside. This provision has not been found necessary when using oxygen as carrier gas, but it has been found essential in related work, when using hydrogen or argon as carrier gas and combusting over an oxide catalyst. The combustion train is connected to the absorption cell via two Flaschenträger tubes, the first filled with silica gel and the second with Anhydrone; it is followed by the manganese dioxide tube. Connections are made with suitable heavy-wall rubber tubing (Fig. 2). The silica gel drying tube is used because of the large amount of water to be removed from the gas stream. The silica gel may be regenerated by removing the taps and placing the tube in a drying oven overnight.

Burette: A 10-ml microburette, calibrated in 0.01 ml, is suitable.

Reagents

If the organic solvents contain too much water as supplied, they must be dried. Redistillation will reduce the water concentration to a fairly low value. Residual water may be removed by shaking with Drierite or a suitable molecular sieve material.

Acetone: This is analytical reagent grade. The water content should be reduced to not more than 0.02%. Dry acetone is hygroscopic and must be stored in a screw-capped bottle, preferably over a drying agent such as Drierite.

Pyridine: The water content should be reduced to not more than 0.02%. Anhydrous pyridine can be purchased, but it may be necessary to redistil this before use if it is not of analytical reagent grade.

Methyl isobutyl ketone (MIBK): This is an alternative to pyridine and should have a similar water content.

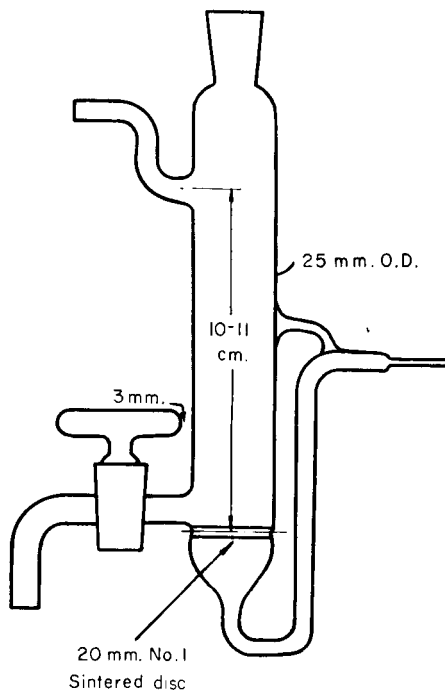


FIG. 1.—Absorption cell.

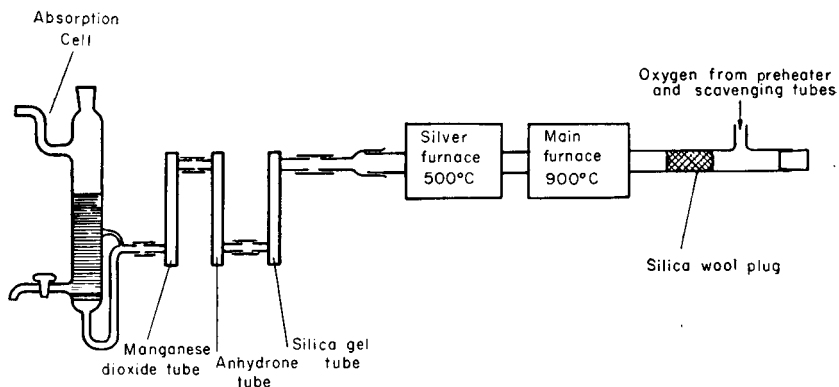


FIG. 2.—Combustion train.

Thymol blue: This should be a solution containing 0.1 g per 100 ml in water-free methanol, and should be prepared afresh once per week.

Sodium hydroxide (0.1M or 0.2M in methanol): Dissolve dry pellets in water-free methanol. Water present should be removed by shaking the solution with Drierite.

Sodium hydroxide (0.005M in methanol/pyridine or methanol/MIBK): Dilute 5 ml of the 0.1M solution in methanol to 100 ml with pyridine or MIBK. The factor will be somewhat less than 0.005M

because of the presence of small amounts of carbon dioxide in the reagents. This titrant should be standardised daily and renewed after 3 or 4 days.

Sodium hydroxide (0.02M in methanol/pyridine or methanol/MIBK): Dilute 10 ml of the 0.2M solution in methanol to 100 ml with pyridine or MIBK. The solution should be restandardised at suitable intervals.

Sucrose solutions (1.5 g per 100 ml in water): The distilled water is thoroughly boiled to remove all carbon dioxide before the solution is made up.

Method for Carbon in Aqueous Solution

Standardisation of titrant

Weigh about 0.80 mg of sucrose into a platinum boat and introduce into the combustion tube. If a suitable micro balance is not available, transfer 50 μ l of the standard sucrose solution on to the silica wool plug by means of an Agla micrometer syringe fitted with a 3-in. hypodermic needle. Close the combustion tube and adjust the oxygen flow to 50 ml/min. Fill the absorption cell with 25 ml of acetone and add 0.1 ml of thymol blue indicator.

Titrate the acidity in the acetone with the 0.005M titrant to the first blue-green colour. Wait 5 min, finally adjust the solution colour to the first clear blue and zero the burette. Apply gentle heat to the silica wool plug with a small gas flame. When the water has volatilised, move the burner slowly along the combustion tube as far as the main furnace to drive the water and volatile organic material into the combustion zone. Return the burner to the silica wool plug, and heat for 3 min at red heat to oxidise any residual carbonaceous material, then pass the burner along the combustion tube a second time as far as the main furnace. Titrate the carbon dioxide continuously as the combustion proceeds. It is easy to maintain the upper part of the absorbing solution a full blue colour even while the lower part is yellow because of the absorption of carbon dioxide. A temporary excess of titrant has no adverse effect; where possible, the solution should not be allowed to become entirely yellow, except momentarily. No loss of carbon dioxide has been observed on this account and certainly no loss is occasioned by this occurring for a few sec.

When it is evident that all of the carbon dioxide has passed into the absorption cell—this normally takes 10 to 15 min from the commencement of the combustion, with a further 5 min added as a safety margin—the solution is adjusted to the correct end-point colour, the titre recorded and also the time elapsed since commencing the combustion.

As previously mentioned, there is noticed, especially with 0.005M titrant, a small drifting on of the end-point, which is dependent on the amount of water and methanol present in the system. Added to this are any such factors as diffusion of carbon dioxide into the oxygen stream, *etc.* Allowance for this drift is made in the following way. When the main titre has been noted, the oxygen is allowed to flow for a further 10 min and any increment in the titre is recorded. The rate of drift is calculated and the appropriate volume subtracted from that first noted to give the net titre equivalent to the carbon dioxide alone. The rate of drift tends to vary from determination to determination, and from day to day, over a small range usually between 0.02 and 0.04 ml in 10 min, so that for accurate work, this calculation should be made for each determination. The end-point is sharp to 0.01 ml. It is assumed that the rate of drift is constant throughout the titration.

When sucrose is used for standardisation, the factor is calculated from

$$F = \frac{3.5054 \times \text{weight of sucrose (mg)}}{\text{net titre (ml)}} \times \frac{M}{100}$$

Analysis of an aqueous solution of organic carbon

It is necessary when analysing a solution of a volatile organic compound to introduce the absorbent and titrate it to the initial end-point before introducing the sample. In order to prevent the acetone running down through the sinter when the combustion tube is opened, a tap on one of the drying tubes is closed before opening the combustion tube. When nitrogen is absent the manganese dioxide tube may be omitted.

Procedure. This is exactly as for standardising the titrant, except that the absorbent must be titrated to the initial end-point before the sample is introduced. Up to 100 μ l of sample is injected onto the silica wool plug, the combustion tube quickly closed, the drying tube tap opened and the combustion commenced.

The carbon content is given by

$$\%C = \frac{\text{Net titre (ml)} \times F \times 12.01}{\text{Volume of sample } (\mu\text{l})}$$

Results: (i) *Recovery of carbon.* A synthetic solution of methanol in boiled distilled water was made containing 0.1121 g of carbon/100 ml. Aliquot portions of this solution were delivered into the

combustion tube from an Agla micrometer syringe. The titrant was 0.005M with pyridine as diluent. A blank was carried out on 100 μ l of the boiled distilled water (1.6 μ g of carbon) and allowance made for this. The results are shown in Table I.

TABLE I

Volume of solution ^a taken, μ l	Carbon taken, μ g	Carbon found, μ g	Error, μ g
100	112.1	109.9	-2.2
		114.0	+1.9
75	84.1	82.7	-1.4
		85.0	+0.9
50	56.1	56.1	0.0
		56.6	+0.5
25	28.0	27.2	-0.8
		29.5	+1.5

^a Solution of methanol (0.1121 g carbon/100 ml) in boiled distilled water.

(ii) *Recovery of carbon in the presence of nitrogen, sulphur and chlorine.* In order to test the recovery of carbon in the presence of nitrogen, sulphur and chlorine, a solution of methanol containing 0.0902 g of carbon/100 ml was made up in a boiled solution, 1N with respect to each of nitric, sulphuric and hydrochloric acids. This solution therefore contained 90.2 μ g of carbon plus approximately 1.4 mg of nitrogen, 1.6 mg of sulphur and 3.5 mg of chlorine per 100 μ l. A series of 100- μ l portions was combusted as before with the manganese dioxide tube in place.

The relatively large amount of nitrogen dioxide in the gas stream is effectively removed by the manganese dioxide, in the absence of which the indicator is rapidly bleached. The carbon found was 90.3, 90.7, 90.3 and 90.7 μ g.

(iii) *Effect of water on the quantitative recovery of the carbon in a solution.* Amounts of water up to 125 mg (larger amounts were not examined) affect neither the oxidation of the organic matter nor the sweeping over of the carbon dioxide into the absorption cell. The drops of water which always condense in the beak of the combustion tube and the upper part of the silica gel drying tube show no tendency to absorb and retain carbon dioxide. To test this a 125- μ l sample containing 28.0 μ g of carbon (as methanol) was combusted. The carbon dioxide was rapidly and quantitatively swept into the absorption cell despite the fact that the ends of the combustion and silica gel tubes were full of water droplets. The carbon found was 28.4 μ g, after allowance had been made for a blank carried out on the same volume of boiled distilled water (2.0 μ g of carbon).

Analysis of aqueous solutions containing both organic carbon and alkali metal carbonate

The need sometimes arises to determine organic carbon in solutions also containing alkali carbonate.

Rapid release of carbon dioxide from sodium and potassium carbonates takes place when heated to 950° in contact with silica wool. It seems likely that this takes place through reaction of the alkali with the silica. As a result of this some attack on the combustion tube takes place where it is wetted by such a sample. To avoid this it is recommended that where samples containing more than very small amounts of alkali carbonate have to be examined, they should be transferred on to a porcelain boat filled with powdered silica. The silica should be renewed periodically. The temperature resulting from the use of a Meeker burner (950°) is sufficient to ensure rapid and quantitative release of the carbon dioxide from sodium and potassium carbonates within about 2 min.

No significant release of carbon dioxide takes place when an aqueous solution of sodium carbonate is heated to 200° in contact with silica for a limited time; this affords a means of differentiating between organic and sodium carbonate-carbon in the same sample, assuming that the organic components present volatilise at temperatures not much in excess of 200°. The sample is heated in contact with powdered silica to 200° for a limited time when the carbon compounds volatile at this temperature are volatilised. After titration of the carbon dioxide derived from these, the sample is heated to 950° to decompose the alkali carbonate. This procedure has been found to work satisfactorily for an aqueous solution of ethylene glycol (b.p. 197.2°) and sodium carbonate.

Potassium carbonate does decompose slowly in contact with powdered silica at 200° but does not do so in platinum. Therefore when it is desired to determine volatile organic carbon only in the presence

of potassium carbonate the sample should be transferred to a platinum boat and heated to 200°; the total carbon is determined on a separate aliquot on silica.

Work has not been carried out on carbonates other than sodium and potassium. In the case of magnesium and calcium carbonates the determination of total carbon should proceed easily; the differentiation between organic and carbonate carbon would depend on the ability to choose a temperature at which the organic material would be volatilised and the carbonate remain undecomposed.

Organic carbon of a sufficiently volatile nature and dissolved carbon dioxide in the same solution could be separately determined by adding to the sample sufficient sodium hydroxide to combine with the carbon dioxide, then applying the foregoing procedure.

Procedure. For solutions of organic carbon (b.p. $> 200^\circ$) in the presence of sodium carbonate, fill a porcelain boat (ca. $25 \times 5 \times 3$ mm.) with finely ground silica. Ignite for a few min in a Meker burner flame. Place the boat in the combustion tube and adjust the acidity of the absorbent as already described. Transfer to the boat up to 100 μ l of sample. Raise the temperature of the boat gradually to 200° over a period of about 5 min and maintain at that temperature for a further 5 min. (An electric heater is necessary for this.) Remove the heater. Titrate the carbon dioxide derived from the sample and when all of the carbon dioxide has been swept into the cell (5 min after removing the heater), adjust the end-point colour and record the titre. Now heat the sample with a full Meker burner for 5 min, titrate the carbon dioxide evolved, and 5 min after removing the burner, adjust the end-point colour and record the titre. The end-point drift is established as before.

When potassium carbonate is present, transfer an aliquot of the sample to a platinum boat and heat as before to 200° to determine the organic carbon. If the total carbon is required, determine this on a separate aliquot transferred to a porcelain boat containing silica.

Results. A blank of 2 μ g of carbon on 100 μ l of boiled distilled water has been subtracted from the results given where appropriate.

(i) *Recovery of carbon from a solution of sodium carbonate.* A solution of sodium carbonate was made up in boiled distilled water containing 0.1001 g of carbon/100 ml. A series of 100- μ l portions was injected onto a silica wool plug and heated to 950° with a Meker burner for 5 min. The carbon found was 99.1, 100.3, 101.0, (96.4) μ g.

Similar samples were injected into a porcelain boat filled with powdered silica and heated in the same way. The carbon found was 102.7, 99.6 and 99.7 μ g.

When 100- μ l portions of this solution were placed in a platinum boat, the release of carbon dioxide was much slower, and only 90% of the carbon was recovered after 5–8 min heating at 950°. This supports the supposition that rapid release of the carbon dioxide takes place through reaction of the alkali with the silica.

(ii) *Recovery of carbon from a solution of potassium carbonate.* A similar solution to the above was made containing 0.0994 g of carbon/100 ml, a 100- μ l portion transferred to a porcelain boat plus silica and heated to 950°. The carbon found was 99.4 μ g.

(iii) *Recovery of carbon from a solution of ethylene glycol plus sodium carbonate.* A solution of ethylene glycol plus sodium carbonate in boiled distilled water was made containing 0.0896 g of organic carbon plus 0.1002 g of carbonate carbon/100 ml.

Replicate 100- μ l portions were injected into a porcelain boat filled with silica. The temperature of the boat was raised by means of an electric heater so as to attain 200° after 6 min, 210° after a further 1 min and then maintained there for a further 3 min. The heater was then removed and the determination concluded as already described.

The results are recorded in Table II.

Method for Carbon in Organic Compounds

In view of the precision attained in the analysis of small amounts of carbon in aqueous solutions it would appear that quite useful results could be obtained in the analysis of, say, 100- μ g samples of organic compounds. The precision in this case could doubtless be increased by reducing the size of the absorption cell and the volume of acetone and reducing the oxygen flow to 20 ml/min, at which flow

TABLE II

Organic carbon found, μ g	Error, μ g	Carbonate carbon found, μ g	Error, μ g
89.2	-0.4	103.5	+3.3
89.4	-0.2	101.4	+1.2
89.0	-0.6	100.9	+0.7
87.7	-1.9	102.2	+2.0

Solution of ethylene glycol (0.0896 g carbon/100 ml) plus sodium carbonate (0.1002 g carbon/100 ml) in boiled distilled water; 100- μ l samples.

rate the empty tube method still operates satisfactorily. This possibility was not tried because of the lack of a submicro balance.

Procedure. The application of the procedure to the analysis of milligram samples of organic compounds was investigated by using 0.02M titrant in methanol/pyridine. An Anhydrone tube was placed at the exit of the combustion tube, and a manganese dioxide tube between this and the absorption cell. The sample, containing 1.5–2.0 mg of carbon, was weighed into a platinum boat, combusted in the usual way and the carbon dioxide titrated continuously as before. The titrant was standardised by the combustion of approximately 4-mg samples of sucrose.

The end-point was sharp to 0.005 ml and the drift at the end-point varied between 0.02 and 0.03 ml/10 min. The titrant decreased in strength about 1% per day.

Results. The results are shown in Table III. A single standardisation using sucrose was carried out for each set of determinations. The compounds were all Organic Analytical Standards (B.D.H., Ltd., England).

TABLE III.—CARBON IN ORGANIC COMPOUNDS USING 0.02M TITRANT

Compound	Weight taken, mg	Theoretical	Carbon, %	
			Found	Deviation
<i>Series 1</i>				
<i>p</i> -Nitroaniline	3.000	52.17	52.20	+0.03
<i>p</i> -Chlorobenzoic acid	3.128	53.70	53.81	+0.11
Sulphonal	4.410	36.82	36.88	+0.06
<i>m</i> -Dinitrobenzene	3.820	42.87	43.10	+0.23
<i>Series 2</i>				
Sulphonal	4.500	36.82	37.03	+0.21
<i>p</i> -Bromobenzoic acid	4.122	41.82	41.79	-0.03
<i>S</i> -Benzylthiuronium-chloride	3.268	47.40	47.58	+0.18
Benzoic acid	2.400	68.84	68.86	+0.02
Naphthalene	2.122	93.71	93.78	+0.07
8-Hydroxyquinoline	2.570	74.47	74.68	+0.21
Phenylthiourea	2.615	55.23	55.41	+0.18

Precision of method. The errors in these determinations are almost entirely on the positive side, which indicates that the titrant factors used in both sets were slightly high.

From the known carbon content of each compound analysed, a value for the factor of the titrant can be calculated. The percentage deviations of these factors from their mean, including those from the two sucrose determinations, were calculated. The probable error was found to be 0.13%. The average sample weight was 3.38 mg. A 0.13% error in weighing this sample would correspond to an error of 4.2 μ g. The known probable error of a single weighing on the balance used is about 3 μ g, so that almost all of the errors in the values for % of carbon found would be caused by sample weighing errors, provided that error in the factor were eliminated.

Automatic Operation

It should be easy to operate the titration automatically by employing a photoelectric end-point detector coupled to a motor-driven syringe burette for delivery of the titrant. A photoelectric end-point detector, such as that described by Fog and Jellum⁵ which used two photocells, registering both colours of the indicator, should be very suitable.

Coulometric Generation of Titrant

The advantages of coulometric generation of titrant are well known, especially where generation proceeds with 100% efficiency. In this case not only would the preparation of titrant and its standardisation be avoided, but the need for regular restandardisation of the titrant because of its instability would be eliminated.

Although some work has been done on this, with encouraging results, it has not yet been possible to examine the technique thoroughly, and the following remarks must be considered with this in mind.

Alkali was generated by electrolysis of potassium iodide dissolved in dry acetone using a spiral platinum cathode and either a silver gauze anode in the same cell, or a platinum anode in the second half of a double compartment cell. Thymol blue in methanol (0.1 ml of 0.1% solution) was added as

visual indicator. On passage of current through the cell, alkali is liberated instantaneously at the cathode as shown by the indicator. The current was integrated with a low inertia motor because this enabled the rate of generation to be varied according to the concentration of carbon dioxide entering the cell during a determination. The low inertia motor used was a type 913 made by Electro Methods Ltd., with counter unit. It is considered that a low voltage type 915 with dial would be more accurate.

The absorption cell already described (Fig. 1) was used with a platinum spiral cathode in the upper part of the absorbing solution and a piece of silver gauze as anode. The advantage of this arrangement was that the cell resistance was low and a high generating current could be employed (up to 200 mA). In order to avoid the need to clean or renew the silver gauze anode a double compartment cell was constructed with a spiral platinum electrode in each half (Fig. 3). The iodine liberated at the anode could then be run off between determinations. The disadvantage of this cell (using a No. 2 10-mm

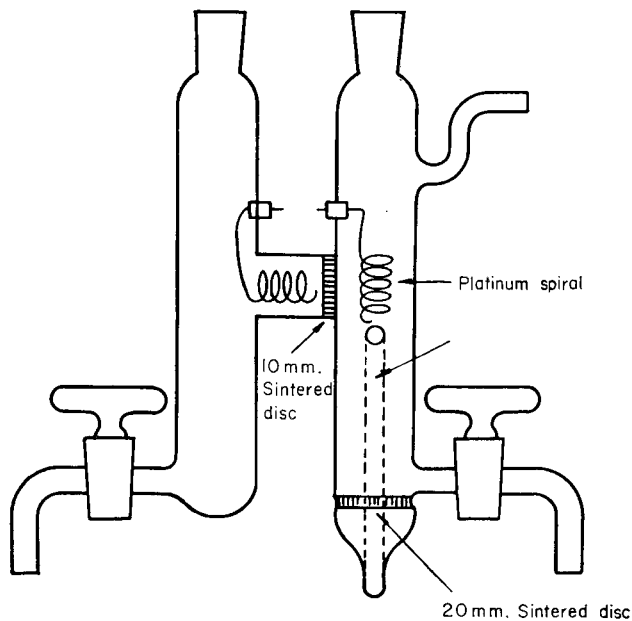


FIG. 3.—Cell for coulometric titration.

sinter between the two halves) was that the high resistance between the electrodes limited the generating current to a maximum of 70 mA because, apparently, of the heat generated at the sinter. A coarser sinter would probably remedy this.

Procedure. Powdered potassium iodide was shaken with dry acetone to form a saturated solution (ca. 1 g/100 ml). A suitable quantity (25 ml) was placed in the absorption cell plus 0.1 ml of indicator. The anode side of the double compartment cell was filled to the same level as the absorption side. A suitable d.c. potential was applied across the electrodes through a rheostat and switch. A generating current of 30 mA was found suitable for the experiments carried out, with an occasional need to increase it to 70 mA when the concentration of carbon dioxide entering the cell was large. The

TABLE IV.—COULOMETRIC TITRATION OF CARBON DIOXIDE.

Weight of carbon taken, mg	Weight of carbon found, mg	Net counter units obtained	CU/mg C
0.760	0.761	49.4	65.0
0.517	0.515	33.4	64.7
0.434	0.435	28.2	65.0
0.334	0.331	21.5	64.3
0.220	0.222	14.4	65.5
0.207	0.205	13.3	64.3

titration procedure was exactly analogous to that already described, and a similar correction for a small drift at the end-point was made.

Results. The low inertia motor with counter unit used gave a change of 748.2 counter units per faraday, or assuming a 100% generating efficiency, 62.3 counter units per mg of carbon where 0.1 unit was the smallest division on the counter unit.

Samples of sucrose providing weights of carbon from 0.2 to 0.76 mg were combusted and the carbon dioxide absorbed and titrated in the double compartment cell.

The results are recorded in Table IV. The carbon found was calculated using the mean counter units per mg of carbon (CU/mg C) from the three largest weights of carbon taken (64.9). This corresponds to a generating efficiency of 96.0%.

Considering the likely error in integration for the smaller amounts of carbon (1%) together with possible weighing errors (1%), the values for CU/mg C are very consistent.

Acknowledgement—The author wishes to thank the Directors of the Distillers Company Limited for permission to publish this work.

Zusammenfassung—Eine Methode zur Bestimmung von Submilligramm-Mengen von organischem Kohlenstoff in wässrigen Lösungen wird beschrieben. Eine Probe von bis zu 100 μ l wird in einem Belcher-Ingram-Ofen mit "offenem Rohr" verbrannt, das CO_2 in Aceton absorbiert und kontinuierlich mit 0,005 m NaOH in Methanol/Pyridin oder Methanol/Methylisobutylketon titriert; Thymolblau dient als Indikator. Für Kohlenstoffmengen zwischen 0 und 100 μ g beträgt die Genauigkeit $6 \pm 2 \mu$ g, sodaß der Kohlenstoffgehalt einer 100 μ l—Probe der wässrigen Lösung auf $\pm 0,002\%$ absolut bestimmt werden kann. Das Verfahren kann auch auf Lösungen mit organischem und Carbonatkohlenstoff angewandt werden; in geeigneten Fällen kann man beide in derselben Probe nebeneinander bestimmen. Kohlenstoffmengen bis 500 μ g können mit demselben Titranten bestimmt werden, grössere Mengen mit einem konzentrierteren Titranten. Die selbe Methode lässt sich zur Kohlenstoffbestimmung in Milligrammproben organischer Verbindungen verwenden. Ein Verfahren zur coulometrischen Erzeugung des Titranten in der Lösung wird beschrieben; so wurden Kohlenstoffmengen bis 800 μ g bestimmt.

Résumé—Une méthode est décrite de dosage du carbone organique en solution aqueuse, pour des quantités de l'ordre du microgramme. Un échantillon de 100 μ l maximum est calciné dans un four de Belcher-Ingram, et l'anhydride carbonique formé absorbé dans l'acétone est dosé d'une manière continue par une solution à 0,005 N de soude dans le mélange méthanol/pyridine ou méthanol/méthyl-isobutyl-cétone, l'indicateur utilisé étant le bleu de thymol. Pour des quantités de carbone comprises entre 0 et 100 μ g, la précision atteint $6 \pm 2 \mu$ g; ainsi, le carbone contenu dans 100 μ l peut être dosé à $\pm 0,002\%$. Le procédé peut également être appliqué à des solutions contenant à la fois du carbone organique et du carbone sous forme de carbonate. Dans les cas favorables il est possible de différencier la provenance du carbone dans un même échantillon. L'utilisation du même réactif permet de doser jusqu'à 500 μ g de carbone, et de plus grandes quantités peuvent être dosées avec un réactif plus fort. Ce même procédé peut aussi être utilisé pour le dosage du carbone dans des échantillons de composés organiques de l'ordre du milligramme. On décrit le procédé de production coulométrique interne du réactif, utilisé pour doser des quantités de carbone supérieures à environ 800 μ g.

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RADIOCHEMICAL SEPARATION OF STRONTIUM BY AMALGAM EXCHANGE

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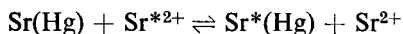
(Received 3 December 1962. Accepted 22 December 1962)

Summary—The radiochemical separation of strontium by an amalgam-exchange technique has been critically evaluated with a saturated aqueous solution of potassium chloride as an exchange medium. With an optimised procedure strontium yields of about 34% were obtained, although mineral acids and alkalis above 0.1M decrease this yield considerably because of decomposition of the amalgam. In studies with tracers of 16 different elements, representative of the Periodic Table, this technique gave considerably better decontamination than does the fuming nitric acid procedure. The simple separation can be carried out in 8 min with no special equipment required, while application of the method to fall-out rain-water samples requires about 40 min. This procedure can also be easily adapted to the preparation of a ^{90}Y -free source of ^{90}Sr .

THE principle of isotopic exchange between a dilute amalgam of a metal and its ions in solution has proved to be very useful for rapid radiochemical separation procedures. Our recent studies on the separation of cadmium³ and indium⁶ show that excellent decontamination can be obtained in a simple 10-min procedure. Indeed, this decontamination is often at least an order of magnitude better than that afforded by the best separation technique previously available.

Preliminary work in this laboratory¹ also indicated the possibility of employing this novel technique for the rapid separation of strontium. In the present paper a critical study of this separation method has been made. Because a detailed evaluation of separations for strontium had already been made by Sunderman and Meinke,⁷ this study provided a good opportunity for the comparison of this new type of separation with optimum methods which are considered standard. This evaluation was particularly timely because of the great interest in radiochemical separations of strontium for fall-out analyses.

When a dilute amalgam of strontium is contacted with an aqueous solution containing radioisotopes of strontium, the radioactive strontium will selectively exchange with inactive strontium in the amalgam. The necessary condition for this exchange is that the concentration of inactive atoms of strontium in the amalgam should be much greater than that of its radioisotope in solution. The exchange can be represented as follows:



where the asterisk denotes a radioisotope of strontium. The amalgam is then removed and the radioactive strontium is recovered by shaking with 2M hydrochloric acid.

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EXPERIMENTAL

Apparatus

A 0.5-oz Boston-round bottle with polyethylene insert screw cap (Plax Corp., Bloomfield, Conn., U.S.A.) was used for agitating the amalgam during separation. It was clamped in a mechanical shaker (Wrist-Action Shaker, Model 33, Burrell Corp., Pittsburgh, Pa., U.S.A.), to which an extension arm of 12 in. was connected to give additional radial action.

The beta-radioactivity measurements were made with a Nuclear-Chicago proportional counter.

Low-level beta measurements were made in a Tracerlab CE-14 Low Background Beta Counter with a mylar window of 0.9 mg/cm² and having a counting efficiency of 40% for ⁹⁰Sr. An anticoincidence circuit was used in the system.

Reagents

Mercury: Baker and Adamson, analytical reagent grade, further purified by washing with dilute nitric acid, followed by rinsing with distilled water.

Strontium chloride: Baker Analysed Reagent.

Potassium chloride: Baker Analysed Reagent.

Sodium nitrate: Baker Analysed Reagent.

All other chemicals used in this work were also of analysed reagent grade.

All radioisotopes used as tracers have been described [Table I² and Table II⁷].

⁹⁰Y-free ⁹⁰Sr: ⁹⁰Y was extracted into 2 ml of 0.1M dibutyl phosphate from 2 ml of equilibrium solution ⁹⁰Sr-⁹⁰Y in 0.1M nitric acid.⁴ Pure ⁹⁰Sr tracer remains in the aqueous layer.

Strontium amalgam: Place 60 g of pure mercury in an electrolytic vessel as the cathode, and add 10 ml of a saturated aqueous solution of strontium chloride. Electrolyse for 15 min at 7.5–8.0 V and 2.5–3.0 A, using a platinum anode. Strontium deposits in the mercury cathode forming the amalgam. Keep the surface of the mercury cathode constantly covered with a layer of strontium chloride crystals to prevent decomposition of amalgam by electrolyte; otherwise decomposition will greatly reduce current efficiency. Wash the amalgam with benzene and dry with air to determine its composition (about 1%). Store the amalgam in an air-tight bottle for at least 3 hr and wash with benzene before use. It has a pasty consistency and sticks to the sides of the containing vessel; it will keep its strength without decomposing for about 2 weeks.

Amalgam-exchange procedure

Place in a bottle 2 ml of a saturated aqueous solution of potassium chloride, containing tracers of contaminating ions plus microgram amounts of inactive strontium, and agitate well to ensure thorough mixing. Radioactive strontium and non-radioactive interferences are used for yield determination. For practical samples make neutral to litmus paper and keep the volume below 4 ml. Add 100 μ l (ca. 1.36 g) of strontium amalgam containing 1% strontium by weight (ca. 14 mg). Shake for 3 min. Remove the supernate by suction and dry the amalgam with absorbent tissue paper. [Do not wash the amalgam or activity will be lost through decomposition of amalgam by water]. Transfer the amalgam to a bottle containing 2 ml of 2M hydrochloric acid and shake for 3 min. Remove a 100- μ l aliquot of the aqueous layer containing separated strontium isotopes, evaporate on a counting plate and count. Total time for the separation is 8 min.

Procedure for rain-water samples

To 500 ml of rain-water add ca. 200 mg of calcium carrier [as 1.2 g of Ca(NO₃)₂·4H₂O] and stir the solution to ensure thorough mixing. Precipitate the calcium as calcium carbonate with ca. 100 ml of 5% ammonium carbonate solution. Digest the precipitate on a hot plate for ca. 5 min and separate by centrifugation of successive 50-ml portions. Wash the precipitate with 5% ammonium carbonate solution, then dissolve in a minimum of 6M hydrochloric acid. Adjust the pH of the solution to ca. 7 by neutralising the excess acid with ammonia solution to the litmus colour change. If the volume of solution is greater than 4 ml, evaporate to ca. 4 ml. Saturate the solution with potassium chloride and perform the amalgam exchange as above. Total time for the entire separation is about 40 min.

DISCUSSION AND RESULTS

Strontium amalgam was first prepared by reducing a saturated aqueous solution of strontium chloride with sodium. The amalgam thus prepared was not pure, however, but contained a small amount of sodium; therefore, the preparation was done electrolytically. The main difficulty with the electrolytic method lies in the fact

that the amalgam is readily decomposed by the aqueous strontium chloride electrolyte. Unsuccessful attempts were made to minimise such decomposition by the use of different strontium salts, such as the nitrate, bromide, chloride and acetate, as well as other solvents, such as absolute alcohol. The extent of this decomposition was finally reduced when the surface of the mercury cathode was covered with a layer of strontium chloride crystals.

In order to determine an optimum separation procedure, a number of trial separations were made in which the shaking time, the concentration of the amalgam and the exchange medium, as well as the composition of the exchange medium, were varied.

The main difficulty encountered in selecting a suitable exchange medium lies in the fact that strontium amalgam is readily decomposed by aqueous solutions and acids. Saturated aqueous potassium chloride solution was used to keep such decomposition to a minimum. Typical yields for 3-min shaking times and 1% amalgams for 0.1*M* hydrochloric acid, 0.5*M* hydrochloric acid, 0.5*M* sodium nitrate, 0.5*M* potassium chloride and saturated aqueous potassium chloride were 15%, 8%, 46%, 47% and 57%, respectively. Absolute alcohol saturated with potassium chloride gave a 19% yield.

The exchange yield is also dependent upon the time of agitation, increasing with time and reaching a maximum at about 3-min, before beginning to decrease gradually. This is probably because of decomposition of the amalgam upon prolonged agitation.

As the amount of strontium in the amalgam was increased from 0.3% to 0.6%, 1.0% and 1.7%, the exchange yield was 41%, 53%, 57% and 58%, respectively. Therefore, a 1% strontium amalgam was used in the standard separation procedure.

Self-absorption problems complicate the measurement of beta emitting ^{90}Sr in the amalgam so that studies were made of a number of back-extractants to strip strontium from the amalgam into an aqueous solution. It proved difficult to quantitatively strip out the strontium. A solution of 2*M* hydrochloric acid was finally selected as the best of a number of stripping reagents, although it recovers only about three-fifths of the product in a 3-min agitation time.

The resultant optimum total procedure has been described above and gives a final yield of about 34% strontium. The entire separation procedure takes about 8 min. To obtain this yield, however, it is necessary to follow exactly the procedure outlined above, otherwise low yields will result because of decomposition of the amalgam.

Purging the system with nitrogen does not produce any appreciable increase in this yield, but does cause precipitation of some potassium chloride from the saturated aqueous solution.

Interferences

Mineral acids, such as hydrochloric, hydrofluoric, nitric, phosphoric and sulphuric, seriously interfere with the amalgam-exchange procedure even at concentrations as low as 0.1*N*. Sodium hydroxide and ammonia solutions also interfere, but to a lesser extent. Some results of our interference studies are given in Table I. This appreciable decrease in the strontium yield is mainly because of decomposition of the amalgam. Thus, the best yield is obtained with a neutral solution. This serious

TABLE I.—EFFECT OF ACIDS AND ALKALIES ON STRONTIUM YIELD IN INITIAL EXCHANGE STEP

Substance	Concentration, <i>N</i>	Yield of ⁹⁰ Sr, %
HCl	0.05	14
HCl	0.1	11
HCl	0.5	9
HF	0.1	10
HF	0.5	7
HNO ₃	0.1	7
HNO ₃	0.5	5
H ₂ SO ₄	0.1	5
H ₂ SO ₄	0.5	3
H ₃ PO ₄	0.1	8
H ₃ PO ₄	0.5	5
NaOH	0.1	16
NaOH	0.5	11
NH ₄ OH	0.1	18
NH ₄ OH	0.5	12

Maximum yield in neutral solution under these conditions = 34%

drawback of the method limits its scope and general applicability, although the yield is quite insensitive to various salt concentrations.

One would expect similar problems in application of the amalgam-exchange technique in separations of isotopes of calcium and barium because both calcium and barium have much the same reactive nature as that of strontium amalgam and are readily decomposed by acids.

Decontamination

Decontamination studies were made of this strontium amalgam-exchange procedure using tracers of 16 different elements representative of the Periodic Table. The results are summarised in Table II and are compared in Fig. 1 with the decontamination data of the 80% nitric acid precipitation method.⁷ Although the yield of strontium is low, the degree of separation obtained from a number of other elements is considerably better than the corresponding separation in the fuming nitric acid method.

In the precipitation methods for strontium, antimony is a prominent contaminant, but decontamination is improved by about a factor of 10 in the amalgam-exchange method. The tin contamination in this method is somewhat greater than for precipitation, probably because of reduction of tin by the amalgam. Selenium shows relatively low contamination. When selenium tracer was brought in contact with the amalgam, some of the selenium was precipitated. For this reason the amalgam was washed with water prior to drying with tissue paper, while with other tracers the amalgam was only dried with the paper.

In general, the decontamination values obtained by this method are not as good as those obtained with the cadmium and indium amalgam-exchange procedures.^{3,6} This might be related to the high reducing power of the strontium amalgam for ions of many elements below strontium in the Electromotive Series. It may be possible to obtain a better decontamination for some of these impurities by scavenging with sodium amalgam. However, only a few preliminary experiments have been made on this approach.

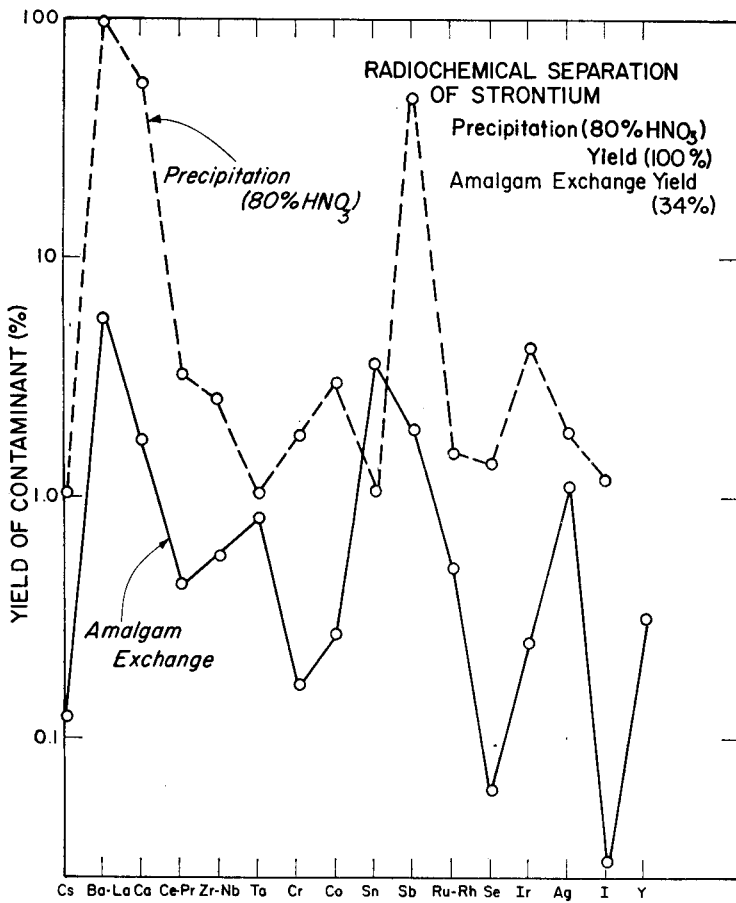


FIG. 1.—Experimental contamination for two types of strontium separations

Applications

The simple amalgam-exchange procedure can be readily used for the separation of ^{90}Sr from its daughter product ^{90}Y . In another area the amalgam-exchange procedure cannot be used directly for the separation of strontium from fall-out rain-water samples because of volume limitations in the sample. An indirect method, such as that described above, whereby the strontium is precipitated on calcium carbonate carrier can be used, however. Chemical recovery of strontium was determined to be $34 \pm 2\%$ by adding a known amount of strontium tracer (10^5 – 10^6 cpm) to 500-ml samples of distilled water and carrying out the separation in exactly the same manner as for rain-water samples.

Several rain-water samples obtained from the School of Public Health of the University of Michigan in Ann Arbor were analysed for radio-strontium by this procedure. The samples had been collected at the Willow Run Meteorological Department during the month of July, 1962. Gross activity of the samples was also determined by evaporating a total of 20 ml in 2-ml portions on a stainless steel planchet. All of the samples were counted through a mylar window of 0.9 mg/cm^2

TABLE II.—SEPARATION OF STRONTIUM AND CONTAMINANTS (AMALGAM-EXCHANGE PROCEDURE)^a

Tracer ^b	Weight, μg^c	Reduction potential, V^d	% Separated
¹³¹ I	C.F.; I ⁻	e	0.03
¹³⁷ Cs	C.F.	-2.92	0.12
¹⁴⁰ Ba- ¹⁴⁰ La	C.F.	-2.90, -2.52	5.45
⁹⁰ Sr	C.F.	-2.89	34 ± 2
⁴⁵ Ca	C.F.	-2.87	1.7
¹⁴⁴ Ce- ¹⁴⁴ Pr	C.F.	-2.48, -2.47	0.42
⁹¹ Y	C.F.	-2.37	0.32
⁹⁵ Zr- ⁹⁵ Nb	C.F.	-1.53, -1.1	0.57
¹⁸² Ta	970	-0.81	0.83
⁵¹ Cr	2.5	-0.74	0.16
⁶⁰ Co	2	-0.28	0.27
¹¹³ Sn	270	-0.14	3.7
¹²⁴ Sb	3.5(SbO ⁺)	+0.21	1.9
¹⁰⁶ Ru- ¹⁰⁶ Rh	6(RuCl ₅ ⁻)	+0.60, +0.25	0.5
⁷⁵ Se	11.5 (SeO ₃ ⁼)	+0.74	0.06
¹⁹² Ir	1 (IrCl ₆ ⁼)	+0.77	0.25
^{110m} Ag	16	+0.80	1.08

^a Average of duplicate runs except for ⁹⁰Sr, which is the average of five runs. Error is "standard deviation."

^b Elements listed in order of their reduction potentials.

^c Weight of inactive element present before separation. C.F. = carrier free.

^d Standard reduction potential of lowest stable oxidation state to the elemental state. Data taken from Latimer.⁵

^e Iodine in its lowest reduced state.

on the Tracerlab low-level beta counting system. The results are summarised in Tables III and IV.

Attempts were also made to apply this procedure to other environmental samples, such as milk and grass. Unfortunately, such samples require a long preparation time prior to the short amalgam-exchange step, thereby losing the time advantage of water samples.

TABLE III.—DETERMINATION OF RADIO-STRONTIUM IN RAIN-WATER SAMPLES

Sample no.	Counting time, min	Counts	Net cpm	Amount of radio-strontium, $\mu\text{c/ml}$	Average of duplicate runs, $\mu\text{c/ml}$
1	30*	528	16.3	1.09×10^{-7} $\pm 0.04 \times 10^{-7}$	1.07×10^{-7}
1	30*	510	15.7	1.05×10^{-7} $\pm 0.04 \times 10^{-7}$	
2	35*	539	14.1	0.94×10^{-7} $\pm 0.04 \times 10^{-7}$	0.93×10^{-7}
2	35*	529	13.8	0.92×10^{-7} $\pm 0.03 \times 10^{-7}$	
3	50†	525	9.3	0.60×10^{-7} $\pm 0.04 \times 10^{-7}$	0.62×10^{-7}
3	50†	546	9.7	0.64×10^{-7} $\pm 0.03 \times 10^{-7}$	

Errors are "standard deviation"

* Background = 1.3 cpm

† Background = 1.2 cpm

TABLE IV.—DETERMINATION OF GROSS ACTIVITY IN RAIN-WATER SAMPLES

Sample no.	Counting time, min	Counts	cpm	Back-ground cpm	Net cpm	Volume of sample, ml	Gross activity, $\mu\text{c}/\text{ml}$
1	50	565	11.3	1.2	10.1	20	5.7×10^{-7}
2	50	510	10.2	1.2	9.0	20	5.1×10^{-7}
3	80	488	6.1	1.2	4.9	20	2.75×10^{-7}

Standard deviation of the counting rate is *ca.* 5%.

The amalgam-exchange procedure for the separation of radioisotopes of strontium is rapid and relatively selective. Although the over-all yield of strontium is rather low (*ca.* 34%), the improved decontamination it affords over other standard separation steps makes it worthy of consideration. Although acids and alkalies interfere markedly, salts generally have little effect; thus, rough neutralisation to a litmus colour change is usually sufficient for satisfactory results. The technique is rapid and can be easily applied to practical samples, such as rain-water. Furthermore, it eliminates the necessity for working with highly corrosive reagents.

Acknowledgements—This work was supported in part by the U.S. Atomic Energy Commission. The stay of one of us (I. Q.) was also supported by a training scholarship from the U.S. Agency for International Development. The assistance of Charles A. Pelletier and others of the University of Michigan School of Public Health in furnishing the environmental samples is gratefully acknowledged.

Zusammenfassung—Die radiochemische Abtrennung des Strontiums mittels Amalgamaustausches in gesättigter, wässriger Kaliumchloridlösung wurde kritisch untersucht. Unter optimalen Bedingungen wurde eine Strontiumausbeute von 34% erzielt. Säuren und Basen in Konzentrationen höher als 0,1 M erniedrigen die Ausbeute beträchtlich, da das Amalgam zersetzt wird. Studien mit Tracern von 16 verschiedenen Elementen, die einen repräsentativen Durchschnitt des periodischen Systems darstellten, haben gezeigt, dass diese Arbeitsweise eine wesentlich bessere Decontaminierung ergab, als die Methode mit rauchender Salpetersäure. Eine Trennung kann innerhalb von 8 Minuten durchgeführt werden, wenn keine besonderen Vorkehrungen nötig sind. Regenwasser bedarf einer Zeit von etwas 40 Minuten. Die Methode kann leicht zur Gewinnung von Y^{90} -freien Sr^{90} adaptiert werden.

Résumé—La séparation radiochimique du strontium au moyen d'un amalgame d'échange a été étudiée systématiquement en utilisant une solution aqueuse saturée de chlorure de potassium comme milieu d'échange. Dans les meilleures conditions, on obtient environ 34% de strontium bien que les acides minéraux et les bases en concentration supérieure à 0,1 M abaissent considérablement le rendement par décomposition de l'amalgame. Les essais effectués avec 16 radio-traceurs différents, typiques de la classification périodique des éléments, montrent que cette technique permet une décontamination bien meilleure que celle obtenue par le procédé à l'acide nitrique fumant. La séparation simple peut être effectuée en 8 minutes, sans appareillage spécial, alors que la méthode d'entraînement à l'eau de pluie nécessite environ 40 minutes. Ce procédé peut également être facilement adapté à la production de Sr^{90} purifié de Y^{90} .

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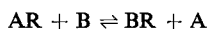
AN ANALYTICAL APPROACH TO CHELATING RESINS

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(Received 6 December 1962. Accepted 19 February 1963)

Summary—Adsorption of lead and copper ions on the chelating resin Dowex A-1 is compared with that on the ordinary ion exchanger Dowex 50. The change in conditional capacity with the change in medium to which the metals are bound in solution is shown, as well as the additional information to be gained through chelating resins, which cannot be obtained with the ordinary type of exchanger. The exchange equilibria investigated show that a reaction of the type



may be readily controlled by binding the metals in solution to a suitable complexing agent. This widens the scope of metal separation facilities.

INTRODUCTION

THE chelating resins, such as Dowex A-1, represent a new group of ion exchangers. The chelating function which is a feature of their make-up and the effects resulting from it give them a wide range of applications. On the other hand, this type of ion exchanger raises new problems with regard to the parameters whose influence must be ascertained before their analytical properties may be understood and defined.

The first review of chelating resins, published by Hale¹ in 1956, described the methods of their synthesis and stressed their analytical and industrial importance. Practical applications are the concentration of small quantities of metal ions, *e.g.*, copper, cobalt, or nickel, as achieved by Turse and Rieman² in an ammoniacal medium and by Christell, Forberg and Westermarck³ in sodium triphosphate.

Before attempting further applications it would appear advisable to investigate whether the information available on the behaviour of chelating agents in solution on the one hand and that of ion-exchange processes on the other could assist in pointing out the special analytical properties of the chelating resins. In this paper an attempt is made to clarify two of the problems arising in this connection:

- (1) the differences between the adsorption curves of ordinary ion exchangers and those of the chelating resins;
- (2) the relation between the affinity of the metal ions in solution to the chelating resin and the composition of the solution medium from which they are adsorbed.

RESULTS AND DISCUSSION

Adsorption curves for single metal ions

In order to reply to the first problem mentioned above, adsorption curves were derived for two metals, copper and lead, the behaviour of which is well known in solution. Two types of media were chosen. One was a system of acetic acid and sodium acetate, with which the metals form a weak complex ($\log K_{Cu} = 3$; $\log K_{Pb} = 4$); the other was of glycine, with which they form strong complexes

($\log K_{Cu} = 15.3$; $\log K_{Pb} = 8.9$). Because of the chelating nature of the Dowex A-1 resin, different capacities for the two metals may be expected as a result of a change in medium.

Fig. 1 shows the adsorption curves of copper from the acetate medium onto Dowex A-1 and onto the strong cation exchanger Dowex 50. Examination of Fig. 1 shows two fundamental differences between these types of ion exchanger:

(a) The capacity of Dowex A-1 for copper in this medium and at the given pH is greater than that of Dowex 50. Although the stability constant of the copper-acetate complex is small, it is sufficient for reducing the maximal capacity of Dowex 50,

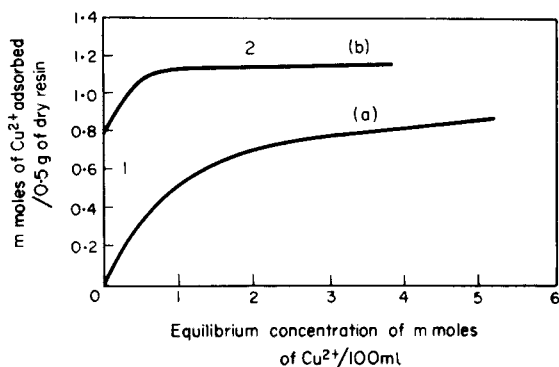
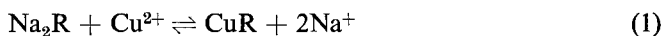


FIG. 1.—Adsorption of copper from a 0.2M acetate medium (pH 4.5): (a) adsorption on Dowex 50, (b) adsorption on Dowex A-1.

which as a rule is 4–5 meq/g of dry resin. In the present case the capacity dropped to 3.5 meq/g, and a further reduction may be expected with increasing buffer concentration or when a different buffer, having a higher stability constant with copper, is introduced into the solution.

(b) The shift of the equilibrium in the reaction



to the right is greater for Dowex A-1 than for Dowex 50. This becomes clear from the difference in the shape of the two curves in Fig. 1. Curve (a) resembles the Langmuir isotherm as described by Boyd and coworkers⁴ who described the adsorption of various metals on cation exchangers, while curve (b) consists of two straight lines linked by a short and steep curve. The first straight line, 1, of curve (b) coincides with the ordinate, indicating the strong shift of reaction (1) to the right. This shift is analogous to the behaviour of complexing agents, *e.g.*, EDTA, which form stable complexes with metals such as copper, lead, *etc.*, in water. It points to the practical application of extracting metals from very dilute solutions on Dowex A-1, which cannot be done efficiently by the ordinary ion exchangers or by other separation methods. Line 2 of the curve (b) is the plateau of maximum capacity of Dowex A-1 (4.8 meq/g of dry resin) in the medium indicated, the value of which corresponds to the maximum capacity of the common ion exchangers in the absence of a competing complexing agent.

Fig. 2 shows that when changing over from an acetate to a glycine medium, the extent of adsorption also changes. The capacity of Dowex 50 in this medium is

negligible, while Dowex A-1 adsorbs appreciable amounts of copper and lead. It is interesting to note that the maximum capacity for copper from this medium dropped to 3.3 meq/g as against 4.8 for the acetate medium of similar concentration and pH. This illustrates well the competition between glycine and Dowex A-1 for the metal ion.

Preliminary experiments have shown that the capacity is further reduced the stronger the complexation in solution. In the case of copper, for instance, the total capacity in a 0.2M citrate medium is 1.5 meq/g, while in a tartrate medium it is 0.8 meq/g.

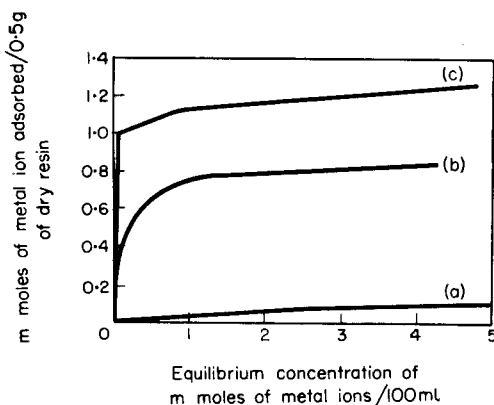


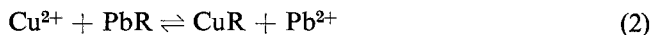
FIG. 2.—Adsorption of copper and lead from a 0.2M glycine medium (pH 4.5): (a) adsorption of copper and lead on Dowex 50, (b) adsorption of copper on Dowex A-1, (c) adsorption of lead on Dowex A-1.

This means that here is a case of “conditional capacity” in analogy to “conditional stability constants” of metal complexes in solution, as defined by Kolthoff,⁵ Ringbom⁶ and others.

Curve (c) in Fig. 2 shows that the capacity for lead ions is greater than that for copper ions. This is because of the large difference in the stability constants of copper and lead with glycine. The difference in capacity for the various metals is no indication of the strength with which they are bound to the chelating ion exchangers. This point will become clearer from the experimental set-up for the exchange reactions, which will also assist towards answering the second problem posed in the *Introduction*.

Exchange reactions

In order to define the effect of the type of medium in analytical separations on Dowex A-1, the competition of lead and copper for the resin was measured in different media and the results expressed by means of the replacement reaction:



The equilibrium constant of this reaction will depend on the conditions under which the experiments are conducted, such as pH, temperature, ionic strength, *etc.* Equation (2) will have an equilibrium constant in the form of the quotient defined by Argensinger and Davidson:⁷

$$K_m = \frac{m_{\text{Pb}^{2+}} N_{\text{Cu}}}{m_{\text{Cu}^{2+}} N_{\text{Pb}}} \quad (3)$$

where m = molarity of metal ions in solution,
and N = mole fraction of the metals in the resin phase.

This is an apparent and not a thermodynamic constant, because the activity coefficients of the metals in solution and in the resin phase have been neglected; but it provides practical information as to the separation possibilities of two metals with the aid of Dowex A-1.

Determination of K_m

If equation (3) is written in its logarithmic form

$$\log \frac{N_{\text{Cu}}}{N_{\text{Pb}}} = \log K_m + \log \frac{m_{\text{Cu}}^{2+}}{m_{\text{Pb}}^{2+}} \quad (4)$$

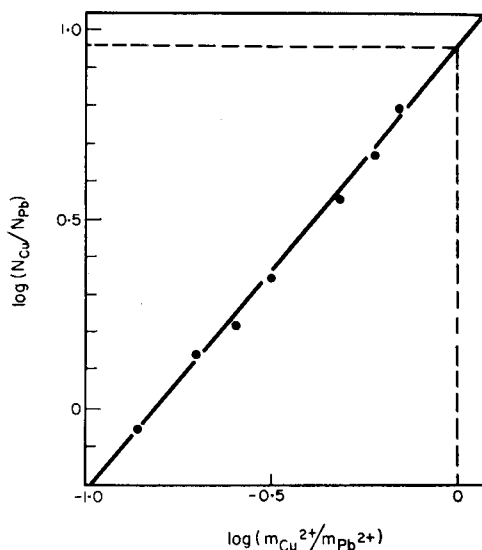


FIG. 3.—Exchange adsorption of copper and lead on Dowex A-1 in a 0.2M acetate medium (pH 4.5).

then the graphic correlation of $\log \frac{N_{\text{Cu}}}{N_{\text{Pb}}}$ versus $\log m_{\text{Cu}}^{2+}/m_{\text{Pb}}^{2+}$ will produce a straight line, the intersection of which with the y-axis will be $\log K_m$.

In practice, the exchange reaction may be carried out in two different ways:

(i) The resin is saturated with lead ions. Different concentrations of copper solutions are then added to constant quantities of lead-saturated resin and, after equilibrium has been reached, the resin is analysed for copper and lead.

(ii) Fixed quantities of both metals in a solution of certain volume are added to the resin in its sodium form and brought to equilibrium. This is permissible, because sodium does not compete with either metal. Method (ii) was preferred because equilibrium is more quickly attained [2 hr compared with 24 hr by method (i)].

The identity of results by the two methods was proved by the fact that the points from both fell on the same straight line.

Fig. 3 gives $\log k_m = 0.96$ in a 0.2M acetate medium. It is interesting to note that this result is analogous to the competing equilibria of the same two metals with

EDTA in solution. The thermodynamic constants of copper and lead with EDTA are $\log K_{\text{Cu-EDTA}} = 18.8$ and $\log K_{\text{Pb-EDTA}} = 17.9$, and $\log \frac{K_{\text{Cu-EDTA}}}{K_{\text{Pb-EDTA}}} = 0.9$.

In the case of the glycine medium, competing complexations exist, as shown in Fig. 4, where the slope of the straight line is much smaller and the point of intersection with the y-axis gives $\log K_m = -0.62$. This proves that from this medium lead is adsorbed preferentially, which also becomes clear from the appreciable difference in the thermodynamic stability constants of the copper and lead glycinate.

The preference of the ion exchanger for copper in an acetate medium—and conversely its preference for lead in a glycine medium—shows that the direction of equation (2) may be determined at will by selecting the proper complexing medium in solution.

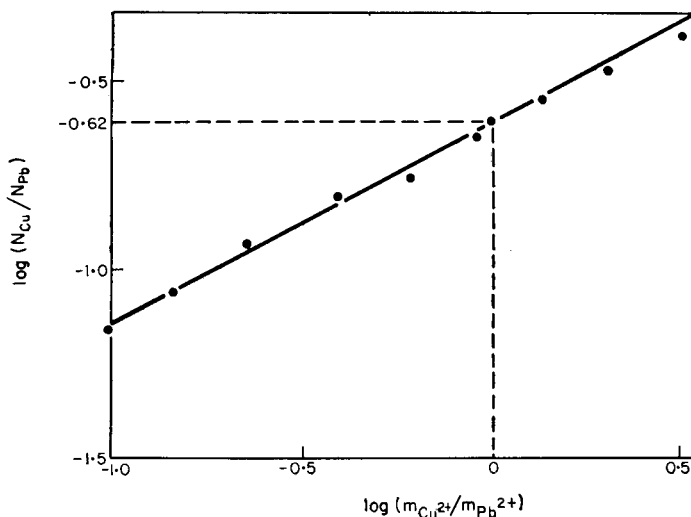


FIG. 4.—Exchange adsorption of copper and lead on Dowex A-1 in a 0.2M glycine medium (pH 4.5).

EXPERIMENTAL

Reagents

0.2M Standard copper solution: Prepared by dissolving 15.908 g of reagent grade copper^{II} oxide in nitric acid (1:1), evaporating excess acid and making up to 1 litre.

0.2M Standard lead nitrate solution: Prepared by dissolving 66.25 g of analytical grade lead nitrate, dried at 100°, in distilled water and making up to 1 litre.

0.1M Standard EDTA solution: Prepared by dissolving 37.21 g of pure disodium dihydrogen ethylenediaminetetra-acetate dihydrate in distilled water and making up to 1 litre.

0.5M Acetic acid-0.5M sodium acetate buffer solution: Prepared by dissolving 68 g of sodium acetate in distilled water, adding 30 ml of glacial acetic acid and making up to 1 litre. The pH of this solution is 4.5.

Glycine: Analytical-grade solid.

Dowex A-1 chelating resin: Prepared in the sodium form and dried at 105°.

Adsorption experiments

A series of copper or lead solutions, containing varying amounts of metal ion (0.2–6 mmoles), was prepared by measuring the appropriate volume of metal ion stock solution into a 100-ml volumetric flask, neutralising with sodium hydroxide and adding the required amount of complexing agent. In the case of the experiments carried out in an acetate medium, 20 ml of the 1M acetate buffer solution were added and the volume was made up to 100 ml; in the case of the experiments in solutions

containing glycine, 1.5 g of the solid substance was introduced into the solution. The pH was adjusted with a Beckman model H pH meter to 4.5 and the volume made up to 100 ml.

These solutions were then introduced into 250-ml beakers, each containing 0.500 g of dry resin. The beakers were now placed on a magnetic stirrer plate for 2 hr to achieve equilibrium; the resin was then separated from the solution by filtration, washed, and the metal ions adsorbed on it were eluted with 6*M* nitric acid.

In a subsequent series of similar experiments, the behaviour of the resin in contact with solutions containing varying amounts of copper and lead (while their total sum was kept constant: 6 mmoles/100 ml), was investigated. Table I shows the concentrations employed and the results obtained in a glycine medium.

TABLE I.—ADSORPTION DATA OF COPPER-LEAD MIXTURES IN A 0.2*M* GLYCINE MEDIUM (pH 4.5).

Pb ²⁺ taken, mmoles/ 100 ml	Cu ²⁺ taken, mmoles/ 100 ml	Pb ²⁺ found in resin, mmoles	Cu ²⁺ found in resin, mmoles	Pb ²⁺ found in solution, mmoles	Cu ²⁺ found in solution, mmoles
5.5	0.5	1.15	0.080	4.35	0.42
5.0	1.0	1.10	0.130	3.90	0.87
4.5	1.5	1.07	0.165	3.44	1.33
4.0	2.0	1.05	0.178	2.95	1.82
3.5	2.5	1.01	0.222	2.50	2.28
3.0	3.0	0.96	0.270	2.04	2.73
2.5	3.5	0.93	0.304	1.57	3.20
2.0	4.0	0.88	0.352	1.12	3.65

Analysis of eluted metals

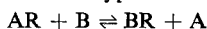
After elution, all solutions were evaporated to dryness in order to remove excess acid. Solutions containing one metal ion only were titrated directly, in an acetate medium, with standard EDTA solution using a mercury electrode⁸ for end-point detection. In the presence of both copper and lead ions, their sum was determined by direct titration with standard EDTA solution; copper was determined polarographically in another aliquot as its EDTA complex.⁹ Polarograms were run in a 0.2*M* acetate buffer solution containing 0.1*M* EDTA, from 0.0 to -0.7 V vs. S.C.E.

CONCLUSION

The adsorption and exchange equilibrium curves in this work point a way towards solving the two problems posed in the *Introduction*. It has been shown that the medium to which the metals are connected in solution exerts a decisive influence on the adsorption of a chelating ion exchanger. This is analogous to the effect of the medium in competing equilibria in soluble chelates pointed out by Reilley, Schmid and Sadek,¹⁰ Cheng,¹¹ Hulanicki,¹² and others. In order to predict the influence of the medium on the measure of adsorption of different components, information additional to the ordinary data such as pH, ionic strength, *etc.*, is required, namely the quantity of competing substances and their stability constants with the metal ions in solution.

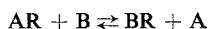
Acknowledgement—The author wishes to thank Miss H. Friedmann for her valuable help in the execution of the experiments preliminary to this work.

Zusammenfassung—Die Adsorption von Blei und Kupfer an Dowex A-1 wird mit der an gewöhnlichen Ionenaustauschern verglichen. Die Änderungen der Adsorptionskapazität mit Änderung des Mediums wird studiert und es wird gezeigt, dass chelierende Austauscher zusätzliche Informationen geben, die beim Arbeiten mit gewöhnlichen Austauschern nicht erhalten werden können. Die studierten Austauschgleichgewichte waren vom Typ



und es wurde gefunden, dass leichte Kontrolle möglich ist, indem man die Metalle in der Lösung mit geeigneten komplexierenden Reagenzien bindet. Auf diese Art werden die Möglichkeiten von Metalltrennungen erweitert.

Résumé—Les adsorptions des ions Pb et Cu sur résine complexante Dowex A-I sont comparées à celles obtenues avec une résine échangeuse d'ions normale. L'étude montre un changement de la capacité conditionnelle avec le changement du milieu auquel les ions en solution sont liés; l'emploi de résine complexante fournit également une information supplémentaire ne pouvant être obtenue avec une résine échangeuse normale. Les équilibres d'échange d'ions étudiés montrent qu'une réaction du type:



peut être contrôlée en complexant les métaux en solution avec un réactif approprié. Possibilités d'extension du problème à la séparation des métaux.

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SELECTIVE DETERMINATION OF TRACE QUANTITIES OF SILVER USING SORPTION OF $\text{Ag}(\text{NH}_3)_2^+$ ON SILICA

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(Received 12 December 1962. Accepted 19 February 1963)

Summary—It is possible to adsorb silver, in the form of $\text{Ag}(\text{NH}_3)_2^+$, quantitatively on silica from solutions of pH higher than 8.5, even in the presence of EDTA. Conditions are described for the determination of trace amounts of silver in the presence of gram amounts of copper, mercury, cadmium, zinc, nickel, bismuth and iron.

RECENTLY the quantitative sorption of metal-ammonia complexes on silica has been studied.^{1,2} The relatively small sorption capacity of silica, however, only permits the separation of trace quantities of metals. Because the stabilities of the complexes with ammonia do not differ appreciably, the results obtained were not satisfactory (especially for the separation of trace amounts of one metal from a large amount of another metal) when the masking effect of other complex-forming reagents or change of pH of the solution used for the sorption process were encountered. There is one exception, however, namely, the complex $\text{Ag}(\text{NH}_3)_2^+$, which under suitable conditions is sorbed on silica even in the presence of a large excess of EDTA. EDTA complexes of anionic nature are not sorbed on silica and this effect increases the selectivity of the sorption of the $\text{Ag}(\text{NH}_3)_2^+$ complex.

Silver was sorbed from alkaline solutions even in the absence of ammonia, probably as colloidal silver hydroxide (pK 2.3). This could be explained as the absorption of the colloid species on the very large surface of the silica and not as sorption, which is more in the nature of an ion-exchange effect. The sorption of silver hydroxide under these conditions is inhibited even at relatively small concentrations of EDTA. This is undoubtedly because of the formation of the silver-EDTA complex (pK_κ 7.2) which is of anionic nature and thus interferes with the analytical application of the sorption process.

In the present paper the sorption of the $\text{Ag}(\text{NH}_3)_2^+$ complex on silica in the presence of EDTA has been studied. The results obtained were used as the basis of a method for the determination of microgram amounts of silver in the presence of relatively high concentrations of a series of metals.

EXPERIMENTAL

Reagents

Silica: Silica of pore size 85 Å and particle size 0.15–0.20 mm, activated at 120°,³ was used for the sorption, which was carried out on a column of 160 mm internal diameter and 50 mm height. The pH of the silica was adjusted to the required value by washing with a suitable buffer solution.

5 × 10⁻⁴ M silver nitrate solution: 5 × 10⁻² M silver nitrate solution was prepared by dissolving pure silver metal in nitric acid and subsequently diluted to 5 × 10⁻⁴ M.

0.1 M 1,10-Phenanthroline solution: Prepared by dissolving 18 g of reagent grade 1,10-phenanthroline in hot water, acidifying with 5 drops of acetic acid and diluting to 1 litre.

1M EDTA solution: Prepared by dissolving 372 g of reagent grade EDTA in warm water, making alkaline with aqueous ammonia (1:1), then diluting to 1 litre. The pH of the resulting solution should be 8.

Buffer solutions: Prepared by potentiometric neutralisation of suitable acids (acetic or boric acid) with aqueous ammonia. All buffer solutions were prepared so as to have a concentration of *ca.* 1M.

Other solutions used were prepared from reagent-grade chemicals and were standardised using recommended procedures.

Apparatus

Optical densities were measured with a Pulfrich photometer (Zeiss, Jena, E. Germany) which had an arrangement for objective measuring—Elpho II. pH values were measured with a glass electrode and pH meter Multoscop V (Lab. potřeby, Prague, Czechoslovakia).

Influence of pH on sorption of $\text{Ag}(\text{NH}_3)_2^+$ on silica

The sorption of $\text{Ag}(\text{NH}_3)_2^+$ on silica was evaluated colorimetrically. Silver was determined as the yellow complex of silver^{II} with 1,10-phenanthroline in acetic acid solution.⁴ This method was sufficiently sensitive and rapid for the determination of silver in pure solutions containing of the order of 1 μg of silver/ml.

The influence of pH on the sorption of $\text{Ag}(\text{NH}_3)_2^+$ on silica was studied under kinetic conditions similar to those employed during the analysis. The sorption of 2 ml of 5×10^{-4} M silver nitrate solution in a total volume of 25 ml, containing 5 ml of 1M buffer solution (ammonia + suitable acid), was carried out at a flow rate of 1.5–2.0 ml/min. Subsequently, the column was washed with 10 ml of the same buffer solution diluted to 0.1M, then with 25 ml of redistilled water. The sorbed $\text{Ag}(\text{NH}_3)_2^+$ was eluted with 25 ml of water acidified with 1 ml of glacial acetic acid. To the eluate were added 15 ml of glacial acetic acid, 2 ml of 0.1M 1,10-phenanthroline and 0.5 g of ammonium persulphate. After dissolution of the latter by thorough shaking, the solution was diluted to 50 ml and allowed to stand for 30 min. The optical density was then measured (5-cm cell, S 41 filter) at 410 m μ using a blank of the same composition but free from silver. A 100% recovery was considered to be obtained for an optical density which was the same as for the solution containing the same amount of silver as the sample, this silver from the solution being sorbed on silica under the same conditions as the analysed solution (Fig. 1, curve 1).

The effect of both pH and EDTA concentration was examined by a similar procedure but, instead of the buffer solution, 2.5 ml of 1M EDTA solution were used and the pH was adjusted potentiometrically with aqueous ammonia (1:1) or sulphuric acid (1:1) (Fig. 1, curve 2).

The curves in Fig. 1 show that, in the absence of EDTA, the sorption of silver on silica is quantitative at pH 7.5, but in the presence of excess of EDTA it is quantitative at pH 8.5. The results

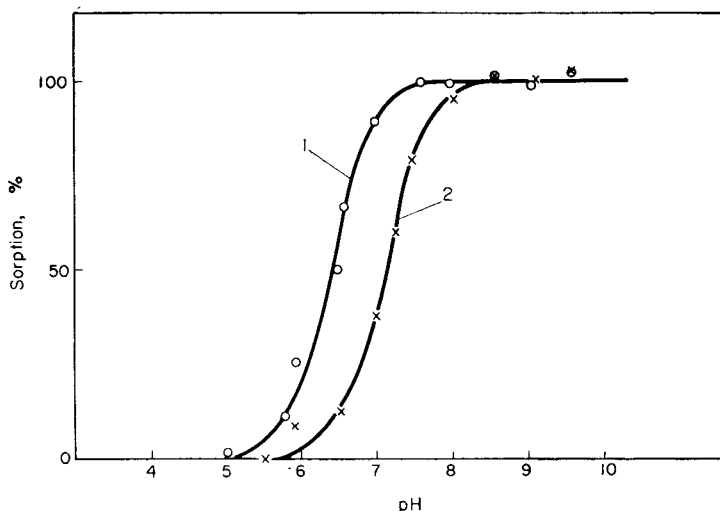
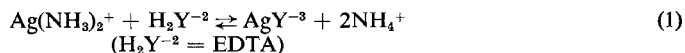


FIG. 1.—Influence of pH on sorption of $\text{Ag}(\text{NH}_3)_2^+$ on silica: (1) in the presence of buffer solutions of ammonia/acetic acid or boric acid, (2) in the presence of 0.1M EDTA.

obtained indicate the similarity in stability of the complexes of EDTA and ammonia;¹ it is possible, however, to eliminate this effect of EDTA by increasing the pH (concentration of ammonia):



Neither citric acid nor sodium citrate (1 g/25 ml) influenced the sorption of $\text{Ag}(\text{NH}_3)_2^+$.

Influence of column flow rate and ionic strength of solution on sorption of $\text{Ag}(\text{NH}_3)_2^+$

The influence of these factors was studied under kinetic conditions and under the same experimental conditions as employed during the study of the effect of pH. At pH 8.5 it is possible to sorb quantitatively 100 μg of silver from a volume of 25 ml at a maximal flow rate of 2 ml/min.

The sorption is not influenced by the ionic strength; this was studied using salts with practically no complex-forming properties, *e.g.*, potassium nitrate and sodium sulphate. Even then, when the total volume of 25 ml of solution contained as much as 10 ml of a saturated solution of these salts, the sorption of 50 μg of silver was quantitative.

Influence of pore size and particle size of silica

The sorption of $\text{Ag}(\text{NH}_3)_2^+$ is influenced by the pore size of the silica as is the case for ferroin;¹ with decrease in particle size, the sorption capacity of silica increases rapidly. The results of kinetic measurements on silica of particle size 0.15–20 μm (relatively small resistance and of sufficient capacity) have shown that at pH 8.5 and flow rate 2 ml/min, 0.75 mg of silver are quantitatively sorbed. Because only the sorption of trace concentrations of silver was studied, the sorption capacity of silica of smaller particle size was not determined.

$\text{Ag}(\text{NH}_3)_2^+$ is sorbed well enough on silica of pore size 32, 65 and 85 \AA , but silica of pore size 150 \AA was unsuitable for the quantitative sorption of silver (as was found for ferroin²).

Accuracy of determination of traces of silver sorbed on silica as $\text{Ag}(\text{NH}_3)_2^+$

The accuracy of the method for the determination of silver was investigated under the conditions described above. Silver was sorbed at pH 8.5 and determined colorimetrically as yellow $\text{Ag}(\text{phen})_2^{2+}$. Quantitative sorption was obtained in the concentration range 0.5–7.5 μg of silver/ml. The average error was found to be $\pm 1.7\%$.

Selectivity of determination of silver

All metals which form complexes with ammonia or which readily hydrolyse to form hydroxo-complexes or hydroxides, are sorbed on silica. This means that at pH 7.5, when $\text{Ag}(\text{NH}_3)_2^+$ is sorbed quantitatively, the sorption (complexes with ammonia or hydroxocomplexes) or adsorption (colloidal hydroxides) of many metals occurs. The selectivity of the sorption, however, and even the selectivity of the determination is increased by using EDTA which does not interfere in the sorption process at pH 8.5 (see Fig. 1). The average error in the presence of 1 g of EDTA/25 ml was found to amount to $\pm 2.3\%$. The chelates of EDTA with many metals are not sorbed on silica and even gram amounts of these metals could be masked for the determination of silver, by using this reagent.

The masking of metals which do not form stable complexes with EDTA (antimony, tin, *etc.*) was attempted with citric acid which does not interfere with the sorption of $\text{Ag}(\text{NH}_3)_2^+$ (see above). The results, however, were not satisfactory, and the reasons for this are under further investigation.

The masking effect of EDTA was examined in the following way: To a mixture of 1 ml of 5×10^{-4} M silver nitrate solution and 5–20 ml of a 1M solution of the interfering metal (as its nitrate or sulphate), a sufficient amount of 1M EDTA solution (in molar ratio 1:1) was added and the pH of the solution was adjusted with ammonia to 8.5–9. Silver was then sorbed at a flow rate of 1.5–2 ml/min, on a silica column previously washed with 25 ml of a solution containing 2.5 ml of 1M EDTA solution at pH 8. After the sorption of silver the column was washed with 10 ml of 0.1M EDTA solution (pH 8.5) and 25 ml of water, the silver was eluted with dilute acetic acid and its concentration determined colorimetrically as yellow $\text{Ag}(\text{phen})_2^{2+}$. To the eluate were added 15 ml of glacial acetic acid, 2 ml of 0.1M phenanthroline solution and 0.5 g of ammonium persulphate, and the resulting solution was diluted to 50 ml. The optical density of the solution was measured in a 5-cm cell at 410 $m\mu$. The amount of silver was calculated using a calibration curve obtained by the measurement of standard silver solutions under identical conditions. The procedure is suitable for the determination of 0–15 μg of silver/ml. For the final determination of silver in the eluate any other sufficiently sensitive and reliable procedure can, of course, be used.

This procedure for the determination of trace amounts of silver can be carried out in the presence of all metals which at pH 8.5 form complexes with EDTA so stable that the normal tendency for hydrolysis or formation of ammonia complexes is eliminated. The determination of silver in the

TABLE I

Additional element, g	Silver taken, μg	Silver found	
		μg	Error, % rel
Cu 1·2	53·5	52·6	-1·7
Hg 2·0	53·5	54·7	+2·3
Cd 2·2	53·5	51·8	-3·1
Zn 1·3	53·5	54·0	+0·5
Ni 1·1	53·5	50·4	-4·0
Fe α 1·3	53·5	56·3	+5·0
Bi 2·1	53·5	54·5	+1·9

α pH value for sorption was 9·3.

presence of some such metals was studied and the results obtained are given in Table I. They show that trace amounts of silver can be reliably determined in the presence of gram amounts of the different metals.

The described procedure was tested by the analysis of electrolytic copper (Outokumpu Oy, Metallitehdas, Finland). Instead of the specified $1 \times 10^{-3}\%$ of silver, $0\cdot92 \times 10^{-3}\%$ of silver was found, a difference of -8% rel.

Acknowledgement—The author would like to thank Mr. J. Štěřba (Research Institute of Natural Medicaments, Prague) for the kind provision of samples of silica.

Zusammenfassung—Aus einer Lösung mit einem pH grösser als 8,5 kann man Silber in der form von $\text{Ag}(\text{NH}_3)_2^+$ auch in Gegenwart von EDTA quantitativ an Silicagel adsorbieren. Es wurden Bedingungen zur Bestimmung von Spuren Mengen Silber neben Grammengen von Cu, Hg, Cd, Zn, Ni, Bi und Fe ausgearbeitet.

Résumé—Il est possible d'adsorber quantitativement l'argent sur la silice, sous forme de $\text{Ag}(\text{NH}_3)_2^+$, à partir de solutions de pH supérieur à 8,5 et même en présence d'EDTA. Description des conditions de dosage des traces d'argent en présence de fortes quantités de cuivre, mercure, cadmium, zinc, nickel, bismuth et fer.

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8-ACETOXYQUINALDINE AS AN ANALYTICAL REAGENT PRECIPITATION OF THORIUM

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(Received 11 January 1963. Accepted 13 February 1963)

Summary—Thorium can be precipitated from homogeneous solution as the 1:4 chelate, $\text{Th}(\text{C}_{10}\text{H}_8\text{ON})_4$, by 8-hydroxyquinaldine generated by the hydrolysis of 8-acetoxyquinaldine. The use of this ester yields a precipitate with physical characteristics distinctly superior to those of the precipitate produced in a conventional way by 8-hydroxyquinaldine, but purity is attained under somewhat more restrictive conditions. Reasons for this are discussed.

INTRODUCTION

THE precipitation of metal 8-hydroxyquinolates (oxinates) from homogeneous solution by the hydrolysis of 8-acetoxyquinoline has recently been investigated.^{1-5,24} The advantages of this technique have prompted our study of a related compound, 8-acetoxyquinaldine (2-methyl-8-acetoxyquinoline), as a source of homogeneously generated precipitant. An earlier interest in thorium directed our attention first to this element.

The reagents 8-hydroxyquinoline and 8-hydroxyquinaldine, formed by the hydrolysis of these esters, differ in their action towards metal-ions in at least three ways: under comparable conditions, a given metal-ion is precipitated at a lower pH by 8-hydroxyquinoline than by 8-hydroxyquinaldine, for reasons discussed elsewhere;⁶ aluminium is precipitated by oxine but not by its 2-methyl derivative;⁷ and thorium is precipitated as a "compound" of not quite 1:5 stoichiometry by the former of these reagents,^{1,8} but as a chelate of 1:4 stoichiometry, $\text{Th}(\text{C}_{10}\text{H}_8\text{ON})_4$, by the latter.^{6,9} The difference in the behaviour of these reagents towards aluminium and thorium is probably caused by a steric effect of the methyl group in the 2 position in 8-hydroxyquinaldine, close to the co-ordinating nitrogen atom.

The present work establishes conditions under which thorium is precipitated from homogeneous solution as the 1:4 chelate of 8-hydroxyquinaldine, and accounts for differences between precipitation by this means and by the direct use of 8-hydroxyquinaldine in a conventional procedure.

EXPERIMENTAL

Reagents

Unless otherwise specified, all chemicals were reagent grade.

Thorium: The thorium nitrate (tetrahydrate) was a highly purified product (Code 103, Lindsay Chemical Co., West Chicago, Illinois, U.S.A.). Stock solutions, kept at a pH below 2 with either hydrochloric or nitric acid, were standardised titrimetrically, substantially by the EDTA method of

Fritz and Ford,¹⁰ the EDTA solution having been standardised against zinc¹¹ (99.999%, Johnson, Matthey & Co., Ltd., London, England).

8-Acetoxyquinaldine: Most of the experiments were performed with reagent obtained from Burdick and Jackson Laboratories, Muskegon, Michigan, U.S.A., and a few of them with our own reagent, prepared by the method of Büchi *et al.*,¹² from 8-hydroxyquinaldine (obtained from Aldrich Chemical Co., Milwaukee, Wisconsin, U.S.A., and further purified by steam distillation). The two products gave similar results. Because the compound hydrolyses readily, it was stored in a desiccator over phosphorus pentoxide and under nitrogen. Solutions were prepared, as required, by dissolving the appropriate amount of 8-acetoxyquinaldine in 1.0 ml of 90% formic acid and 2.0 ml of glacial acetic acid followed by dilution to 10 ml with water (100 mg of 8-acetoxyquinaldine is equivalent to 28.8 mg of thorium, for the 1:4 chelate).

Apparatus

Weights and all volumetric ware were calibrated.

Measurements of pH were made with a Beckman Model G pH meter (Beckman Instruments Inc., South Pasadena, California, U.S.A.) using a 40498 glass electrode in association with a saturated calomel reference electrode. The pH values of precipitation were determined by measurements made on the filtrates at room temperature.

The thermobalance was a Chevenard-type photographically recording instrument (TBP Nr. 27, S.A.D.A.M.E.L., La Chaux de Fonds, Switzerland). The rate of heating was 2.5°/min, and the sensitivity was 0.85 mm/mg.

Precipitation of thorium with 8-acetoxyquinaldine

Preliminary experiments gave information about appropriate concentrations of reagents and about temperature and time of digestion. Under the conditions of our experiments, the maximum amount of 8-hydroxyquinaldine that could conveniently be used was about three times the stoichiometric quantity because the volatilisation of the reagent became troublesome, particularly at the higher pH values.

As judged by the appearance of a precipitate, the rate of hydrolysis of 8-acetoxyquinaldine increases with increasing pH, as does that of 8-acetoxyquinoline in the same pH range;^{13,14} for example, at 70°, with 200% excess of reagent, a precipitate appeared in about 25 min at pH 5.0, and in about 3 min at pH 5.8. At room temperature, hydrolysis is of course slower.

Excellent crystals of the chelate were obtained (Fig. 1); these were larger the lower the pH of precipitation, probably as a consequence of the slower rate of hydrolysis.

Procedure: To 50 ml of thorium solution (0.7 mg of thorium/ml) 10 ml of a freshly prepared solution of 8-acetoxyquinaldine (*vide supra*) were added, then the pH was adjusted by means of 3.0M aqueous ammonia, added drop by drop with vigorous stirring, the measurement being made by pH meter. (To allow for drift during precipitation, the pH was adjusted to a higher value than that desired after precipitation: about 0.1 unit higher at pH 5.3; about 0.5 unit at pH 5.9.) The solution was warmed for 2 hr at 70°, then filtered through a medium-porosity fritted-glass crucible and the precipitate washed, using for the transference and washing 75–100 ml of hot (70°) water. The precipitate was dried for 2 hr at 105–110°, cooled in a desiccator, and weighed as $\text{Th}(\text{C}_{10}\text{H}_8\text{ON})_4$.

Determination of 8-hydroxyquinaldine (HQ) contents of precipitates

Procedure: Preferably 100–120 mg of the dry precipitate, obtained by the procedure given above, were weighed, transferred to an iodine flask, and dissolved in 50 ml of warm 4M hydrochloric acid. After the addition of 50 ml of water, the 8-hydroxyquinaldine (HQ) content of the solution was determined by the bromometric procedure used in earlier work.⁶

TABLE I.—PERCENTAGE OF 8-HYDROXYQUINALDINE (HQ) IN PRECIPITATES*
(theoretical, for $\text{ThQ}_4 = 73.63\%$)

Excess of reagent, %	Precipitation at pH ≤ 5.65			Precipitation at pH > 5.65		
	HQ, %	No. of detns.	Stand. dev.	HQ, %	No. of detns.	Stand. dev.
125	73.46	16	0.13	73.11	15	0.36
150	73.52	4	0.17	73.26	7	0.10
200	73.66	13	0.20	73.48	7	0.16

* Precipitates dried for 2 hr at 105–110°

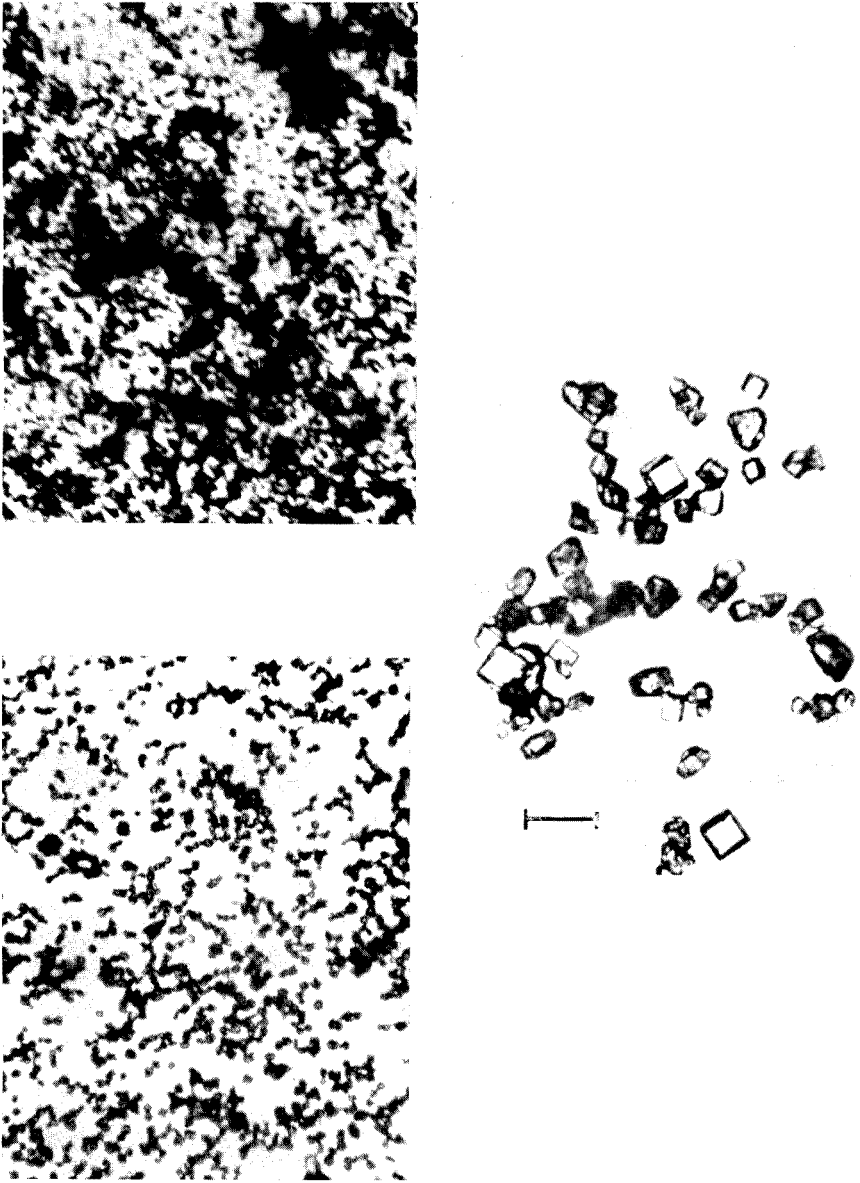


FIG. 1.—Photomicrographs of thorium 8-hydroxyquinoldinate (all at the same magnification; the "marker" represents 0.1 mm):—
Upper left: conventional precipitation; 70% excess reagent; pH 5.5,
Lower left: precipitation from homogeneous solution; 125% excess reagent; pH 5.5,
Right: precipitation from homogeneous solution; 125% excess reagent; pH 5.3.

RESULTS AND DISCUSSION

Fig. 2 shows that, as the excess of precipitant is increased, the pH for both the beginning and the peak of precipitation is decreased, as might be expected. Under the conditions of these experiments, with an excess of reagent of 125%, precipitation is not quite quantitative as the chelate, ThQ_4 , although it comes within 2–3% of it at pH 5.6–5.7. With an excess of reagent of 150%, precipitation of the chelate is at least 99% complete* at pH 5.5–5.6; and with an excess of 200%, this degree of completeness is attained at pH 5.4–5.5.

The downward trend of the precipitation curve beyond pH 5.65 when the excess of reagent is 125% is probably caused by an increasing replacement of Q^- in the

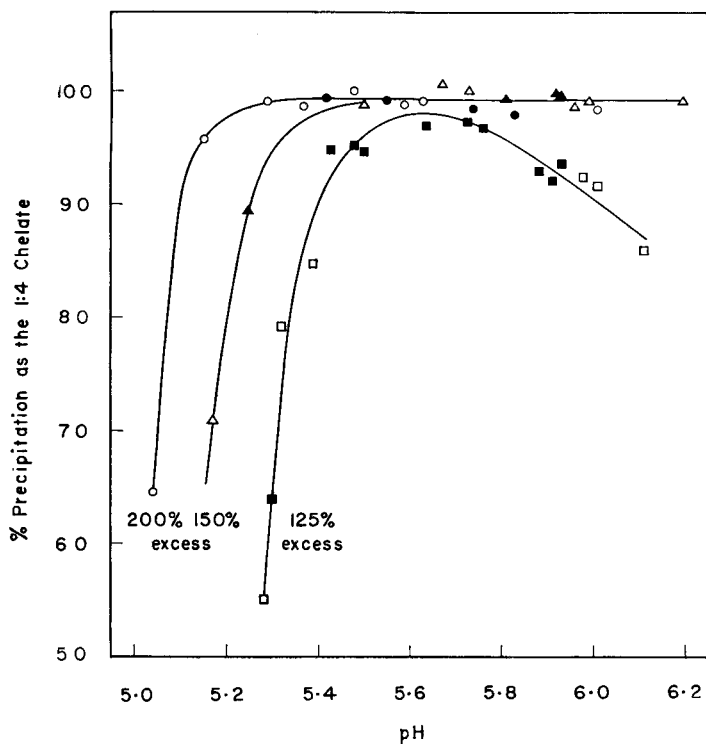


Fig. 2.—Precipitation from homogeneous solution of $\text{Th}(\text{C}_{10}\text{H}_8\text{ON})_4$ in relation to pH of precipitation and excess of reagent. (Thorium in original solution = $0.7 \text{ mg/ml} = 3 \times 10^{-3} \text{ M}$; the solid symbols represent the average of two or three determinations.)

precipitate by OH^- (*i.e.*, partial precipitation of the thorium as hydrous thoria or a basic thorium chelate or both). With increasing pH of precipitation, the decrease in the weight of precipitate is progressive: in experiments with 125% excess of reagent, not shown in Fig. 2, at pH 6.8 the weight obtained was *ca.* 85% of that expected for ThQ_4 ; at pH 7.8 it was *ca.* 80%. Similarly, with increasing pH the 8-hydroxyquinaldine (HQ) content of the precipitate decreases: from 73.5% (theoretical, for ThQ_4 , 73.6%) to *ca.* 64% at pH 7.5 and to <60% at pH 9. In fact, there is evidence (in

* This figure, and the data of Fig. 2, are calculated from the EDTA titre of the thorium solution. All EDTA titrations gave highly precise results, but yielded a value for the thorium solution 0.8% lower than gravimetric determinations by precipitation of hydrous thoria with either hexamethylenetetramine¹⁵ or aqueous ammonia,¹⁶ followed by ignition to thorium dioxide.

Table I, which relates to the data of Fig. 2) that in our experiments pure chelate was obtained only with 200% excess of reagent at the higher acidities. In both the lower and higher pH ranges, the HQ in the precipitate increases with increasing excess of reagent; for a given excess, the HQ is higher when the pH is below 5.65 than when it is above it; only with an excess of 200% at the lower pH values does the HQ content accord strictly with that of ThQ_4 .

Precipitates judged from their weight and HQ content to be appreciably contaminated by OH^- yielded thermograms different (by virtue of discontinuity at about 355°) from that of the pure chelate.

An earlier study⁶ showed that, at the same concentration, thorium can be precipitated quantitatively as the chelate over a wide range of pH (6.1–11.5) by the direct use of 8-hydroxyquinoline, even though the excess of reagent is only 70%. Why, then, with an excess of 125% is chelate precipitation less complete (or the precipitate less pure) when the reagent is generated homogeneously?

This substantial difference in the two methods probably stems from the very different concentrations of the anion, Q^- , during adjustment of the pH. In the non-homogeneous method, more than enough 8-hydroxyquinoline to precipitate all of the thorium is present before pH adjustment begins, distributed among various species: H_2Q^+ , HQ, Q^- and Th-Q soluble complexes such as ThQ^{3+} and ThQ_2^{2+} . As the pH is raised, the ionisation of HQ to Q^- , of course, increases and all of the other (mobile) equilibria involving Q species are affected. With increasing pH, the "favoured" soluble Th-Q complex changes from ThQ^{3+} to ThQ_2^{2+} to ThQ_3^+ (compare the thorium-oxine complexes¹⁷) until eventually ThQ_4 precipitates. Throughout, Q^- is in competition with OH^- for the thorium; the fact that ThQ_4 can be precipitated at pH values as high as 10 and 11 testifies to the stability of the Th-Q soluble complexes and to the low intrinsic solubility (in the sense of Irving and Williams¹⁸) of ThQ_4 .

In the homogeneous method, however, at a given pH the extent of formation of Th-Q complexes is very much less—or, rather, hydroxo complexes are formed before the formation of Th-Q complexes can become appreciable. The damage is done during the raising of the pH to a value appropriate for quantitative precipitation, at which time very little generation of HQ or Q^- by the hydrolysis of 8-acetoxyquinoline has occurred. The pH and excess of reagent being what they are in these experiments, the Th-OH complexes would, given time, be converted to Th-Q complexes, but it is reasonable to expect this conversion to be slow—indeed, it is slow⁶—because of the polynuclear olated nature of the thorium hydroxo complexes.^{19–21} If, on the other hand, 8-acetoxyquinoline were allowed to hydrolyse appreciably before pH adjustment, the precipitation would not be from homogeneous solution (unless the pH were raised by, say, the hydrolysis of urea; but then urea, not 8-acetoxyquinoline, would be the basis of the precipitation from homogeneous solution).

The competition for thorium involves acetate ion as well as Q^- and OH^- . Experiments showed that the precipitation curve (125% excess reagent) is raised significantly when the acetate is reduced 25%. Reduction in the concentration of formate causes no significant shift in the curve, suggesting that thorium-formate complexes have lower stability than thorium-acetate complexes.

It is unfortunate that the conditions for the quantitative precipitation of ThQ_4 are more restrictive when 8-acetoxyquinoline rather than 8-hydroxyquinoline is used, because the physical characteristics of the chelate are distinctly better when it is

produced homogeneously than when it is formed by a conventional method (compare the two photographs on the left in Fig. 1). Perhaps the features of both procedures can be obtained in a homogeneous method using 8-hydroxyquinaldine and urea.

8-Hydroxyquinaldine is of particular interest as a precipitant for thorium: it is one of the very few organic reagents which have been shown to react with thorium to yield a pure stoichiometric compound of good thermal stability;* the compound has an attractive gravimetric factor (0.2683); it can be used for other kinds of thorium determinations, e.g., bromometric⁶ and polarographic.²³

An element such as copper, which is less prone than thorium to hydrolysis and whose chelates form at a significantly lower pH, is precipitated from homogeneous solution through 8-acetoxyquinaldine much more satisfactorily. Studies involving this and other metal-ions are in progress.

Acknowledgements—We are grateful to the National Research Council of Canada for financial support, and we acknowledge the assistance of Mr. J. A. Thomson with some of the experiments.

Zusammenfassung—Thorium kann aus homogener Lösung als 1:4-Chelat $\text{Th}(\text{C}_{10}\text{H}_8\text{ON})_4$ mit 8-Hydroxychinaldin (2-Methyloxin) gefällt werden, das durch Hydrolyse von 8-Acetoxychinaldin erzeugt wird. Die Verwendung des Esters liefert einen Niederschlag, dessen Eigenschaften deutlich besser sind als bei der üblichen Fällung mit 8-Hydroxychinaldin, aber es müssen bestimmte Bedingungen genauer eingehalten werden, damit der Niederschlag rein ist. Gründe dafür werden diskutiert.

Résumé—Le thorium peut être précipité de ses solutions homogènes sous forme de chélate 1/4, $\text{Th}(\text{C}_{10}\text{H}_8\text{ON})_4$, au moyen de l'hydroxy-8-quinaldine (2-méthylloxine) obtenu par hydrolyse de l'acetoxy-8-quinaldine. L'emploi de cet ester fournit un précipité dont les propriétés Physiques sont nettement supérieures à celles du précipité obtenu par la voie habituelle au moyen d'hydroxy-8-quinaldine. Seule une pureté satisfaisante n'est atteinte que sous quelques restrictions; discussion.

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INFRARED DETERMINATION OF CHLORATE IN THE PRESENCE OF OTHER OXYHALOGEN ANIONS

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(Received 21 January 1963. Accepted 24 February 1963)

Summary—Small quantities of chlorate may be determined in the presence of perchlorate, bromate, iodate, periodate, and many other substances by measurement of the $20.4\text{-}\mu$ chlorate absorption band. Quantities of potassium chlorate ranging from about 0.1 to 1.0 mg in 300-mg potassium bromide disks can be determined with errors of about 2%. The disk technique is applicable to aqueous solutions via the freeze-drying process. Cations affect the measured absorbance values, but this problem is easily circumvented by a simple ion-exchange step.

THE common spectrophotometric methods for determining chlorate are based upon its oxidising power and are subject to serious interferences from other oxidants, such as bromate.^{1,2} It is thus of interest to consider the possibility of determining chlorate by means of a more characteristic property than its oxidising ability. Infrared catalogues^{3,4} and other papers^{5,6} present spectra which suggest that a fairly selective infrared determination might be developed. Sulphate, nitrate and nitrite have been determined by infrared spectrophotometry utilising potassium bromide disks prepared by freeze-drying aqueous solutions of these ions,^{7,8,9} and on the basis of the work reported here it appears that this technique may be applied advantageously to chlorate in certain analytical situations.

The chlorate ion exhibits three main infrared absorption bands, at about 10.3, 16.2 and $20.4\ \mu$. Slight shifts in these wavelengths depending upon the cation accompanying the chlorate have been reported.^{4,6} The spectra shown in Figs. 1 and 2 indicate that the $20.4\ \mu$ band would be the least subject to interferences from the other oxyhalogen anions. The catalogue of Miller *et al.*⁴ shows, in fact, that relatively few compounds absorb at this wavelength.

In the method reported here, 300 mg of potassium bromide are added to the aqueous solution containing from about 0.1 to 1.0 mg of potassium chlorate, the solution is freeze-dried, and a disk is pressed from the resulting powder. No difficulty is encountered with redox reactions in the solution provided it is neutral. If it were acidic, of course, chlorate would be destroyed by reaction with bromide. Fractional milligram quantities of chlorate were determined in the present work, but there is wide latitude for scaling the method up or down simply by varying the volume of solution and the quantity of potassium bromide taken for freeze-drying.

EXPERIMENTAL

Apparatus and reagents

Infrared spectra were recorded with a Perkin-Elmer KBr Model 137 Infracord spectrophotometer. The freeze-drying operation and the pressing of the potassium bromide disks have been described.^{8,9}

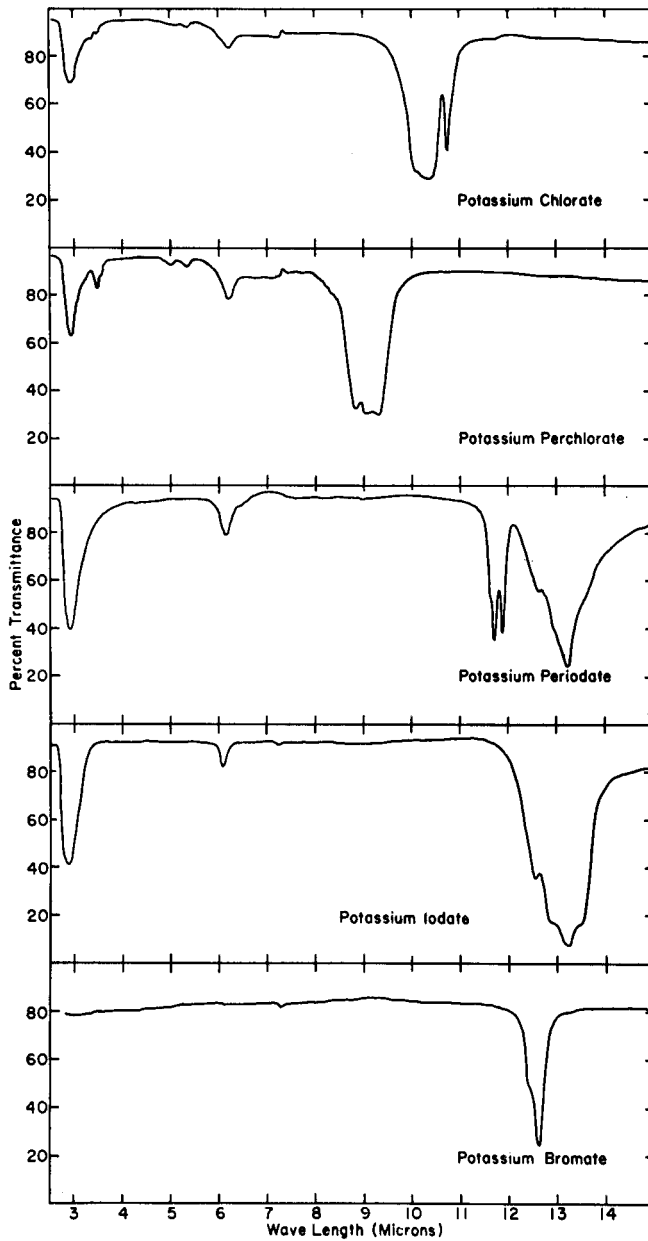


FIG. 1.—Spectra in the rock salt region (0.5 mg of indicated compound in 300-mg KBr disks; freeze-dried preparations).

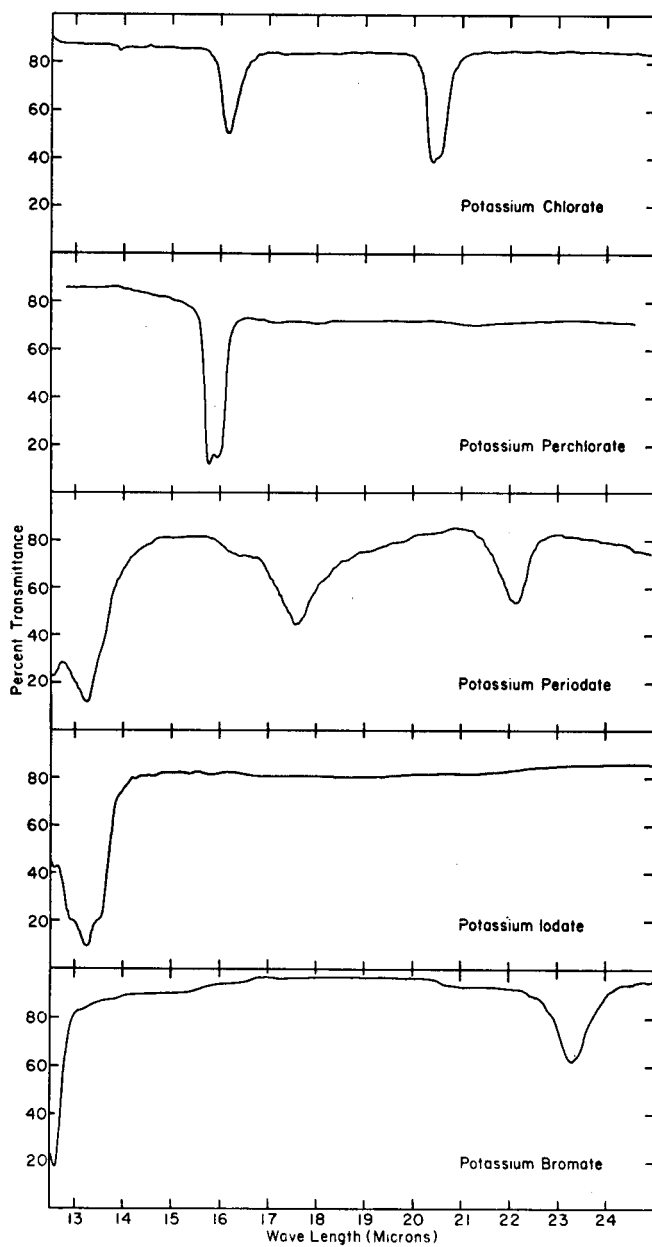


FIG. 2.—Spectra in the KBr region (0.5 mg of indicated compound in 300-mg KBr disks; freeze-dried preparations).

A special grade of potassium bromide for infrared work, manufactured by E. Merck, Darmstadt, Germany, was obtained from Terra Chemicals, Inc., New York, N.Y., U.S.A. All other chemicals were of reagent grade.

Pure potassium chlorate solutions

One-ml aliquots of a series of solutions containing from 0.1 to 1.0 mg of potassium chlorate were mixed with 1-ml aliquots of a solution containing 300 mg of potassium bromide/ml and subjected to the freeze-drying process. Disks were pressed from the resulting powder, and their spectra were scanned from 19 to 22 μ with a 300-mg potassium bromide disk in the reference beam. Values of I and I_0 were measured using the base-line technique, and the absorbance values were calculated. The disks were weighed and the absorbances were corrected to a 300-mg basis to compensate for losses in transferring and pressing the powder. The base-line is very easy to draw, as may be seen from the potassium chlorate spectrum shown in Fig. 2. The calibration curve obtained in this way is shown in Fig. 3, where it may be seen that Beer's law is followed over the concentration range studied.

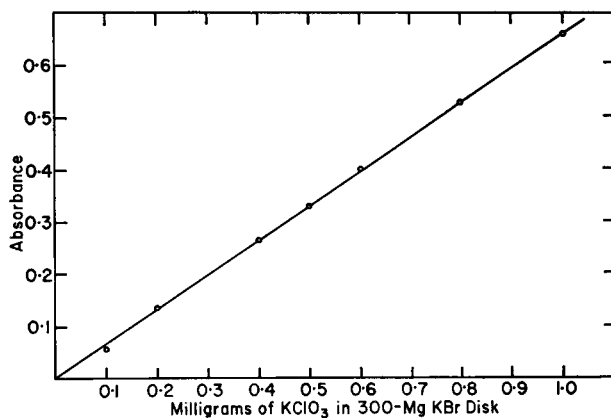


FIG. 3.—Typical calibration curve obtained with freeze-dried samples (absorbance measured at 20.4 μ)

RESULTS AND DISCUSSION

Forty-five solutions containing from 0.2 to 1.0 mg of potassium chlorate/ml were analysed by the infrared method. The average relative deviation of these samples was 1.9%.

Cation effects

Solutions of magnesium chlorate lead to chlorate absorbance values identical with those obtained with potassium chlorate until about 0.3 mg of chlorate in a 300-mg potassium bromide disk is exceeded. Negative deviations from Beer's law are then seen, and low results are obtained using a working curve prepared with potassium chlorate solutions. For example, an error of 16% was found with a disk containing 1 mg of chlorate as the magnesium salt.

Sodium chlorate solutions follow Beer's law, but the slope of the curve is less than that of a curve where the chlorate is taken as the potassium salt. An error of 14% was found in the analysis of a sodium chlorate solution containing 0.6 mg of chlorate when a calibration curve based on potassium chlorate was used. Errors of similar magnitude were found with barium chlorate. With strontium chlorate, on the other hand, chlorate absorbance values were the same, within experimental error, as those obtained with the potassium salt.

It is clear that the absorbance at 20.4μ varies significantly as the cation accompanying the chlorate is changed. That this occurs in spite of the fact that potassium ion predominates in the solutions taken for freeze-drying suggests that solid solutions are not obtained in this process but that the various metal chlorates are to some degree segregated in the potassium bromide matrix. Similar results were found for the effect of cations on the sulphate band at 9μ .⁷ In any case, the calibration curve should be prepared using a metal chlorate having the same cation as occurs in the unknown chlorate solutions. In cases where this is beyond control, it is best to pass the unknown chlorate solution through a column of a cation exchanger in the potassium form, thereby ensuring that extraneous cations will not affect the results. In the present work, a 10×1 cm column of Dowex 50W- X12 was found satisfactory.

Other oxyhalogen anions

Table I shows the effect of potassium perchlorate upon the determination of chlorate. As much as 8 mg of this compound has no effect upon the results for

TABLE I.—DETERMINATION OF 0.34 mg OF CHLORATE IN THE PRESENCE OF PERCHLORATE

KClO ₄ added, mg	ClO ₃ ⁻ found, mg	Error, mg	Relative error, %
2	0.343	0.003	0.9
4	0.341	0.001	0.3
8	0.340	0.000	0.0
12	0.364	0.024	7.1
15	0.354	0.014	4.1
19	0.357	0.017	5.0
30	0.357	0.017	5.0
38	0.364	0.024	7.1
45	0.357	0.017	5.0

0.34 mg of chlorate. Larger quantities of perchlorate do seem to have an effect, although not a very large one. Curiously, after a maximum tolerable amount of perchlorate has been exceeded, further increases seem to exert no additional effect. Although the reason for this behaviour is obscure, one may take advantage of it by adding potassium perchlorate to all standard and unknown samples. In an experiment where 15 mg of potassium perchlorate were added to all of the samples, the errors in the chlorate determination dropped from 4 to 7% as seen in Table I to about 2%, about the same as the error expected in the complete absence of perchlorate.

Table II shows a few results obtained with chlorate samples to which both

TABLE II.—DETERMINATION OF CHLORATE IN SYNTHETIC MIXTURES WITH PERCHLORATE AND BROMATE

KClO ₃ taken, mg	KClO ₄ added, mg	KBrO ₃ added, mg	KClO ₃ found, mg	Error, mg	Relative error, %
0.200	19.0	0.400	0.200	0.000	0.0
0.400	23.0	5.00	0.390	0.010	2.6
0.600	30.0	1.00	0.605	0.005	0.8
1.00	30.0	5.00	1.01	0.010	1.0

perchlorate and bromate were added. It is seen that bromate does not interfere in the quantities studied. Similarly, it was found that the presence in the disk of 5 mg of potassium iodate had no effect upon the absorbance of the chlorate band and, likewise, 5 mg of potassium metaperiodate did not interfere.

Acknowledgement—The authors gratefully acknowledge the support of this work by the U.S. Atomic Energy Commission through Research Contract No. AT-(40-1)-2046.

Zusammenfassung—Für die Bestimmung kleiner Mengen von Chlorat neben Perchlorat, Bromat, Jodat, Perjodat und vielen anderen Verbindungen eignet sich die Messung der Chloratabsorption bei $20,4 \mu$. 0,1 bis 1 mg Kaliumchlorat in etwa 300 mg schweren Kaliumbromidpreßlingen können mit einer Unsicherheit von etwa 2% bestimmt werden. Auf wäßrige Lösungen läßt sich die Preßtechnik über das Gefriertrocknungsverfahren anwenden. Kationen beeinflussen die gemessene Absorption, aber diese Schwierigkeit läßt sich durch Ionenaustausch leicht umgehen.

Résumé—Dans l'analyse des petites quantités de chlorate en présence de perchlorate, de bromate, d'iodate, de périodate et de nombreuses autres substances, il peut être avantageux d'appliquer aux échantillons envisagés la mesure de la bande d'absorption des chlorates à $20,4 \mu$. Des quantités de chlorate de potassium comprises entre 0,1 et 1,0 mg dans des pastilles de 300 mg de bromure de potassium peuvent être déterminées avec une erreur de c'environ 2%. La technique des pastilles peut être employée pour les solutions aqueuses après dessiccation. Certains cations peuvent affecter les valeurs des mesures d'absorption, mais ce problème est facilement éludé par un simple échange d'ions.

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THE COMPLEXOMETRIC ANALYSIS OF PYRO- AND TRIPHOSPHATES—I

STABILITY CONSTANTS OF THE PROTON AND METAL COMPLEXES OF THE ACIDS

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(Received 30 January 1963. Accepted 15 February 1963)

Summary—The stability constants of the proton and some metal complexes formed by pyro- and triphosphoric acids at 25° have been evaluated from potentiometric titration measurements.

PENTASODIUM triphosphate (tripolyphosphate) is extensively used as a component of detergents. The content of pentasodium triphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) in industrial tripolyphosphates often exceeds 90%, the remainder consisting mainly of sodium pyro- and orthophosphates. The various components are usually determined after their isolation by chromatography¹⁻³ or by ion exchange,^{4,5} but the analyses are time-consuming.

In the following we present the results of attempts to develop a direct method for the analysis of various phosphates that is based on complexometric titration. As reliable data on the magnitudes of the stability constants of the proton and metal complexes of the phosphates were few in number, it was necessary to evaluate these constants. In this, the first paper of this series, we describe the determination of the stability constants of the proton and a number of metal complexes of pyro- and triphosphoric acids; the second paper of the series will deal with the practical performance of the complexometric analyses.

EXPERIMENTAL

Apparatus and chemicals

All the pH measurements were made with a recording pH meter, a Metrohm Potentiograph model E 336, equipped with a glass electrode of type EA 107 X and a calomel electrode of type EA 402. The potentiograph readings were checked with standard buffer solutions.

The ionic strengths of the solutions were adjusted to 0.1 by adding the necessary quantity of sodium nitrate. The concentrations of the components titrated were approximately 10^{-3} mole/litre.

Solutions of the acids were prepared by passing aqueous solutions of their recrystallised sodium salts through columns of Dowex 50 X 8 cation-exchange resin in the hydrogen form.

Solutions of metal nitrates were prepared from analytical-grade salts. The metal ion concentrations of the solutions were determined by complexometric titration with EDTA.

The measurements were all carried out at 25°.

Acid-base titrations were performed with a 0.1M sodium hydroxide solution prepared by diluting the contents of a Titrisol ampoule containing 0.1 mole of sodium hydroxide (E. Merck AG) to 1 litre with redistilled, carbon dioxide-free water.

The titrations of the free acids were carried out as follows. About 1 millimole of acid and 10 ml of 1M sodium nitrate were added to a titration vessel and diluted to 100 ml. The variation of the pH of the solution on slowly adding 0.1M sodium hydroxide was recorded with the Metrohm Potentiograph.

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THE STABILITY CONSTANTS OF THE PROTON COMPLEXES
OF THE ACIDS

Orthophosphoric acid is stable in aqueous solution, but pyro- and triphosphoric acids are unstable, although their hydrolysis proceeds very slowly at room temperature. The titration curves of solutions of the last two acids that had been stored for 18 days at room temperature did not differ essentially from the curves for solutions of the acids prepared immediately before the titrations by passing solutions of their salts through ion-exchange resin columns. If pyro- and triphosphoric acid solutions are boiled, the acids are quantitatively hydrolysed to orthophosphoric acid within a short time.

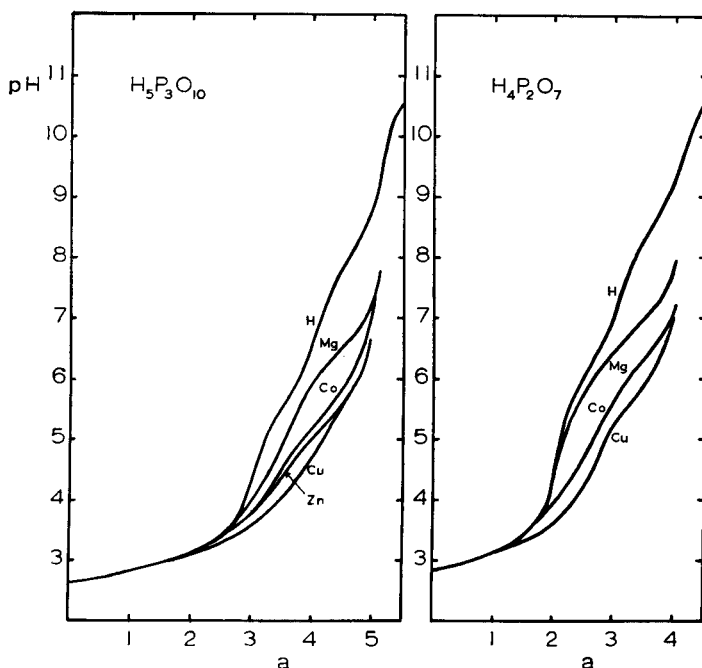


FIG. 1.—pH as a function of the number (*a*) of moles of sodium hydroxide added per mole of acid for pyro- and triphosphoric acids.

The curves H relate to titrations of the acids with no metal nitrate present and the other curves to titrations with equimolar amounts of a metal nitrate (cation indicated) and acid present.

The values of the stability constants of the proton complexes of the two acids reported in the literature (see Table III) differ greatly; this probably results from the difficulty of preparing solutions of the pure acids. For the preparation of the solutions of the acids, we used their sodium salts which had been recrystallised so many times that the presence of other phosphates could not be detected by chromatography.⁶

The stability constants of the proton complexes were evaluated from the recorded titration curves of the acids which are reproduced in Fig. 1. These curves exhibit no large pH jumps, but fairly abrupt changes in pH resulted when 2 and 3 equivalents of sodium hydroxide had been added per mole of pyro- and triphosphoric acid, respectively. These results are in agreement with those reported by van Wazer and Holst,⁷ who concluded that the acids contain as many readily liberated hydrogen ions as they contain phosphorus atoms.

If we denote the acid in question by H_nX , the calculation of the stability constants of the proton complexes of the acids can be based on the equations (charges omitted):

$$C_X = [H_nX] + [H_{n-1}X] + [H_{n-2}X] + \dots \quad (1)$$

$$pC_X = n[H_nX] + (n-1)[H_{n-1}X] + (n-2)[H_{n-2}X] + \dots \quad (2)$$

where n is 4 for pyrophosphoric acid and 5 for triphosphoric acid, C_X is the analytical concentration of the acid, and p is the degree of protonation of the acid. This last is defined by

$$p = n - \frac{aC_X + [H] - [OH]}{C_X}, \quad (3)$$

where a is the number of moles of sodium hydroxide added per mole of acid.

The stability constants of the various hydrogen complexes of a polyprotic acid are defined by

$$K_n = \frac{[H_nX]}{[H][H_{n-1}X]}. \quad (4)$$

Equations (1) and (2) can be simplified somewhat, depending on the side of the pH jump at $a = n - 2$ from which results are taken for the calculations.

The stability constant, K_1 , of the first proton complex of each acid can be calculated without any very great error by substituting data from the section of the titration curve between the value $a = n - 1$ and $a = n$ in equation (7) derived by eliminating the concentration terms $[HX]$ and $[X]$ from equations (4, $n = 1$), (5) and (6),

$$C_X = [HX] + [X] \quad (5)$$

$$pC_X = [HX] \quad (6)$$

$$K_1 = \frac{p}{(1-p)[H]}. \quad (7)$$

The values in the range between $a = n - 2$ and $a = n - 1$ can be used to evaluate K_2 . When the concentrations $[H_2X]$ and $[HX]$ are eliminated from the equations

$$C_X = [H_2X] + [HX] \quad (8)$$

$$pC_X = 2[H_2X] + [HX] \quad (9)$$

and equation (4) with $n = 2$, it is found that

$$K_2 = \frac{p-1}{(2-p)[H]}. \quad (10)$$

The constants K_3 and K_4 of pyrophosphoric acid and the constants K_3 , K_4 and K_5 of triphosphoric acid cannot be evaluated with sufficient accuracy in the above manner, and it was necessary to employ the graphical method of Schwarzenbach, Willi and Bach.⁸

At values of a less than $n - 2$, the concentrations $[HX]$ and $[X]$ can be disregarded, and we may write

$$C_X = [H_nX] + [H_{n-1}X] + [H_{n-2}X] + [H_{n-3}X] \quad (11)$$

$$p'C_X = (n-2)[H_nX] + (n-3)[H_{n-1}X] + (n-4)[H_{n-2}X]. \quad (12)$$

When the constants for *pyrophosphoric acid* are calculated, the last terms in equations (11) and (12) are zero. By eliminating all concentration terms except [H] from equations (4), (11) and (12), we obtain

$$(2 - p')[H]^2 K_3 K_4 + (1 - p')[H] K_3 = p' \quad (13)$$

This equation is that of a straight line in the xy plane ($x = K_3$; $y = K_3 K_4$) which intersects the x axis at the point A [eq. (15)] and the y axis at the point B [eq. (16)].

When the concentration terms excluding [H] in equations (4), (11) and (12) are eliminated, we find for *triphosphoric acid* that

$$(3 - p')[H]^3 K_3 K_4 K_5 + (2 - p')[H]^2 K_3 K_4 + (1 - p')[H] K_3 = p' \quad (14)$$

which represents a plane in the three-co-ordinate system xyz ($x = K_3$; $y = K_3 K_4$; $z = K_3 K_4 K_5$) which intersects the x axis at the point A and the y axis at the point B,

$$A = \frac{p'}{(1 - p')[H]} \quad (15)$$

$$B = \frac{p'}{(2 - p')[H]^2} \quad (16)$$

The value of p' is given by

$$p' = (n - 2) - \frac{aC_x + [H] - [OH]}{C_x} \quad (17)$$

When values of A and B, determined by substituting corresponding values of a and [H] in equations (15) and (16), are plotted in a two dimensional co-ordinate system, and straight lines are drawn through these values, it is possible to determine a point in the xy plane where all the lines intersect each other. At this point $x = K_3$ and $y = K_3 K_4$.

The constants can also be calculated with the aid of determinants from a series of pairs of values read from the titration curve.

The results of the titrations are shown in Tables I and II.

TABLE I.—TITRATION OF PYROPHOSPHORIC ACID WITH 0.1M SODIUM HYDROXIDE
[$C_x = 1.01 \times 10^{-3}M$. $\mu = 0.1$ (NaNO₃)]

$a = 0.25$	0.50	0.75	1.00	1.25	1.50	1.75	2.00
pH = 2.90	2.98	3.04	3.15	3.24	3.42	3.67	4.20
$a = 2.25$	2.50	2.75	3.00	3.25	3.50	3.75	4.00
pH = 5.55	5.97	6.43	6.90	7.76	8.24	8.75	9.10

TABLE II.—TITRATION OF TRIPHOSPHORIC ACID WITH 0.1M SODIUM HYDROXIDE
[$C_x = 1.00 \times 10^{-3}M$. $\mu = 0.1$ (NaNO₃)]

$a = 0.25$	0.50	0.75	1.00	1.25	1.50	1.75	2.00
pH = 2.70	2.75	2.80	2.85	2.90	2.97	3.05	3.18
$a = 2.25$	2.50	2.75	3.00	3.25	3.50	3.75	4.00
pH = 3.26	3.43	3.75	4.30	5.10	5.58	6.03	6.55
$a = 4.25$	4.50	4.75	5.00				
pH = 7.40	7.86	8.32	8.84				

The equations derived above and the experimental results were used to evaluate the stability constants of the proton complexes of pyro- and triphosphoric acids. Because the aim was to use these values in the mathematical treatment of the complexometric titration of these acids, the logarithms of the stability constants are given only to the first decimal. These values are collected in Table III which includes values previously reported for these acids.

Given the values of the stability constants of the proton complexes of an acid, it is possible to determine the value of the so-called side-reaction coefficient⁹ with the aid of which the concentration of the proton-free anion, X^{n-} , of the acid can be evaluated at any pH. The side-reaction coefficient $\alpha_{X(H)}$ is defined by

$$\alpha_{X(H)} = \frac{C_X}{[X]} = \frac{\sum_{n=0} [H_n X]}{[X]} = 1 + \sum_{n=1} [H]^n K_{H_n X}^H \quad (18)$$

where

$$K_{H_n X}^H = \frac{[H_n X]}{[H]^n [X]} \quad (19)$$

In order to shorten complexometric calculations, values of $\log \alpha_{X(H)}$ for the two acids are plotted as functions of pH in Fig. 2.

TABLE III.—STABILITY CONSTANTS OF THE PROTON COMPLEXES OF PYRO- AND TRIPHOSPHORIC ACIDS.

<i>Pyrophosphoric Acid</i>						
Log K_1	log K_2	log K_3	log K_4	μ	Ref.	
7.8	5.6	1.5	1.0	2	10	
8.9	6.1	1.8	0.8	1	10	
8.5	6.1	2.5		0.1	10	
9.1	6.4	2.2		0.1	10	
9.5				0	11	
9.0	6.4	2.1		0.1	12	
8.7	6.0	1.8	1.7	1	13	
8.3	6.0	2.7	2.5	0.1	This study	
<i>Triphosphoric Acid</i>						
Log K_1	log K_2	log K_3	log K_4	log K_5	μ	Ref.
8.8	5.7	1.6	0.9		1	10
8.8	5.8	2.1	1.1	0.8	1	10
8.7	6.0	2.2			0.1	10
7.8	5.4				0.1	10
9.2	6.5	2.8			0	10
9.5					0	11
8.6	5.7	2.0	1.2	0.5	1	13
7.9	5.6	2.6	2.2	small	0.1	This study

STABILITY CONSTANTS OF THE METAL COMPLEXES OF THE ACIDS

The addition of a metal salt to a solution of a salt of either phosphoric acid leads to an increase in acidity as a result of the reactions



Because of the fact that many metal ions form precipitates with pyrophosphate even in acid solutions, and because our studies had as their aim the selection of a suitable metal for the complexometric determination of pyro- and triphosphates, we determined the stability constants of the complexes formed by these acids and the metals cobalt^{II}, copper^{II}, magnesium and zinc only. In the case of zinc, we succeeded in evaluating only the stability constant of its triphosphate complex because the metal forms an insoluble compound with pyrophosphate.

Because the reaction between a complexing anion and a metal ion may take place very slowly—this is true at least when the metal is magnesium¹⁴—solutions containing the metal ion, the complexing anion and the neutral salt were given time to attain equilibrium before the pH was measured. The curves in Fig. 1 plot the pH values measured for a series of such solutions.

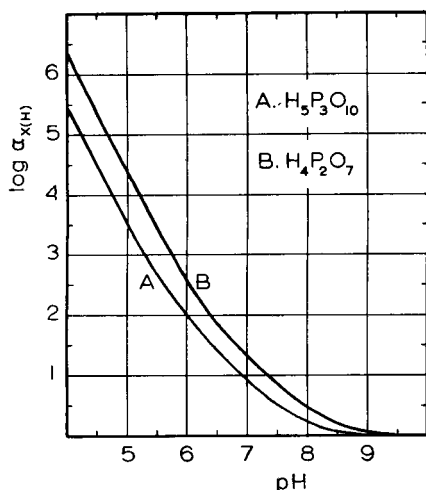


FIG. 2.—Log $\alpha_{X(OH)}$ as a function of pH for pyro- and triphosphoric acids.

Values taken from such a potentiometric titration curve can be used to calculate the stability constants of metal complexes¹⁵ provided that reaction (21) exerts no buffer action at pH values less than 4. In addition, the ionic strength of the solution should remain constant and hence the analytical concentration of the phosphoric acid in question should not exceed 10^{-3} mole/litre.

The value of the equilibrium constant K of reaction (21), given by

$$K = \frac{[MH][H]^2}{[M][H_2X]} = K_{MX}/K_{H_2X}^H \quad (22)$$

where $K_{H_2X}^H$ is defined by equation (19), determines how high the value of the stability constant K_{MX} must be so that the simple potentiometric method can be applied. At the middle point of the buffer range, $[MX] = [M] = [H_2X] = C_X/2$. It follows from equation (22) that the value of K_{MX} must be less than $10^{9.6}$ for pyrophosphoric acid and less than $10^{8.7}$ for triphosphoric acid.

TABLE IV.—EVALUATION OF THE STABILITY CONSTANTS OF METAL COMPLEXES OF PYRO- AND TRIPHOSPHORIC ACIDS

$$[C_M = C_X = 1.00 \times 10^{-8} \text{ M. } \mu = 0.1]$$

<i>Pyrophosphoric Acid</i>						
<i>a</i>	2.50	2.75	3.00	3.25	3.50	3.75
M				pH		
Mg	5.85	6.20	6.46	6.70	7.08	7.30
Co	4.65	5.10	5.60	6.00	6.35	6.65
Cu	4.19	4.60	5.18	5.61	5.94	6.26
<i>Triphosphoric Acid</i>						
<i>a</i>	3.50	3.75	4.00	4.25	4.50	4.75
M				pH		
Mg	4.85	5.21	6.00	6.35	6.60	6.74
Co	4.45	4.84	5.12	5.45	5.80	6.30
Zn	4.34	4.64	4.96	5.28	5.65	6.05
Cu	4.00	4.35	4.69	5.14	5.65	6.04

TABLE V.—LOGARITHMIC STABILITY CONSTANTS OF METAL COMPLEXES OF PYRO- AND TRIPHOSPHORIC ACIDS

<i>Pyrophosphoric Acid</i>				
Reference	10	11	16	This study
μ	0.02	0	1	0.1
Mg	$\log K_{HMgX}^H$		6.4	6.0
	$\log K_{MgX}$	5.7	7.2	4.7
Co	$\log K_{HCoX}^H$			5.7
	$\log K_{CoX}$			6.1
Reference	10	10	10	
μ	0.8	1	var	0.1
Cu	$\log K_{HCuX}^H$			5.4
	$\log K_{CuX}$	13.2	8.7	7.3
<i>Triphosphoric Acid</i>				
Reference	10	11	16	This study
μ	0.1	0	1	0.1
Mg	$\log K_{HMgX}^H$	5.8		5.8
	$\log K_{MgX}$	5.8	8.6	5.7
Co	$\log K_{HCoX}^H$			5.4
	$\log K_{CoX}$			6.6
Zn	$\log K_{HZnX}^H$			5.3
	$\log K_{ZnX}$		9.7	6.9
Cu	$\log K_{HCuX}^H$			5.2
	$\log K_{CuX}$	9.8		7.3

The pH values of solutions containing equimolar amounts of acid and metal were determined after the addition of different numbers of moles, a , of sodium hydroxide per mole of acid. The values of the stability constants were determined with the aid of the following equations where C_M and C_X denote the analytical concentrations of the metal and acid in the solution,

$$C_M = [M] + [HMX] + [MX] \quad (23)$$

$$C_X = [H_nX] + [H_{n-1}X] + \dots + [HX] + [X] + [HMX] + [MX] \quad (24)$$

$$pC_X = n[H_nX] + (n-1)[H_{n-1}X] + \dots + [HX] + [HMX]. \quad (25)$$

The value of p is computed from equation (3).

The unknown constants K_{HMX}^H and K_{MX} defined by

$$K_{HMX}^H = \frac{[HMX]}{[MX][H]}; \quad K_{MX} = \frac{[MX]}{[M][X]} \quad (26)$$

can be evaluated by inserting pairs of values read from the titration curves in the equation derived by eliminating all concentration terms except $[H]$ from equations (23), (24) and (25).

The calculations can be simplified by applying the method of successive approximations. A value is taken for $\log K_{HMX}^H$ which is close to the pH of the solution for which $a = n - 1$. If this value is too high, the calculated value of $\log K_{MX}$ will rise with pH, and *vice versa*. When the value chosen for $\log K_{HMX}^H$ is the correct one, the same value of $\log K_{MX}$ will be obtained for every point on the curve in the buffer range in question.

The results from experiments carried out on solutions of ionic strength 0.1 are collected in Table IV and the derived values of the stability constants in Table V.

Acknowledgments—The authors wish to express their gratitude to the *Statens Tekniska Forskningsråd* for financial aid, and to Mrs. G.-M. Gunnarsson, Chem. E., for the performance of the titrations.

Zusammenfassung—Die Dissoziationskonstanten von Pyro- und Triphosphorsäure sowie die Stabilitätskonstanten einiger Metallkomplexe dieser Säuren bei 25°C wurden aus potentiometrischen Titrationsdaten bestimmt.

Résumé—Les constantes de stabilité du proton et de quelques complexes métalliques formés à 25°C par les acides pyrophosphoriques et triphosphoriques ont pu être évaluées à partir des résultats fournis par dosage potentiométrique.

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DETERMINATION OF RHODIUM-103, NEODYMIUM-143, SAMARIUM-149 AND -151, AND GADOLINIUM-155 IN IRRADIATED URANIUM

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(Received 8 February 1963. Accepted 22 February 1963)

Summary—Methods for the determination of rhodium-103, neodymium-143, samarium-149 and -151, and gadolinium-155 in irradiated uranium metal are described. The concentrations of these five isotopes have been determined in a rod of uranium, which had received an irradiation of approximately 850 MWday/ton in a Calder reactor. Rhodium-103 was determined colorimetrically following anion-exchange purification and the lanthanide isotopes by isotope dilution and mass spectrometry, again after ion-exchange purification.

DURING the operation of a nuclear reactor certain long-lived or stable fission products are formed which possess very high neutron-absorption cross-sections. These are generally referred to as reactor poisoning isotopes because of their deleterious effect on the reactivity of the reactor. The rate of build-up of the concentrations of these isotopes is calculable using the appropriate cross-section, fission yield and radioactive decay data. However, where the isotope represents a fission chain termination the errors in calculated concentrations may be considerable because of the cumulative effect of individual errors in the parameters used for the successive decay products. A direct analytical check on the calculated concentrations is clearly of value in such instances and is usually feasible provided that the fuel has received an irradiation dose adequate for the build-up of determinable quantities of the required isotopes.

This paper reports the direct determination of rhodium-103, neodymium-143, samarium-149 and -151, and gadolinium-155 in a uranium metal specimen irradiated to some 850 MWday/ton. The importance of a reactor poison in the operation of a thermal neutron reactor depends essentially on the stability, fission yield and thermal neutron cross-section of the poison. Relevant data for the five isotopes under consideration are listed in Table I. The quoted fission yields are for thermal neutron fission of uranium-235 only.

Theoretical studies on the build-up of reactor poisons have been reported,^{3,4,5} based mainly on the data of Hughes and Schwartz² and Coryell and Sugarman.⁶

TABLE I

Isotope	Half-life	Fission yield, ¹ %	Thermal neutron cross-section, ² barns
Rhodium-103	Stable	3.0	156
Neodymium-143	Stable	6.03	324
Samarium-149	Stable	1.13	40,800
Samarium-151	80 year	0.44	12,400
Gadolinium-155	Stable	0.033	56,200

A mass spectrometric study of some reactor poisons produced in the fission of uranium-233 and -235 and plutonium-239 has been conducted by Bidinosti *et al.*⁸ In the present work, radiochemical separation techniques have been developed to separate the desired elements for analysis.

The choice of separation techniques was based largely upon the desire to avoid, so far as possible, carrier coprecipitation methods because all of the isotopes of interest are stable or long-lived, and subsequent separation of the carrier element, or alternatively chemical yield determinations, would introduce an additional stage in the process. Because the final separation of the three lanthanides would necessarily be achieved by ion-exchange chromatography it was decided to base the entire separation procedure on quantitative ion-exchange methods. Selection of methods for the final determination of each isotope was governed largely by the quantities expected to be present. For rhodium-103, calculations indicated 5–10 $\mu\text{g/g}$ of uranium and therefore simple absorptiometric methods offer adequate sensitivity. No further isotopic analysis is necessary because rhodium-103 is the only stable isotope of the element. In the case of the lanthanides, where 0.2–50 $\mu\text{g/g}$ of uranium is expected, depending on the element concerned, the isotopic complexity of the separated fractions dictated that a mass spectrometric finish be used and an isotope dilution technique⁷ using pure natural lanthanides was evolved.

EXPERIMENTAL

Preparation of Ion-Exchange Columns

Cation-exchange resin, Zeokarb-225, BSS 52-80 mesh, was washed several times with distilled water, converted to the hydrogen-form by washing with 6M nitric acid, washed several times with distilled water again and allowed to dry overnight in a current of air. Anion-exchange resin, Deacidite FF, BSS 52-80 mesh, was converted to the hydroxide-form with 2M sodium hydroxide solution, washed several times with distilled water, then converted to the required anionic form with the appropriate acid. After several further washes with distilled water the resin was dried overnight in a current of air. All columns were packed by slurring the desired weight of resin with water, pouring the slurry into the column and allowing the resin to settle under gravity.

Separation and Determination of Rhodium

Because the irradiated uranium had been dissolved in nitric acid for a previous experiment it was hoped to carry out the separation of rhodium and the appropriate lanthanides in this medium. However, preliminary experiments indicated that the chemistry of rhodium in nitric acid was rather complex and not fully reproducible; the complexity of the ion-exchange column behaviour of rhodium in nitric acid is well illustrated by Table II.

TABLE II

Sample	Rhodium eluted by 10 column volumes of 0.2M nitric acid, %	
	Zeokarb-225	Deacidite FF
Stock rhodium solution in 0.2M nitric acid	95	85
Stock solution evaporated to 8M in nitric acid and diluted to 0.2M	100	50
Stock solution evaporated to dryness and dissolved in 0.2M nitric acid	50	65

In contrast, rhodium in 0.3M hydrochloric acid behaved, as anticipated, as an exclusively anionic complex and consequently the separations were carried out in hydrochloric acid solution.

Procedure

To remove all traces of nitrate ion, 20 ml of the 3M nitric acid solution of uranium (containing 201 mg of uranium/ml) were evaporated just to dryness with eight separate 50-ml portions of 6M hydrochloric acid. After the eighth evaporation the residue was dissolved in 20 ml of 0.3M hydrochloric acid and passed through an ion-exchange column, 12 cm long \times 0.5 cm diameter, containing 2 g of Zeokarb 225 in the hydrogen-form. The evaporation vessel was washed out with three separate 10-ml portions of 0.3M hydrochloric acid and the washings also passed through the column. A flow rate of 0.5 ml. cm⁻². min⁻¹ was used for this elution and all of the eluate was collected in one beaker. This separates rhodium, which behaves as an anionic complex, from the bulk of the fission products (including the whole of the lanthanides). The eluate from the cation-exchange column was then passed down an anion-exchange column, 20 cm long \times 1.7 cm diameter, containing 20 g of Deacidite FF in the chloride form, at a flow rate of 0.3 ml. cm⁻². min⁻¹. The rhodium is completely retained by the resin while the uranium, which is cationic under these conditions, passes through. The column was washed with three column volumes of 0.3M hydrochloric acid to ensure complete removal of uranium and the rhodium then eluted with 125 ml of 4M hydrochloric acid at a flow rate of 0.5 ml. cm⁻². min⁻¹. This volume of 4M hydrochloric acid had been shown by a preliminary experiment to be necessary for the complete elution of the rhodium. On evaporation, the colour of this eluate became slightly yellow and to make absolutely certain that all of the uranium would be removed before the rhodium determination, the eluate was evaporated just to dryness, taken up in 5 ml of 0.3M hydrochloric acid and the uranium removed on a cation-exchange column, 8.0 cm long \times 0.4 cm diameter, containing 1 g of Zeokarb 225 in the hydrogen-form. The column was washed with a further 20 ml of 0.3M hydrochloric acid. All of the eluate was evaporated to dryness, then dissolved in 4 ml of 2M hydrochloric acid.

The rhodium content of this solution was determined by the method described by Sandell⁹ as modified by Maynes and McBryde.¹⁰ A 2-ml aliquot of the eluate was taken, 1 ml of 2M hydrochloric acid and 5 ml of 10% tin^{II} chloride in 2M hydrochloric acid added and the whole heated for 90 min on a water bath. After cooling, the sample was diluted to a volume of 25 ml with 2M hydrochloric acid. Standard samples containing 0 μ g, 10 μ g and 20 μ g of rhodium were prepared in a similar manner. After allowing to stand for 30 min the absorbancies of all of the solutions were measured in large (25-ml volume) 4-cm cells using Ilford 602 filters in a Hilger and Watts Spekker absorptiometer. In view of the low absorbancy reading obtained (see *RESULTS*), a second 2-ml aliquot of eluate was treated to yield a 10-ml final volume. The aliquot was evaporated almost to dryness, taken up in 1.2 ml of 2M hydrochloric acid, 2 ml of 10% tin^{II} chloride in 2M hydrochloric acid added and the solution heated for 90 min on a water bath. After cooling, the volume was made up to 10 ml with 2M hydrochloric acid and the absorbancy measured as before, except that thin (10-ml volume) 4-cm cells were used. A reagent blank and standard rhodium solutions were similarly treated.

Separation and Determination of Neodymium, Samarium and Gadolinium

The lanthanide elements remain adsorbed, together with most of the other fission products, on the cation-exchange column used in isolating the rhodium fraction. To obtain pure lanthanide fractions the following general scheme, each stage of which had been proved in preliminary experiments, was adopted:

- (a) selective elution of zirconium, niobium, alkali and alkaline earth fission products,
- (b) elution of the lanthanide group and purification from uranium and plutonium by anion exchange,
- (c) further purification of the lanthanide fraction by carrier coprecipitation cycles,
- (d) isolation of the required neodymium, samarium and gadolinium fractions by cation exchange using α -hydroxyisobutyric acid.

Procedure

Selective elution of zirconium, niobium, etc. The cation-exchange column was eluted first with 10 ml of 0.5% oxalic acid solution to remove zirconium and niobium activities. This was followed by 10 ml of 1M ammonium chloride solution and 10 ml of 0.3M hydrochloric acid to remove alkali and alkaline earth fission products. The lanthanides, which are strongly held by the resin, are not removed by these treatments.

Separation from uranium and plutonium. The lanthanides, together with uranium and plutonium, were eluted from the cation-exchange column using 200 ml of 11M hydrochloric acid at a flow rate of 0.1 ml. cm⁻². min⁻¹. These elements were adsorbed on a column of anion-exchange resin by passing the eluate through a column, 15.0 cm long \times 1.7 cm diameter, containing 15 g of Deacidite FF in the chloride-form. Elution of this column with 30 ml of 13.3M hydrochloric acid gave an eluate containing the lanthanides, while the plutonium and uranium were retained by the resin as anionic chloride complexes.

Further radiochemical purification. The lanthanide-bearing eluate from the anion-exchange column was evaporated to dryness and dissolved in 5 ml of 0.2M nitric acid. To serve as carrier for the remainder of the procedure, 400 μg of spectrographically pure yttrium as yttrium chloride were then added. Yttrium was selected because it not only carries lanthanides quantitatively but it is also readily separated from them in the final α -hydroxyisobutyric acid/ion-exchange stage and serves as a useful "marker" element to follow the progress of the separation.

The radiochemical purification procedure comprised the following stages. The lanthanides were precipitated as fluorides by adding 0.5 ml of 12.5% ammonium fluoride solution. The precipitate was dissolved in 1 ml of saturated aluminium nitrate solution and lanthanide hydroxides precipitated by addition of 6M sodium hydroxide solution. After dissolution of the precipitate in 0.2M nitric acid, 200 μg of cerium carrier and 0.2 ml of saturated potassium iodide solution were added and, after standing for 10 min, cerium^{IV} iodate was precipitated by addition of 0.5 ml of 0.3M iodic acid solution. The precipitate was centrifuged and washed and the lanthanides in the combined supernate and washings precipitated as hydroxides. After dissolution in 0.2M nitric acid the entire precipitation cycle from fluoride onwards was repeated and the final hydroxide precipitate dissolved in 2 ml of 0.5M nitric acid.

Isolation of individual lanthanides. This was achieved by elution of the lanthanides from a column of Zeokarb-225 cation-exchange resin using α -hydroxyisobutyric acid at controlled pH as eluant.¹¹ The column dimensions were 9 cm in length by 0.3 cm diameter and the resin was graded by sedimentation, the fraction settling through 1 inch of water in 1–4 min being used for the column. The column was packed in water, washed with 0.5M α -hydroxyisobutyric acid made pH 3.2 with aqueous ammonia, and finally washed with water.

The 2 ml of 0.5M nitric acid containing the lanthanides was divided into two 1-ml portions. To each portion 100 μg of spectrographically-pure europium chloride were added, the europium serving as a column "marker" to follow the course of the separation. To one portion only was added 10 μg each of spectrographically-pure natural neodymium, gadolinium and samarium as chlorides. These additions were necessary in order to determine the required isotopes by isotope-dilution mass spectrometry. Lanthanide hydroxides were precipitated from each portion with aqueous ammonia and dissolved in 100 μl of 0.5M nitric acid and each solution submitted to the separation sequence described below.

The lanthanide solution and two 50- μl centrifuge tube water washings were transferred separately to the top of the column and allowed to pass through it under gravity. A small amount of very fine grade Zeokarb-225 was then placed on top of the column to act as a top cover. Elution was commenced using 0.5M (pH 3.2) α -hydroxyisobutyric acid solution. Whilst this eluant will completely separate the individual lanthanides, very large volumes are required to elute the lighter ones and it proved more convenient to adjust the pH of the eluant during the sequence in order to reduce the volume collected. Preliminary experiments indicated that the following scheme was satisfactory. The pH 3.2 eluant was used until yttrium had been eluted, then the pH was increased to pH 3.37 and elution continued until gadolinium and europium had been eluted and finally an eluant of pH 3.75 was used to elute samarium and neodymium. Throughout the elution 200- μl fractions of eluate (one free column volume) were collected and 100 μl of saturated oxalic acid solution added to each fraction to precipitate individual lanthanide oxalates. Using this sequence yttrium oxalate precipitated in fractions 11–20, gadolinium oxalate in fractions 40–52, europium oxalate in fractions 70–82, samarium oxalate in fractions 79–100 and neodymium oxalate in fractions 122–127. In the case of the portion not treated with natural lanthanides the concentration of gadolinium was too low to yield an oxalate precipitate so fractions 40–52 were bulked, 50 μg of spectrographically pure yttrium added as carrier and the precipitation completed. For samarium and neodymium, fractions 95–102 and 121–128, respectively, were bulked.

The six lanthanide oxalate samples (two each for neodymium, gadolinium and samarium) were washed with water and submitted for mass spectrometric analysis, together with samples of the oxalates of the three natural lanthanides added to the second portion of the test solution.

A Metropolitan-Vickers M.S.2 mass spectrometer modified for analysis of solid samples, incorporating triple filament ionisation, was used for the mass spectrometric analyses. Before the loading of every sample the filaments were operated above the normal operating temperature to ensure absence of contamination. New filaments were used for each sample.

RESULTS

Rhodium-103

The absorbancy readings for the two 2-ml aliquots together with rhodium standards are given in Table III.

The results quoted in Column 5 of Table III represent the rhodium-103 concentration because all other isotopes of rhodium are short-lived. Because there is no

TABLE III

Aliquot No.	Sample	Corrected absorbancy	Rhodium/ aliquot, μg	Rhodium/ g of uranium, μg
1 (final volume of 25 ml)	10 μg Rh	0.061	10.0	
	20 μg Rh	0.119	20.0	
	Test solution	0.094	15.7	7.82
2 (final volume of 10 ml)	10 μg Rh	0.140	10.0	
	20 μg Rh	0.280	20.0	
	Test solution	0.213	15.2	7.57

evidence of rhodium contamination in the unirradiated uranium it is assumed that this concentration has arisen entirely from the fission process.

Neodymium-143, samarium-149 and -151, and gadolinium-155

In the following tables the unspiked sample, spiked sample and natural lanthanide are numbered 1, 2 and 3, respectively. All quoted errors are standard deviations.

The isotopic analyses for neodymium are given in Table IV. Isobaric contamination was negligible.

TABLE IV

Isotope	Sample Nd 3, %	Natural abundance, ¹³ %	Sample Nd 2, %	Sample Nd 1, %
142	27.5 \pm 0.5	27.1	2.88 \pm 0.04	0.11 \pm 0.01
143	12.0 \pm 0.4	12.2	27.7 \pm 0.4	29.8 \pm 0.5
144	24.2 \pm 0.4	23.9	21.3 \pm 0.3	20.8 \pm 0.3
145	8.2 \pm 0.2	8.3	19.3 \pm 0.3	20.4 \pm 0.3
146	17.4 \pm 0.3	17.2	16.3 \pm 0.2	15.9 \pm 0.3
148	5.5 \pm 0.3	5.7	8.8 \pm 0.1	9.3 \pm 0.2
150	5.2 \pm 0.3	5.6	3.74 \pm 0.05	3.7 \pm 0.1

It is apparent that the measured ratios for the natural Nd 3 sampled are very close to the literature¹³ data and the latter have therefore been used for calculation purposes.

From the above figures the following results may be derived:—

Total neodymium content of irradiated uranium sample = $44 \pm 1 \mu\text{g/g}$

Isotopic abundance of neodymium-143 = $29.8 \pm 0.5\%$.

The isotopic abundance measurements for samarium are given in Table V. In this case some sample contamination is evident, europium-151 and -153 being present in both the Sm 1 and Sm 2 samples. Because there is no isotope at mass 153 in either natural or fission product samarium the sample was run until the mass peak at 153 had almost disappeared before measurements were made. Natural samarium-144 was present in the fission product Sm 1 sample. Its presence was corrected for on the basis of known natural abundance of the 144 isotope and assuming that Sm 2 was contaminated to the same extent as Sm 1.

Again, measured values on the natural Sm 3 sample agree sufficiently well with accepted data that the latter have been used in the calculations. The results so derived are:—

Total samarium content of irradiated uranium = $6.9 \pm 0.4 \mu\text{g/g}$

Isotopic abundance of samarium-149 = $2.3 \pm 0.1\%$

Isotopic abundance of samarium-151 = $7.4 \pm 0.2\%$.

TABLE V

Isotope	Sample Sm 3, %	Natural abundance, ¹³ %	Sample Sm 2, %	Sample Sm 1, %	Sm 1 corrected for natural contamination, %
144	2.9 ± 0.1	3.1	1.46 ± 0.05	0.32 ± 0.01	—
147	15.2 ± 0.2	15.0	20.1 ± 0.2	23.7 ± 0.5	24.7 ± 0.6
148	11.4 ± 0.1	11.2	6.5 ± 0.2	3.00 ± 0.07	2.1 ± 0.1
149	13.9 ± 0.2	13.8	7.9 ± 0.3	3.45 ± 0.08	2.3 ± 0.1
150	7.3 ± 0.1	7.4	23.5 ± 0.2	35.7 ± 0.8	38.9 ± 0.9
151	—	—	3.7 ± 0.1	6.6 ± 0.2	7.4 ± 0.2
152	26.7 ± 0.3	26.8	23.8 ± 0.2	21.5 ± 0.5	20.8 ± 0.5
154	22.6 ± 0.2	22.7	13.0 ± 0.1	5.7 ± 0.1	3.8 ± 0.1

Because of the extremely small quantity of gadolinium present in the Gd 1 sample and the fact that significant contamination of mass spectra occurred in the mass range 133 to 182, a worthwhile measurement of the isotopic content of gadolinium-155 could not be made. This was further aggravated by contamination from natural gadolinium. Using results from the Gd 2 sample and correcting for the presence of natural samarium and dysprosium at gadolinium masses, an approximate figure of 0.4 of total fission product gadolinium per g of uranium was calculated.

Acknowledgements—The authors are indebted to Drs. J. O. Clarke and J. Leece who were responsible for all of the mass spectrometric measurements on the lanthanides at the Capenhurst Factory of the U.K.A.E.A. during 1958. Tables IV and V are taken from their unpublished results.¹²

Zusammenfassung—Methoden für die Bestimmung von ¹⁰³Rh, ¹⁴³Nd, ¹⁴⁹Sm, ¹⁵¹Sm und ¹⁵⁵Gd in bestrahltem Uranmetall werden angegeben. Die Konzentrationen dieser Isotope wurden in einem mit ungefähr 850 Megawatt-Tage/Tonne in einem Calder-Reaktor bestrahlten Uranstab ermittelt. ¹⁰³Rh wurde nach Isolierung durch Anionenaustausch kolorimetrisch bestimmt, die Lanthaniden durch isotope Verdünnung und Massenspektrometrie, wiederum nach einer Reinigungsstufe mittels Ionenaustausch.

Résumé—On décrit les méthodes de dosage du rhodium-103, du néodyme-143, du samarium-149 et -151, et du gadolinium-155 dans des échantillons irradiés d'uranium. La concentration de ces cinq isotopes a été déterminée dans un bâtonnet d'uranium soumis à une irradiation d'environ 850 mégawatt-jours/tonne. Le rhodium-103 est déterminé par colorimétrie après purification par voie d'échange anionique et les isotopes des lanthanides déterminés par dilution isotopique et spectrométrie de masse, après purification par échange d'ion.

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SEPARATION OF CERTAIN CATIONS FROM MIXTURES OF VARIOUS CATIONS ON ION-EXCHANGE PAPERS—II* ANTIMONY AND ARSENIC

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(Received 13 February 1963. Accepted 20 February 1963)

Summary—Antimony and arsenic have been separated from multi-component mixtures by development with complexing solvents on filter paper impregnated with cation-exchange resin. Comparisons are made with the results of electrochromatographic migrations of the same ions with these solvents as background electrolyte.

PAPER chromatography on ion-exchange papers provides a new and useful approach to analytical procedures for the isolation of particular ions from complex mixtures. With a suitable complexing developer, ions of one or of a few metals may be made to migrate from the mixture as separate and distinct zones. The ions in these zones may then be detected and estimated by appropriate methods. This procedure permits separations without previous segregation of the mixture, and the separations are effective at the lowest concentrations of the ions that can be detected by the most sensitive tests.

The first part of this series¹ demonstrated the separation of silver or thallium from multicomponent mixtures of cations by chromatography on papers impregnated with strong-base anion-exchange resin. Developing solutions were chosen so that either of these two ions remained cationic and migrated while all other ions remained at or near the origin because they precipitated, became anions and underwent ion exchange, or became non-ionic species which were sorbed by the paper.

Cation-exchange papers can be used similarly to separate cations which are converted to non-sorbed anions or non-ionic species (and migrate) from those which precipitate, remain as cations, or become non-ionic or anionic species which are sorbed, and remain at or near the origin. This report demonstrates the separation of antimony or arsenic in this manner.

EXPERIMENTAL

Paper-chromatographic studies

Migration apparatus: Essentially the same procedures as reported earlier¹ were employed, except that the papers were sprayed with the proper zone-revealing reagents immediately after development without drying. Sample solutions were spotted 1 inch apart along the origin, and development required about 2 hr with the solutions and paper used.

Amberlite SA-2 ion-exchange papers, containing about 45% by weight of Amberlite IR-120 strong-acid cation-exchange resin in the sodium form, were used (batch No. 7802-H. Reeve Angel and Co.). The paper was converted to the required form by soaking overnight in a 4% (by weight) solution of an appropriate acid or salt, washing with water and air drying.

Developing solvents: Various aqueous complexing solutions were evaluated as selective solvents for separations. These were prepared from the best grades of chemicals commercially available and had the following compositions: (1) 0.50M tartaric acid, pH 2.2; (2) 0.50M ammonium fluoride,

* Part I: see reference 1.

pH 6.5; (3) 0.050*M* malonic acid, pH 2.2; (4) 0.10*M* diethylenetriamine, pH 11; and (5) 0.020*M* diethylenetriamine and 0.080*M* hydrochloric acid, pH 1.7. These particular solutions were chosen because electrochromatographic studies^{2,3} indicated that they might give useful separations and not interfere with detection tests for the ions.

Initial zones: Single spots of the cations to be studied were developed at a concentration of 0.050*M*. The volumes applied to the paper were as follows: 10 μ l for Ag, Tl, Pb, Cu^{II}, Cd, Co, Ni, Hg^I, Hg^{II}, Fe^{III}, Pt^{IV}, Au, Al, Mg, Zn, Mn^{II}, Cr^{III}, U^{VI} and V^V; 15 μ l for Sb^{III}, Bi and Sn^{IV}; and 25 μ l for As^{III}, Ce^{III}, Ce^{IV} and Ba. These were convenient amounts which allowed identification after development.

Each solvent was also tested with a mixture containing 15 compatible, representative ions. The mixture employed contained Ag, Al, Ba, Cd, Ce^{IV}, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Tl and Zn. Ten μ l of this solution, which was 0.025*M* in each metal ion, was used for an initial zone. Arsenic and/or antimony was added to this mixture on the paper by spotting the mixture and the single ion on the same area of the paper with drying in between.

Detection of zones: Four spray reagents, previously described,¹ served for the detection of all of the ions listed above: 2% aqueous, yellow ammonium sulphide followed by HCl for Ag, Tl, Pb, Cu, Cd, Co, Ni, Hg, As, Fe, Sb, V, Bi, Sn, Au, Pt; alkaline, ammoniacal silver nitrate (Tollen's Reagent) for Mn and Cr; dilute, alcoholic 8-quinolinol followed by ammonia (if necessary) and observation in ultraviolet light for Al, Ce, Mg, Zn, Cr, Sn and U; and fresh, dilute aqueous potassium rhodizonate for Ba. Uranium could also be located as a brown zone when sprayed with 1% aqueous potassium ferrocyanide followed by HCl if necessary.

It was better to spray with ammoniacal silver nitrate and then 6*M* sodium hydroxide (very lightly) separately rather than to mix the two solutions together before spraying. This prevented severe blackening of the paper.

Potassium rhodizonate would locate barium only under slightly acidic conditions. Paper sheets which were neutral or strongly basic were sprayed with 3*M* acetic acid first; those which were strongly acidic were sprayed with the reagent followed by dilute ammonia until the red spot appeared.

Electrochromatographic studies

Each ion listed was subjected to migration in an electrochromatographic system in which the five solvents described above were in turn used as the background electrolyte. The purpose of this was to determine the sign of the charge, if any, on each ion in each solution. Several separations resulted from these studies and have been reported.^{2,3} Complete details of the experimental procedures used for these studies have been previously reported.^{3,4}

The direction of electrochromatographic migration reveals the sign of the electrical charge on ionised substances in solution. In this way one can tell the condition of ions in various complexing solutions. Zones which do not leave the origin (after correction for electro-osmotic flow) either are non-ionic or are precipitated. To differentiate these, a simple chromatographic test was run with the background solution as the wash liquid. If the zone migrates with $R_F = 1$, it is non-ionic; if $R_F = 0$, it is probably a precipitate held mechanically by the paper. Zones which streak from the origin can be non-ionic or precipitated; test-tube experiments with sample solution and background solution were performed to differentiate these. (There is negligible adsorption of ions, at the concentrations used, by the Eaton Dikeman Grade-301 paper employed in these studies, so this effect is unimportant in the interpretation of results.^{5,6})

RESULTS AND DISCUSSION

As a matter of convenience, results are reported for each developing solution rather than according to the ion separated. Results are interpreted based on R_F values, where

$$R_F = \frac{\text{distance travelled by leading edge of solute zone}}{\text{distance travelled by solvent front}} \quad (1)$$

All R_F values and distances of migration given are the average of at least 6 trials with each R_F having a standard deviation of ± 0.04 or less.

Tartaric acid

Solvent (1) caused the separation of antimony from all ions except tin, arsenic and mercury on sodium-form paper and from all ions except tin and mercury on hydrogen-form paper.

With the sodium-form paper, antimony has $R_F = 0.50$ but gives an elongated zone 12 cm in length; this means that the rear boundary of the zone was only 6.0 cm from the origin with the apparatus used. Most of the ions remained stationary at the origin, but several formed diffuse zones trailing back to the origin and in some cases contaminating the antimony zone; these were (distances given are for farthest advance of diffuse zone from the origin): mercury^I and mercury^{II}, 14.5 cm; arsenic, 6.0 cm; tin, 6.5 cm; cerium^{IV}, 3.5 cm; and bismuth, 5.0 cm. The mercury zones and tin zone always contaminated the antimony, while arsenic usually, but not always, did.

With the hydrogen-form paper, antimony has $R_F = 0.39$ and forms a zone 9.0 cm in length. Again, most of the ions remained at the origin (including arsenic) except mercury^I and mercury^{II} which trailed 7.3 cm from the origin, and bismuth and tin which trailed 3.5 and 5.0 cm, respectively. All of these except bismuth contaminated the antimony zone.

Tin, antimony, gold and platinum migrated toward the anode during electrochromatography in paper soaked with the solvent. This fact proved that only these ions are anionically complexed by tartaric acid. Mercury, arsenic and bismuth remained at the origin and all other metals migrated as cations. It was not surprising, therefore, that anionic antimony migrated a relatively long distance and that non-ionic mercury, bismuth and arsenic also showed some migration on the cation-exchange paper. The facts that anionic tin showed limited migration on both forms of paper, that arsenic migrated to some extent on sodium-form paper and not at all on hydrogen-form paper, and that anionic platinum and gold did not migrate at all, indicate that in addition to actual cation and anion exchange, ion-exchange papers sorb ions by various other mechanisms. This is supported by the observation that neither antimony nor tin are sorbed at all by columns of cation-exchange resin.^{7,8} Two sorption effects undoubtedly involved are interactions with the organic network of the resin and paper⁹ and partition between the solution in the resin phase and the flowing solution (which would differ in composition),¹⁰ as well as the normal differences in selectivity that resins of different forms exhibit.¹¹

An attempt was made to cause tin to leave the origin and antimony to migrate in a more compact zone by preparing the test solutions in the 0.50M tartaric acid developer rather than in water acidified with HCl. This technique has been shown to reduce or eliminate trailing in electrochromatography,³ but had no beneficial effect here. On the hydrogen-form paper, the leading edge of the antimony zone moved exactly the same distance and formed only a slightly less diffuse zone (6.0 cm). The rear of the tin zone still remained at the origin, and the front trailed 2–3 cm farther.

Ammonium fluoride

Solvent (2) caused the separation of antimony and arsenic from all other ions and from each other on ammonium-form paper. Arsenic had $R_F = 0.84$ and formed a circular zone 1.6 cm in diameter. Antimony migrated with $R_F = 0.95$ in a flat, wide zone 1.4 cm in height. Average zones of each were separated by about 1.5 cm.

The following ions were found to stay at the point of origin or to move a short distance (below $R_F = 0.10$): Cr, Tl, Pb, Ba, Au, Ag, Al, Bi, Pt, Hg^I, Hg^{II}, Mg, Ce^{III} and Ce^{IV}. Of these, electrochromatography proved that the first six were cationic, the next three were anionic, the next three were non-ionic, and two were precipitated.

The precipitates, non-ions (except Mg) and anions all formed elongated zones streaking from the origin, as did chromium. The following species moved a short distance from the origin (R_F 0.10–0.40): V, U, Sn, Fe^{III}, Zn, Cu, Cd, Ni, Mn and Co. The first four were anions in the solvent, the rest were cations. The separated arsenic proved to be non-ionic, and antimony was anionic.

The closest ions to either separated zone were those of iron ($R_F = 0.34$) and uranium ($R_F = 0.36$) which are known to be strongly complexed by fluoride ions. These were separated from the arsenic zone by 14 cm.

Malonic acid

Solvent (3) caused the separation of arsenic from all other ions on hydrogen-form paper. Arsenic migrated in a circular zone 1.7 cm in diameter with $R_F = 0.91$ and was separated from mercury^I, the closest zone, by 16.0 cm.

The following ions remained as cations (Mn, Cr, Tl, Pb, Cu, Cd, Co, Ni, Ce^{III}, Ce^{IV}, Mg, Ba, U and V) and remained at the origin, as did precipitated Bi, Sb and Ce^{IV}, and non-ionic Ag and Al. The following ions formed diffuse zones migrating a few cm and trailing back to the origin: Sn, Au, Pt, Hg^I and Hg^{II}. (Hg^I trailed 13.2 cm). Of these, Sn was non-ionic; gold and platinum were cationic and mercury (both states) was precipitated. Iron is the only anionic metal in this solvent; its leading edge was 15 cm from the origin, but most was at the origin. As with the fluoride solvent, separated arsenic is non-ionic in this solvent.

Diethylenetriamine

Solvent (4) caused the separation of arsenic from all other ions on sodium-form paper. The paper was used as delivered without a change of form because of the small chance for ion exchange to occur between the solvent and the paper. Arsenic migrated with $R_F = 0.88$ in an elliptical zone 2.9 cm wide and 1.9 cm high.

The following ions were cations in this solvent: Hg^{II}, Zn, Mg, Pb, Cu, Cd, Ni, Tl, Ba, Ag. Of these, only the mercury zone moved at all, streaking 2.5 cm from the origin. Al, Au, Pt, U and V were anionic in the solvent. All formed elongated zones which migrated up to 11 cm from the origin (for vanadium) and trailed back to the origin. Cr, Mn, Fe^{III}, Co, Be, Ce^{III} and Ce^{IV} precipitated and remained at the origin. Sb, Hg^I and Sn were non-ionic and also formed zones trailing back to the origin, but not so diffuse as those above. Non-ionic arsenic was separated by 20 cm from the closest zone (vanadium).

Diethylenetriamine-hydrochloric acid

Solvent (5) also caused the separation of arsenic from all other ions, on hydrogen-form paper. Arsenic had $R_F = 0.91$ and formed a zone 2.0 cm high and 3.5 cm wide. It was separated by 18 cm from the closest ion, cerium.

Electrochromatography proved that arsenic was non-ionic in this solvent also. Platinum and mercury^{II} were the only anions, streaking 5.5 cm and 3.3 cm, respectively. All the cations (Cd, Co, Ce^{IV}, Cu, Fe^{III}, Pb, Ni, Tl, Al, V, U, Mg, Ba, Zn, Cr, Mn and Ce^{III}) remained at the origin except the first three, which formed elongated zones whose leading edges were up to 9.6 cm from the origin and trailed to the origin. Silver was precipitated by the chloride ions in the developer and remained at the origin. Mercury^I disproportionated in this solvent to Hg⁰, which remained at the origin, and Hg^{II}, which migrated as above in an elongated zone. Arsenic and tin

were non-ionic, tin streaking 2.0 cm. Bismuth and gold were not studied electrochromatographically in this solvent. Both formed elongated zones trailing back to the origin so were no doubt non-ionic or anionic in character.

CONCLUSIONS

Paper chromatography on filter paper loaded with strong-acid cation-exchange resin in various forms, with aqueous complexing solutions as developers, has provided rapid, simple procedures for the isolation of antimony or arsenic from complex mixtures. As in most differential-migration methods, the behaviour of individual ions was subject to some variation. The separations described herein are reproducible when specified concentrations and pH values are maintained, even though R_F values and the sizes of individual zones may vary somewhat from run to run.

Exploratory studies were performed using cations representative of most elements of the Periodic Table. Arsenic or antimony have been proven separable, therefore, from virtually all ions, including the alkali metals, which would remain at the origin in every case. This was proven in several experiments with radioactive potassium, rubidium and caesium in several of the solvents. Had we chosen to study the separation of various pairs or triplets of ions, complete and absolute separations of a tremendous number of combinations could be reported.

Separations of this type have many advantages over chemical methods of separation. Very small quantities of the desired ions can be completely separated. The separated ions are in a form readily suitable for detection and quantitative analysis, and there is no necessity for a preliminary fractionation of any kind. These separations of antimony and arsenic should be widely applicable as in clinical practice, forensic chemistry, or agricultural analysis.

The following generalisations can be made concerning the migration of various species on strong-acid cation-exchange paper. Anionic or non-ionic species may migrate with the solvent front (R_F close to 1) in compact zones, as did antimony in solvent (2) and arsenic in solvents (2), (3), (4), and (5). However, anionic or non-ionic species can show limited migration, as did aluminium and tin in solvent (4). When this occurs, the solutes can form elongated, diffuse zones trailing back to the origin, or compact zones at the origin [as did gold and platinum in solvent (1)]. Anions generally form more diffuse zones than non-ions (the leading edge of the zone is farther from the origin). Ions which precipitate are usually found at the origin in a very compact zone because the paper holds these zones mechanically. Cations usually are found at the origin in a compact zone. Because of normal differences in resin selectivity, however, cations sometimes migrate a short distance, in a compact zone [manganese in solvent (2)]. In exceptional cases, some cationic species form diffuse zones streaking a short distance from the origin [cerium^{IV} in solvent (1); chromium in solvent (2); gold and platinum in solvent (3); and cerium^{IV}, cadmium and copper in solvent (5)]. With these ions, interactions other than simple ion exchange are probably involved (see below).

Caution must be exercised in predicting the possible separation of two or more charged or uncharged species by ion-exchange paper chromatography. Some cations migrate (or streak) farther than some anions on cation-exchange paper. For example, the leading edge of the cationic manganese zone was 6.7 cm from the origin in solvent (2), while the leading edge of the anionic platinum zone migrated only 5.0 cm in the

same system. As with all differential migration procedures, experimental verification is the only way to be sure that any specific result will occur.

Comparison of the R_F values for arsenic in the four solvents in which it migrated as a compact zone indicates that interactions may occur with the paper or the resin (or both) other than simple ion exchange (because arsenic is non-ionic), and that the degree of interaction is quite similar in all the solvents.

Acknowledgment—This work was performed in part at the Argonne National Laboratory, Argonne, Illinois, under the auspices of the United States Atomic Energy Commission, while one of the authors (J.S.) was a Resident Research Associate during the summers of 1961 and 1962. Charles W. Cline was a participant in Lafayette's N.S.F. Undergraduate Research Participation Program during the academic year 1962-3.

Zusammenfassung—Antimon und Arsen wurden aus Mischungen mit vielen Bestandteilen durch Entwicklung mit komplexbildenden Lösungsmitteln auf mit einem Kationenaustauscher imprägnierten Filtrierpapier abgetrennt. Vergleiche mit den Ergebnissen der elektrochromatographischen Wanderung derselben Ionen mit solchen Lösungsmitteln als Grundelektrolyten werden angestellt.

Résumé—L'antimoine et l'arsenic ont pu être séparés de mélanges comportant de nombreux composés, par développement au moyen de solvants complexants sur papier filtre imprégné d'une résine échangeur de cations.

Comparaison avec les résultats de migration électrochromatographique obtenus avec les mêmes ions et les mêmes solvants utilisés comme électrolytes de base.

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THE AIR-OXIDATION OF VANADIUM^{IV} IN ALKALINE SOLUTION

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(Received 2 March 1963. Accepted 21 March 1963)

Summary—The air-oxidation of vanadium^{IV} in alkaline solution proceeds *via* the reduction of the aerial oxygen to peroxide. The initial rate of oxidation is proportional to the concentration of sodium hydroxide; iron^{III} catalyses the reaction and chromium^{III} inhibits it. At concentrations of vanadium not less than 0.002*N*, the rate of oxidation is controlled by the rate of diffusion of aerial oxygen. Under suitable conditions, quantitative recovery of vanadium as vanadium^V is obtained.

No air-oxidation of vanadium^{IV} occurs in strongly acid solution,¹ but in alkaline solution the standard redox potential of the vanadium^{IV}-vanadium^V system becomes sufficiently less positive (-0.74 and -0.85 v in 1*N* and 3*N* sodium hydroxide, respectively²) for such oxidation to occur. Jackson³ found that below pH 2.45 oxidation at 14° was negligible over a period of 1 week: above this pH, the rate of oxidation rapidly increased.

EXPERIMENTAL

Reagents

Solutions of vanadium^{IV} in 0.1*N*-sulphuric acid were prepared from GPR vanadium pentoxide by reduction with sulphur dioxide,⁴ and those of vanadium^V in 1*N* sulphuric acid from AnalaR ammonium metavanadate by the method of Rao, Murty and Rao.⁵ All other reagents were of AnalaR quality.

A number of reagents are known⁶ to contain small amounts of impurities that can reduce vanadium^V. Here the chief source of this error is the sodium hydroxide; the content of reducible impurity of several specimens of GPR and AnalaR grade was about 0.2 μ eq/g (compared with about 0.005 μ eq/g for AnalaR sulphuric acid). The concentration of this impurity was reduced to less than 0.01 μ eq/g in the following way: 40 g of sodium hydroxide pellets were swirled with 70–80 ml of water; when dissolution was complete, the solution was heated to boiling and 1 g of sodium peroxide was added, in small portions at a time, with swirling. The peroxide decomposed rapidly, but not violently, and no frothing occurred. The solution was boiled gently for 30 min more and then allowed to cool, and was diluted to 250 ml to give 4*N* sodium hydroxide.

Method

The reaction between vanadium^{IV} and oxygen in alkaline solution was studied by adding sodium hydroxide solution to a stirred standard solution of vanadium^{IV}. After the desired time had elapsed, the solution was acidified. Amperometric (dead-stop) determinations were then made of either the residual vanadium^{IV} by means of permanganate or the vanadium^V produced by means of iron^{II}.

Tests showed that the distilled water and stock solutions were saturated with oxygen. In distilled water the concentration of dissolved oxygen at saturation is 0.0012*N* at 15°; in solutions of electrolytes it is less, being about 0.0006*N* in 2*N* sodium hydroxide at 15°. In a typical reaction mixture of 5–6 ml of 1*N* sodium hydroxide and 10 ml of 0.005*N* vanadium^{IV} in 0.1*N* sulphuric acid at 15°, the concentration of dissolved oxygen was found to be 0.0011*N*.

MECHANISM AND KINETICS

(A) Dissolved Oxygen in Excess

Table I gives a qualitative summary of many consistent determinations made with aliquots of the same solutions of vanadium^V. The results in (*d*) were the same

whether the chromium^{III} was added before or after the air-oxidation, but before acidifying. The differences between (c) and (b) or (d) and (b) increased with the concentration of vanadium^{IV} present at the beginning of the air-oxidation.

TABLE I.—TITRATIONS BY IRON^{II} IN ACID SOLUTION

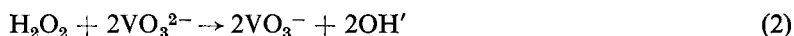
Treatment	Titre compared with the direct titration of the vanadium ^V
(a) Chromium ^{III} added	the same
(b) Vanadium ^V alone, or with chromium ^{III} added, and air-oxidation in 1 <i>N</i> sodium hydroxide	the same
(c) Vanadium reduced to vanadium ^{IV} and air-oxidation in 1 <i>N</i> sodium hydroxide	slightly high
(d) As (c), but chromium ^{III} added	high
(e) Chromium ^{III} alone and air-oxidation as in (b) and (c)	nil

The high results in (c) and (d) cannot be caused by impurities in the reagents because there is no corresponding error in (b). The high result in (d) cannot be due to air-oxidation of chromium^{III} [cf. (e)] or to the induced air-oxidation of chromium^{III} because the same result is obtained by adding the chromium^{III} immediately before acidifying.

It is postulated that the high results in (c) and (d) are caused by the formation of peroxide during the air-oxidation of vanadium^{IV}. The reaction can be formulated as follows:



followed by:



Reaction (1) is undoubtedly the result of several successive reactions; O_2' and HO_2 are probably formed as intermediates.

Direct tests with vanadium^{IV} and hydrogen peroxide in alkaline solution showed that the two overall reactions are comparable in rate, but that reaction (2) is somewhat slow at the concentrations prevailing during the air-oxidation. Thus, provided an excess of oxygen is initially present, peroxide should accumulate during the air-oxidation and some peroxide should remain when all the vanadium^{IV} has been oxidised.

This is in agreement with the experimental results. The higher results in (d) compared with (c) are caused by the oxidation of the chromium^{III} by the peroxide formed. In (c) the peroxide formed reacts only very slowly with the iron^{II} in the titration (see below).

Under the optimum conditions for the production of peroxide, *i.e.*, in the presence of a large excess of dissolved oxygen, the amount of free peroxide remaining corresponds to not more than one quarter of the maximum allowed by reaction (1). As the initial concentration of vanadium^{IV} is increased, this proportion of free peroxide finally present decreases, and, with an excess of vanadium^{IV}, the peroxide remaining becomes negligible.

A detailed examination of the kinetics was not attempted. As expected, an equation of the type

$$-d[\text{vanadium}^{\text{IV}}]/dt = k[\text{oxygen}][\text{vanadium}^{\text{IV}}]$$

does not describe the results satisfactorily.

Effect of hydrogen peroxide on the titration by iron^{II}

The peroxide formed in the alkaline oxidation is of less consequence because at the low concentrations encountered here it reacts only slowly with iron^{II} in acid solution. The results given in Table II were obtained for titrations of 20 ml of 0.0008*N* vanadium^V by approximately 0.02*N* iron^{II} at 20°C in a solution 1*N* to sulphuric acid and 0.5*M* to orthophosphoric acid.

TABLE II

Conditions	Titre, ml	Titre calculated if the peroxide reacted quantitatively with iron ^{II} , ml
No addition of peroxide	0.880	—
Solution 10 ⁻⁴ <i>N</i> to peroxide	0.883	0.995
Solution 10 ⁻³ <i>N</i> to peroxide	0.9	2.05

The observed increases in the titres correspond to only a few per cent of the peroxide present. The presence of hydrogen peroxide at the end-point causes a drift in the values of the amperometric current because of the slow oxidation of iron^{II}. Such a drift was detected when, in the experiments summarised in Table I, relatively large concentrations of vanadium^{IV} had been air-oxidised and this is additional evidence for the formation of peroxide.

The peroxide formed is usually too dilute to be detected by the colour of pervanadium. In the last titration mentioned above, the vanadium was initially present as pervanadium and the solution was distinctly red. The end-point coincided with the discharge of this colour.

Effect of some variables

The rate of oxidation by dissolved oxygen is greatly increased as the concentration of sodium hydroxide is increased, the *initial* rate being proportional to the concentration of sodium hydroxide. The results in Table III are for solutions initially 0.0008*N* to vanadium^{IV} at 15°.

TABLE III.—EFFECT OF CONCENTRATION OF SODIUM HYDROXIDE

Normality of sodium hydroxide	0.006	0.056	0.18	0.37	0.92	1.9	3.8
Percentage of vanadium ^{IV} oxidised after 1 sec	—	—	12	18	30	65	90
after 10 sec	26	48	76	95	100	100	100

Traces of iron catalyse the reaction, whilst chromium^{III} inhibits it (Table IV). The air-oxidation of chromium^{III} is very slow, *e.g.*, 0.001 equivalents-% per day for 0.05*M* chromium^{III} in 1*N* sodium hydroxide.

TABLE IV.—EFFECT OF IRON AND CHROMIUM.
(All solutions initially 0.0008*N* to vanadium^{IV})

	Percentage of vanadium ^{IV} oxidised after 1 sec in 0.3 <i>N</i> -sodium hydroxide at 18°				
	Added iron ^{III} , <i>M</i>	nil	10 ⁻⁵	10 ⁻⁴	10 ⁻³
Chromium absent	20	34	85	*	
Solution 0.031 <i>M</i> to chromium ^{III}	3	4	10	17	

* When the concentration of iron^{III} is greater than 10⁻³*M*, precipitation occurs and oxidation of the vanadium is incomplete. In the presence of chromium^{III}, this precipitation is inhibited.

Between 15 and 50°, a rise of 10° increased the rate of reaction in 0.3*N* sodium hydroxide by a factor of 1.4.

(B) Diffusion-controlled Conditions

If the vanadium^{VI} is in excess of the dissolved oxygen, initially the vanadium^{IV} reacts rapidly with the oxygen in solution, and this is followed by a slower oxidation of the remaining vanadium^{IV} at a rate equal to the rate of diffusion of atmospheric oxygen into the solution.

Experiments were made with solutions stirred without perturbation of the surface, in which the concentration of vanadium^{IV} was varied between 0.003 and 0.008*N*, the liquid-air interface between 7.5 and 70 cm², and the time between 3 and 30 min; consistent results were obtained for the rate of oxidation of vanadium^{IV} per cm² of interface.

The presence of iron^{III} did not increase the rate of this oxidation. Between 15 and 50°, a rise of 10° increased the rate of oxidation by a factor of about 1.15. The rate of air-oxidation of vanadium^{II} in 2*N* sulphuric acid was the same as that of vanadium^{IV} in 0.3*N* sodium hydroxide.

At higher concentrations of sodium hydroxide, the rate of oxidation was decreased as shown in Table V.

TABLE V

Normality of sodium hydroxide	0.06	0.31	0.88	3.7	6.6
Rate of oxidation at 15°, $\mu\text{eq. min}^{-1} \text{cm}^{-2}$	0.30	0.31	0.31	0.16	0.05

Presumably the lower solubility of oxygen in the more concentrated solutions is accompanied by a reduced rate of diffusion.

ANALYTICAL APPLICATION

As the oxidation of vanadium^{IV} by oxygen in alkaline solution has been shown to be rapid and complete, and as the oxidant is inactivated on acidification, the reaction may be of use in the determination of vanadium. The oxidation of vanadium^{IV} to vanadium^V before titrating with iron^{II} sulphate is a common operation in vanadium determinations and requires not only quantitative oxidation but also easy and complete removal of the excess of oxidising agent. The problem is unexpectedly difficult, as is evidenced by the continuous attention that it has received, and various reagents, namely nitric acid,⁸ permanganate, persulphate,⁹ perborate,¹⁰ bromate,¹¹ perchloric

acid¹² and ozone,¹³ have been proposed; all of these leave something to be desired, particularly when the concentration of vanadium is small.

The recovery of vanadium^V after air-oxidation of vanadium^{IV} was determined as follows. For 40-mg quantities of vanadium, 10-ml aliquots of 0.073*N* vanadium^V solution were treated with sulphur dioxide in the presence of 1*N* sulphuric acid, this treatment being followed by expulsion of the excess of sulphur dioxide in a stream of

TABLE VI.—RECOVERY OF 40 mg OF VANADIUM*

Method	0.02 <i>N</i> iron ^{II} sulphate, ml		
	Direct titre, ml	Titre after applying method, ml	Difference %
Air-oxidation	34.79 ± 0.003 (3)	34.77 ± 0.02 (3)	-0.06 ± 0.07
	34.80 ± 0.003 (3)	34.82 ± 0.014 (4)	+0.06 ± 0.05
Permanganate-azide	33.76 ± 0.003 (4)	33.67 ± 0.016 (4)	-0.27 ± 0.05
Silver-persulphate	33.64 ± 0.006 (4)	33.77 ± 0.09 (6)	+0.39 ± 0.28

* The ± values are standard deviations from the mean; the figures in parentheses are the number of determinations.

carbon dioxide. The solution was made 0.5*N* to sodium hydroxide, which gave a total volume of about 35 ml. As the vanadium^{IV} is in excess of the dissolved oxygen, the solution was aerated until oxidation was complete. The solution was then made 1*N* to sulphuric acid and 0.5 *M* to phosphoric acid, and was titrated amperometrically by 0.02*N* ferrous sulphate (Table VI). For 2.4-mg quantities of vanadium, 10 ml of

TABLE VII.—RECOVERY OF 2.4 mg OF VANADIUM

0.01 <i>N</i> iron ^{II} sulphate, ml	Direct titre	4.742	4.747	4.812	4.755
			4.741	—	4.813
	Titre after applying air-oxidation method, ml	4.742	4.749	4.814	4.757
		—	4.750	—	4.756
	Difference, %	nil	+0.05	+0.03	+0.03

0.004753*N* vanadium^V solution were diluted with 70 ml of 0.2*N* sulphuric acid. An excess (1.5 ml) of 20-vol hydrogen peroxide was added, and the solution was boiled until the decomposition of the pervanadium was complete and for a further 5 min. (This procedure converts vanadium, whatever its initial valency, into a mixture of ~98% of vanadium^V and ~2% of vanadium^{IV}; all traces of peroxide are decomposed.¹⁴ The air-oxidation of the remaining vanadium^{IV} produces insufficient peroxide to affect the titration). The solution was allowed to cool to 20°, and 8 ml of 4*N* sodium hydroxide were added with swirling. After 5 min, the solution was acidified and titrated as above by 0.01*N* iron^{II} sulphate (Table VII).

The titres thus obtained were compared with the "direct titre" of an untreated aliquot of vanadium^V solution. Air-oxidation of the vanadium^V solution showed that less than 0.02% of the vanadium was present as vanadium^{IV}. In Table VI, the recovery of vanadium^V by two well-known methods¹⁵ is presented for comparison.

Small differences between groups of direct titres are due to small differences in the concentrations of the iron^{II} solutions used.

The recovery of vanadium^V by air-oxidation is evidently quantitative under the conditions used. The reaction is thus a useful one where rapid and complete oxidation of vanadium in pure solution is required to be followed by a titration with a reducing agent. It is specially recommended for very dilute standard vanadium^V solutions which, under acid conditions, are often slightly reduced because of the presence of dust or organic impurities. The method has proved to be as satisfactory at vanadium concentrations of $3 \times 10^{-5}N$. It cannot be used in the presence of ions that are precipitated by alkali. Small amounts of iron (*i.e.*, insufficient to be precipitated by the alkali, p. 796) do not interfere. Chromium^{III} interferes by being partially oxidised to chromium^{VI}. Thus, in the determination of 2.4 mg of vanadium, initially present as vanadium^{IV}, the presence of 2.4 mg of chromium^{III} caused a positive error of 2.5%; pre-treatment with hydrogen peroxide in dilute acid reduced the error to +1–1.5%,* most of which is due to oxidation of chromium^{III} during the pre-treatment rather than during air-oxidation. For smaller amounts of chromium^{III}, the error decreases approximately proportionally, but the exact value is somewhat dependent upon the conditions. With 2.4 mg of vanadium and 0.1 mg of chromium, no error was discernible.

Acknowledgement—We thank Imperial Chemical Industries Ltd. (Billingham Division) for awarding a bursary to one of us (G. A. D.), during the tenure of which this work was carried out.

Zusammenfassung—Bei der Luftoxydation von Vanadin(IV) in alkalischer Lösung wird Luftsauerstoff zu Peroxyd reduziert. Die Anfangsgeschwindigkeit der Oxydation ist der NaOH-Konzentration proportional; Eisen(III) beschleunigt die Reaktion, Chrom(III) hemmt sie. Bei Vanadinkonzentrationen um 0,002*N* ist die Oxydationsgeschwindigkeit durch die Andiffusion von Luftsauerstoff bestimmt. Unter geeigneten Bedingungen verläuft die Oxydation zu Vanadin(V) quantitativ.

Résumé—L'oxydation à l'air du vanadium^{IV} en solution alcaline s'effectue par la conversion de l'oxygène de l'air en peroxyde. Le taux initial d'oxydation est proportionnel à la concentration de la soude; le fer^{III} catalyse cette réaction tandis que le chrome^{III} l'inhibe. Pour une concentration de vanadium de 0,002*N*, le taux d'oxydation est soumis au taux de diffusion de l'oxygène de l'air. En opérant dans des conditions convenables on peut récupérer d'une manière quantitative du vanadium sous forme de vanadium^V.

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* We have found¹⁶ that this error can be eliminated by keeping the solution hot for 10 min at pH 7 after the peroxide treatment and before the air-oxidation. At this pH, the residual vanadium^{IV} reduces any chromium^{VI} formed during the pre-treatment with hydrogen peroxide.

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SHORT COMMUNICATIONS

XXXIV. Mitteilung über quantitative organische Analyse: Beitrag zum Studium der Methode zur Bestimmung von Sauerstoff in organischen Substanzen

(Eingegangen am 13. Juni 1962. Angenommen am 16. Februar 1963)

DIE Grundreaktion $\text{CO}_2 + \text{C} = 2\text{CO}$ der direkten Sauerstoffbestimmung in organischen Substanzen wurde bisher nicht im Durchflusssystem unter den bei der Sauerstoffbestimmung üblichen Bedingungen studiert. Zur Zeit haben wir den Konversionsgrad von CO_2 zu CO bei Durchgang durch eine kurze Schicht von Aktivkohle in Abhängigkeit von der Temperatur festgestellt. Die gemessenen Werte, die unter den im experimentellen Teil beschriebenen Bedingungen gewonnen wurden, sind auf Abb. 1 graphisch dargestellt und in der Tabelle I zusammen mit den im stationären Zustand gemessenen Werten² zusammengestellt. Die Resultate zeigen, dass sich die Konversion von CO_2 zu CO in Abhängigkeit von der Temperatur der Kohlenschicht (für den dynamischen Zustand gemessen) von den Angaben für das Gleichgewicht $\text{CO}_2 \xrightleftharpoons{\text{C}} 2\text{CO}$ im stationären Zustand wesentlich unterscheidet.

TABELLE I.—ABHÄNGIGKEIT DER KONVERSION VON CO_2 VON DER TEMPERATUR AUF DER 10 CM KOHLESCHICHT BEI DURCHFLUSS DES TRÄGERGASES 10 ML/MIN. UND DIE ANGABEN FÜR DIE GLEICHGEWICHT

$\text{CO}_2 \xrightleftharpoons{\text{C}} 2\text{CO}$ IM STATIONÄREN ZUSTAND.*

Temperatur, °C	Konversion von CO_2 , % dynamischen Zustand	im stationären Zustand
1200	—	99,94
1140	99,8	—
1120	100,0	—
1100	—	99,85
1080	98,9	—
1060	94,0	—
1050	91,0	99,63
1040	85,0	—
1020	76,5	—
1000	—	99,41
980	57,3	—
950	—	98,68
930	31,6	—
900	—	97,78
880	16,2	—
850	—	93,77
835	7,1	—
785	3,1	—

* Die Werte für den stationären Zustand haben wir der unter Punkt 2 angeführten Literatur entnommen.

Unsere Feststellung gestattet, die Bedingungen zur Sauerstoffbestimmung rationell zu wählen. Die hierbei ausgearbeitete Methodik beabsichtigen wir beim weiteren Studium der Kinetik und des Mechanismus dieser Reaktion anzuwenden. Dazu ist es vorteilhaft die Leitfähigkeitsmethode anzuwenden, die sowohl die Messung des Reaktionsverlaufes auf der Kohle als auch die bequeme Beobachtung der Blindversuche in Abhängigkeit von der Temperatur vor jedem Versuch ermöglicht. Auch andere Arbeitsstellen widmen der Leitfähigkeitsmethode eine gewisse Aufmerksamkeit.³ Gleichzeitig haben wir auf Grund der gewonnenen Erkenntnisse eine Schnellmethode zur

* XXXIII: Literatur Punkt 1.

Sauerstoffbestimmung ausgearbeitet. Die Methode ist genau und gut reproduzierbar, wie Tabelle II und die gefundene Standard-Abweichung $s = \pm 0,11\%$ O₂ zeigen und übertrifft in dieser Hinsicht bisher bekannte Methoden

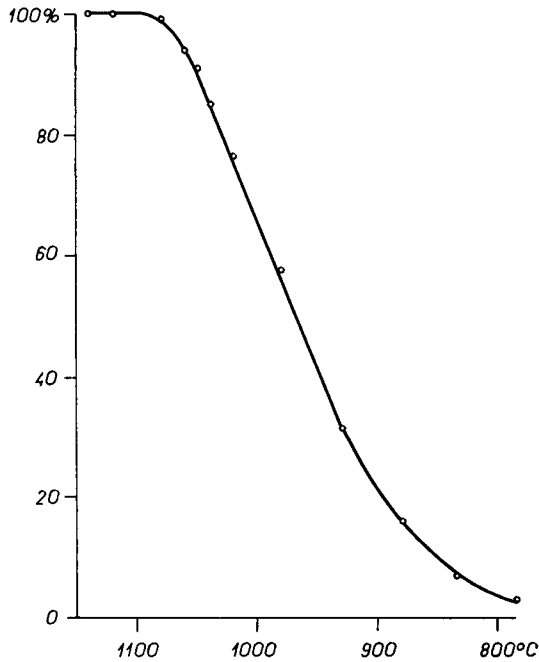


ABB. 1.—Abhängigkeit der Konversion des Kohlendioxydes von der Temperatur der Kohle.

TABELLE II

Substanz	Formel (Mol. Gewicht)	Sauerstoff	
		berechnet, %	gefunden, %
Aethoxynaphthalen	C ₁₂ H ₁₂ O (172,22)	9,29	9,30; 9,28; 9,11
Dimethylterephthalat	C ₁₀ H ₁₀ O ₄ (194,18)	32,96	33,22
Benzoessäure	C ₇ H ₆ O ₂ (122,12)	26,20	26,21; 26,18; 26,20
Salicylsäure	C ₇ H ₆ O ₃ (138,12)	34,75	34,77; 34,72; 34,78

EXPERIMENTELLER TEIL

Verwendete Substanzen

Oxydationskatalysator, Co₃O₄.⁴

Frisch reduziertes Kupfer aus CuO zum Reinigen des Stickstoffs.

Natronasbest und Magnesiumperchlorat zum Auffangen von CO₂ resp. H₂O.

Acetylenruss P 1250, gereinigt durch Glühen im Quarzrohr und Auslaugen mit verdünnter HCl⁵.

CuO für die Oxydation von CO.

0,03N NaOH im Absorptions—Leitfähigkeitsgefäß.

Die Apparatur

Stickstoff als Trägergas (10 ml/Min) wird über Co_3O_4 (3 im Abb. 2), das auf 700°C erhitzt wurde, geleitet und weiter über eine Schicht Kupfer (4) von 35 cm Länge (550°C), Natronasbest (5) und Anhydron (6) in ein Verbrennungsrohr aus Quarz geführt (9). Bei der Sauerstoffbestimmung von organischen Substanzen wurde die Umkehrspülung vorgenommen (8). Bei Messung der Konversionsgrades wird das gasförmige CO_2 mit Hilfe einer speziellen Pipette mit Quecksilbersverschluss in das des Verbrennungsquarzrohr dosiert (zwischen 7 und 9). Der Kohlenstoffkatalysator wird im

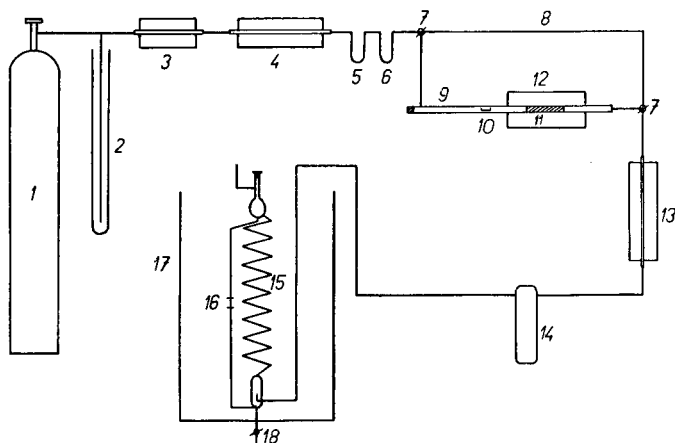


ABB. 2.—Schema der Apparatur zur Sauerstoffbestimmung.

1 Stahlflasche mit Stickstoff; 2 Flüssigkeitsausgleicher mit Öl gefüllt; 3 Co_3O_4 im Quarzrohr im elektr. Ofen (700°C); 4 ca 200 g Cu; 5 Natronasbest; 6 Anhydron; 7 Dreiweghähne; 8 Rückflussstrom des Trägergases; 9 Quarzrohr, Durchmesser 9 mm, Länge 50 cm; 10 Platinschiffchen mit Probe; 11 Zwei 5 cm lange Schichten von Kohle; 12 Elektrischer Ofen für 1150°C ; 13 CuO im elektr. Ofen; 14 Flüssigkeitsdurchflussmesser; 15 Absorptions—Leitfähigkeitszelle; 16 Pt—Elektroden; 17 Wasser—Temperierbad mit Ultrathermostat bei 25°C gehalten; 18 Ausflusshahn.

Verbrennungsrohr in zwei Schichten zu je 5 cm (11), die von einander durch Quarzwatte getrennt sind, untergebracht. Der Katalysator wird mit einem elektrischen Öfchen (12) eigener Konstruktion auf 1120°C , bei der Messung der Konversion von CO_2 auf $800\text{--}1140^\circ\text{C}$ erhitzt. Durch Stromstabilisierung wurde eine Temperaturkonstanz von $\pm 5^\circ\text{C}$ erzielt. Bei Messung der Konversion von CO_2 wird vor das Öfchen mit CuO (13) noch ein Röhrchen mit Natronasbest zum Abfangen des nicht umgesetzten CO_2 eingelegt.

Das Messverfahren

In den Stickstoffstrom (10 ml/Min.) wird das gasförmige CO_2 aus der Dosierpipette mit ca. 2,5 ml Inhalt (760 mm Hg, 0°C) im Laufe von $4\text{--}4\frac{1}{2}$ Min. zugeführt und der Konversionsverlauf gemessen.

Bei der Sauerstoffbestimmung in organischen Substanzen werden unter Umkehrspülung 5–20 mg Substanz im Platinschiffchen in das Verbrennungsrohr eingeführt und mit einem Gasbrenner mit der in der Mikroelementaranalyse üblichen Geschwindigkeit (3–10 Min.) verbrannt. Die Leitfähigkeitsänderung der NaOH—Lösung nach Absorption des entwickelten CO_2 ist bei Konzentrationen von 1,0–3,5 mg O_2 direkt proportional der Sauerstoffmenge in der Probe.

Zusammenfassung—Auf der Apparatur zur Sauerstoffbestimmung mit konduktometrischem Endteil, die mit der Quecksilberpipette ausgestattet ist, wurde die Konversion von CO_2 auf der Kohle in Abhängigkeit von der Temperatur im Durchflusssystem gemessen.

Summary—In the determination of oxygen in organic compounds, using an apparatus with a conductometric finish, the relationship between the temperature and the percentage conversion of oxygen to carbon dioxide has been examined.

Résumé—On a étudié le rapport entre la température et le pourcentage de conversion de l'oxygène en anhydride carbonique dans le dosage de l'oxygène organique, utilisant un mode opératoire s'achevant par conductimétrie.

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Titration of weak acids with tetramethylguanidine as solvent

(Received 29 October 1962. Accepted 24 February 1963)

INTRODUCTION

THE use of 1,1,3,3-tetramethylguanidine as a solvent for the titration of weak acids has recently been suggested.¹ This preliminary work indicated that weak acids titrated gave satisfactory potential inflections in the region of the equivalence point. A glass calomel electrode system was used for the potentiometric detection of the end-point in the earlier investigation.

A study of reference electrodes, of visual indicators, and of the effect of potassium ion on the titration properties was undertaken in this new work.

EXPERIMENTAL

Reagents

Tetramethylguanidine (TMG): Obtained from the American Cyanamid Company and used without further purification. Its blank was 0.40–0.50 ml for 25 ml of TMG, depending upon the extent of exposure of the solvent to carbon dioxide. Used solvent was stored over Ascarite and distilled from Ascarite for further use. (Redistilled solvent had a blank of 0.10 ml for 25 ml of solvent.) TMG boiled at 160–161° at a barometric pressure of 738 mm.

Hexadecyltrimethylammonium hydroxide in isopropyl alcohol: Prepared by the potassium hydroxide method² and used as titrant. The potassium content of titrant prepared by this method may be relatively high (100–200 ppm).³ Therefore, the titrant was passed through a column of Dowex 50 (20–30 mesh) ion-exchange resin. The resulting solution was standardised potentiometrically against benzoic acid with TMG as the solvent (concentration of titrant was 0.1M).

Benzoic acid was Fisher reagent grade. Most of the phenols were Eastman white label; phenol was Allied Chemical reagent grade. All were used without further purification.

Indicators used were azo violet (0.1% in benzene), *o*-nitroaniline (0.15% in benzene) and alizarin yellow (0.1% in ethanol).

Apparatus

Potentiometric titrations were performed with a Beckman "Zeromatic" pH meter. A Beckman general purpose glass electrode No. 4990-80 was used for all titrations. A number of different reference electrodes were investigated. The silver-silver halide references were prepared by the procedure of Meites and Thomas⁴. The titration cell was similar to that used in the previous study.¹ A magnetic stirrer was used for all titrations.

Procedure

A sample containing 1 meq of acid was weighed into a 180-ml Berzelius beaker. Depending on the volume of titrant to be used and on the solubility of the acid in TMG, 25–50 ml of TMG were delivered into the titration cell. In all cases 50 ml/meq of acid were sufficient to dissolve the acid. Two or three drops of indicator were added. The system was de-aerated with nitrogen, and an

atmosphere of nitrogen maintained throughout the titration to prevent the absorption of carbon dioxide. The solvent blank was determined for each series of titrations.

RESULTS AND DISCUSSION

Effect of potassium

Recent work by Harlow³ indicated the importance of the exclusion of small amounts of potassium ion in non-aqueous titrations involving the glass electrode. Using pyridine as solvent, this worker found distortion of titration curves and poor precision when potassium ion was present at concentrations greater than 0.005M. Similar effects (Table I and Fig. 1) were noted when small amounts

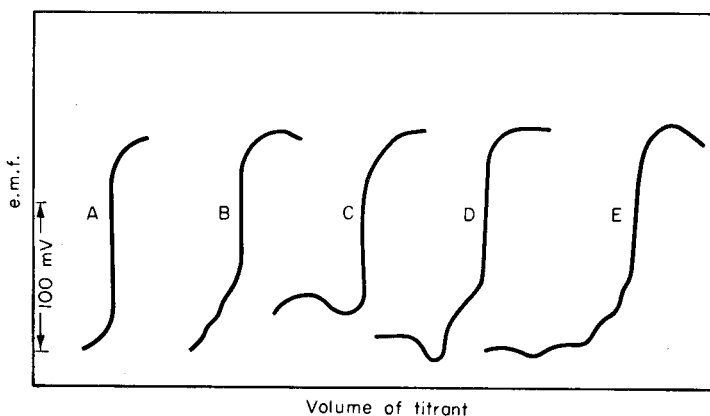


FIG. 1.—Effect of potassium ion on titration of benzoic acid:

- (A) no K^+ , (C) 0.0048M K^+ ,
 (B) 0.0029M K^+ , (D) 0.0055M K^+ ,
 (E) 0.01M K^+ .

TABLE I.—EFFECT OF POTASSIUM ION ON THE TITRATION OF BENZOIC ACID

Concentration of K^+ , M	Recovery of benzoic acid, %
Negligible	100.1
0.0029	102.3
0.0047	105
0.0055	106.7
0.01	105.7

of potassium ion were introduced into the titration system with TMG as the solvent. The high recovery values are consistent with Harlow's belief that the tip of the glass electrode is "titrated" with the potassium ions present. The presence of small amounts of potassium also resulted in large irreproducibility of the initial potential of the titration systems.

Electrodes

To eliminate the possibility of potassium ion leaking from the fibre-type calomel electrode, various other reference electrodes were tried. The results of this study are shown in Table II and indicate advantages of the silver-silver bromide reference electrode containing tetramethylammonium bromide. This electrode did not introduce potassium ion, reached a stable potential in a very short time, and gave a large end-point inflection. Initial potentials were reproducible within 25 mV and a flat S-shaped curve, as shown in Fig. 2, was observed for all titrations using the electrode. Over a 3-week period the potential of this electrode remained quite stable.

Antimony electrodes of the type described by Bishop and Short⁵ were employed for several titrations. Because small inflections, of the order of magnitude of 35 mV, were observed, regardless of the reference system, use of this indicator system was discontinued.

TABLE II.—TITRATION OF BENZOIC ACID IN TMG WITH HEXADECYLTRIMETHYLAMMONIUM HYDROXIDE USING VARIOUS REFERENCE ELECTRODES

Reference electrode	Time for stable potential, min	Total emf change, mV	Recovery of benzoic acid, %
S.C.E. fibre-type with aqueous KCl	3	140	101.4 ± 0.66
S.C.E. with KCl saturated in methanol	2	130	99.6 ± 0.78
S.C.E. with (CH ₃) ₄ NBr instead of KCl	5	150	103.5 ^a
Ag/AgCl with agar containing KCl	<1	155	100.6 ± 0.33
Ag/AgBr agar containing (CH ₃) ₄ NBr	<1	150	100.4 ± 0.45
Silver wire	<1	150 ^b	99.3

^a Average of only 2 results.

^b Silver appears to be attacked by the solvent during the titration.

TABLE III.—DETERMINATION OF PHENOLS USING TMG AS SOLVENT

Compound	Visual recovery, %	Potentiometric recovery, %	Recovery by bromination, %
Phenol	98.6	98.1	99.0
<i>p</i> -Bromophenol	101.2	101.4	101.1
2,4-Dibromophenol	98.9	98.5	99.0
Salicylic acid	99.3	99.1	98.8

Each percentage is the average of at least 3 determinations.

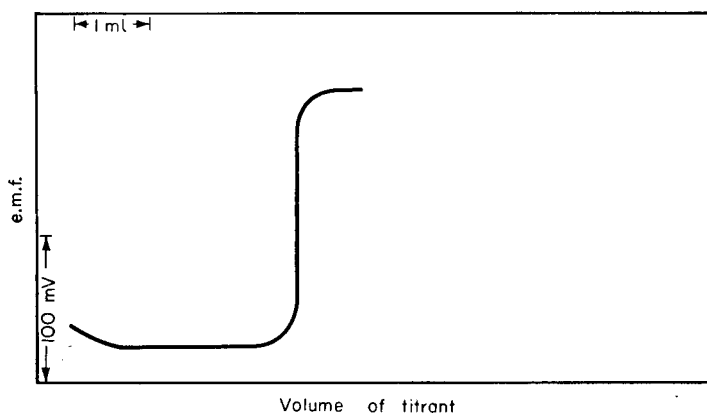


FIG. 2.—Titration of benzoic acid with a glass-silver/silver bromide couple.

Indicators

Figs. 3 and 4 show the colour changes which occur in the titration of benzoic acid with alizarin yellow (orange to blue colour change) and azo violet (red to pure blue colour change) as indicators. Visual end-points of both of these indicators agreed with potentiometric values to 0.2%. *o*-Nitroaniline also changed in the region of the equivalence point, but gave values approximately 1% low. Thymol blue, phenolphthalein and *o*-cresol phthalein did not give a satisfactory colour change at the equivalence point.

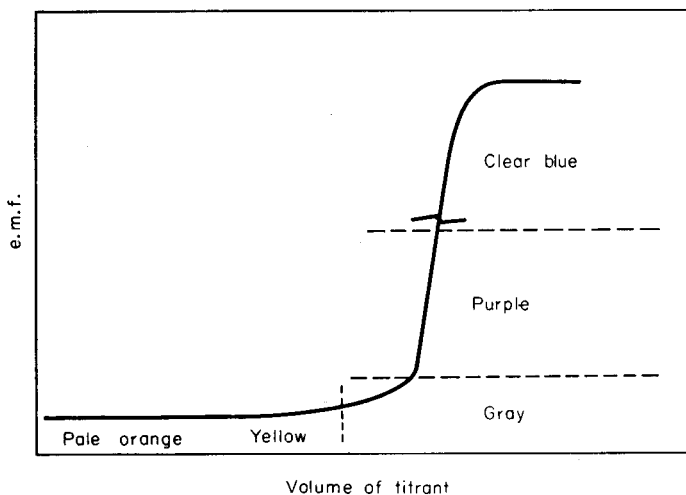


FIG. 3.—Indicator action of alizarin yellow in TMG.

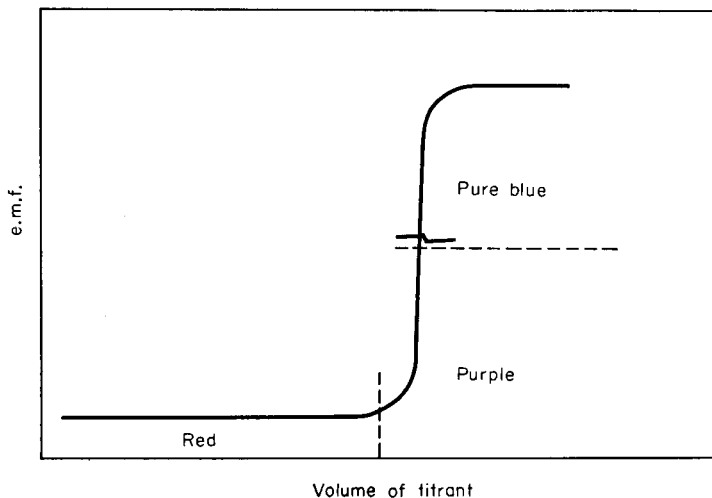


FIG. 4.—Indicator action of azo violet in TMG.

These indicators were also used for phenols, and the results are summarised in Table III. Percentage recoveries of these phenols were in good agreement with those obtained by bromination procedures.

Analysis of acid mixtures

Differentiation of acid mixtures with TMG as solvent was attempted, using such mixtures as perchloric and acetic, hydrochloric and benzoic, or 2,4-dibromophenol and acetic. In every case, the total acid equivalent was obtained but no differentiation appeared. Also, only one inflection was observed for salicylic acid. These facts indicate that this solvent exerts a strong leveling effect on acids.

Acknowledgment—The authors thank the National Science Foundation for support of Margaret Lautenschleger's work in the Undergraduate Research Participation Programme.

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Summary—Indicators and electrode systems for the titration of weak acids in 1,1,3,3-tetramethylguanidine as solvent have been investigated. A glass electrode coupled with a silver-silver bromide reference is found to give the most reliable results. Alizarin yellow and azo violet give results in agreement with potentiometric end-point values. A large potassium ion effect is observed in this solvent. Attempts to differentiate several pairs of acids were unsuccessful, because the solvent showed a strong leveling effect.

Zusammenfassung—Die Indikatoren und Elektrodensysteme zur Titration schwacher Säuren in 1,1,3,3-Tetramethylguanidin (TMG) werden beschrieben. Die Glaselektrode in Verbindung mit einem Silber-Silberbromid-Standard wurde als zuverlässigst gefunden. Alizarin gelb und Azoviolett geben Resultate, die mit den nach der Glaselektrodenmethode erhaltenen übereinstimmen. Versuche verschiedene Paare von Säuren zu differenzieren verliefen erfolglos, da das Lösungsmittel einen zu starken Ausgleicheffekt zeigt.

Résumé—On décrit des indicateurs et des divers systèmes d'électrodes utilisés pour le dosage des acides faibles dans le 1,1,3,3-tétraméthylguanidine (T.M.G.). L'électrode de verre couplée avec une électrode de référence Ag-bromure d'Ag donne les résultats les plus satisfaisants. L'effet d'ion potassium se fait sentir dans ce solvant. Le jaune d'alizarine et certains azoïques donnent des résultats en accord avec les valeurs obtenues en potentiométrie. Des essais pour séparer plusieurs couples d'acides n'ont pas conduit à des résultats satisfaisants en raison de la trop grande action du solvant.

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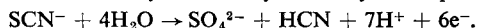
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Electrolytic generation of sulphate for precipitation studies

(Received 4 January 1963. Accepted 18 February 1963)

THE chemical generation of precipitant *in situ* or precipitation from homogeneous solution (PFHS) is widely used in precipitation studies¹ because it permits control of the rate of precipitation, and because it avoids the gross concentration inhomogeneities associated with the use of direct mixing procedures. Electrolytic generation of precipitant should also prove of value in precipitation studies because it makes possible quite precise control of the rate of formation of precipitant (and thus of the rate of precipitation), over a wide range of experimental conditions. Electrolytic generation does not correspond to PFHS, in that the precipitant is formed only at the electrode surface rather than throughout the solution; however, the resulting concentration inhomogeneity can be minimised by using adequate stirring and low current densities.

Nicholson² has discussed the electrolysis of thiocyanate to yield sulphate, by the reaction



This method of generating sulphate has now been further investigated, with the intention of applying it to studies of nucleation and coprecipitation of insoluble sulphates.

EXPERIMENTAL

Apparatus

Coulometric power supply: Sargent constant current coulometric supply (E. H. SARGENT, Chicago, U.S.A.) This instrument reads directly in microequivalents and is calibrated to 0.1%.

Cell: Cylindrical platinum gauze anode, 52 mesh, 120 cm² total surface; platinum wire cathode, isolated from the bulk solution by a glass frit.

Reagents

Reagent grade, used without further purification.

Procedure

Prior to each run the gauze anode was cleaned by soaking in a basic EDTA solution. It was also found necessary to clean the anode electrochemically, by placing it in a dilute solution of perchloric acid and electrolytically depositing hydrogen on it for about 5 min. The electrode was then rinsed, dried and placed in the test solution.

The test solutions were 0.01*F* in barium perchlorate and 0.05*F* in sodium thiocyanate; the required pH was obtained by adding perchloric acid, sodium hydrogen diglycollate, sodium acetate-acetic acid or pyridine-pyridinium hydrochloride. A seed suspension of aged barium sulphate precipitate was added when required. Exactly 200 ml of a test solution were pipetted into the cell and the circuit was closed. Magnetic stirring was used.

At various times 1.00-ml aliquots of the solution were taken and analysed for barium by EDTA titration with metalphthalein indicator.³ The observed decrease in barium concentration was compared to the power supply reading to calculate the current efficiency, here defined as moles of Ba²⁺ precipitated/ $\frac{1}{2} \times$ Faradays.

RESULTS AND DISCUSSION

In preliminary experiments it was observed that the rate of precipitation of barium sulphate was initially zero, then reached a value much higher than that corresponding to the current, and finally approached the value corresponding to the current. This behaviour is a result of the precipitation reaction rather than the electrode reaction. Precipitation does not begin until the supersaturation is sufficient to cause nucleation, but once sufficient nuclei are formed precipitation is quite rapid until the supersaturation is essentially relieved.⁴ To avoid complications from this source in the present study, the solutions were seeded with a suspension of barium sulphate.

As shown in Fig. 1, 100% current efficiency was obtained over a wide range of pH, at currents up to about 50 mA.

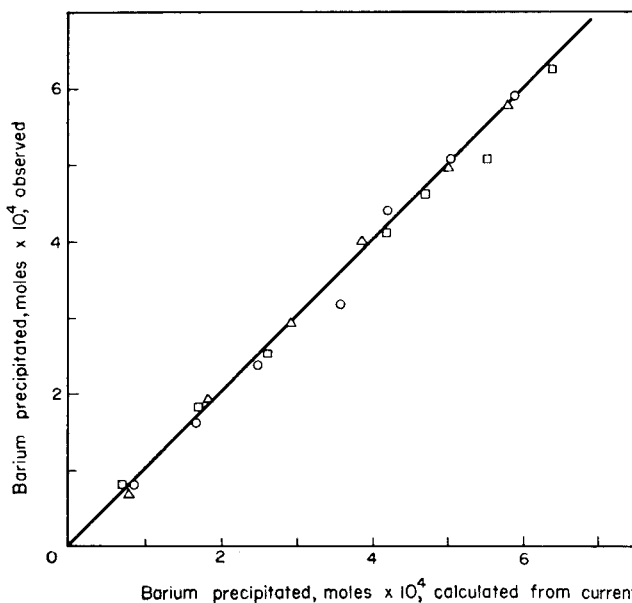


FIG. 1.—Current efficiency in oxidation of thiocyanate to sulphate (solution is 0.05*F* in thiocyanate and 0.01*F* in barium; current density is 0.4 mA/cm²; temperature is 25°):

- Solid line—theoretical for 100% current efficiency,
- pH 1.0 (perchloric acid-sodium perchlorate),
- △—pH 3.0 (formic acid-sodium formate),
- pH 5.2 (pyridine-pyridinium hydrochloride).

The potential at the anode increased during the course of each experiment. At pH 5.2, for example, the anode potential was initially 0.52 V *vs.* SCE, rose to 0.70 in 2 hr, and reached 1.1 V after 1 hr further. This effect is caused by the accumulation of solid barium sulphate on the anode surface, raising the current density. Removal of the precipitate from the electrode results in a return of the anodic potential to 0.52 V.

The extent to which the formation of sulphate ion at the electrode surface (rather than throughout the solution) affects the nucleation process was examined by determining the "critical supersaturation" at which precipitation began. Critical supersaturation ratios of around 24, which are comparable to, or slightly higher than, those obtained by LaMer and Dinegar⁵ and Collins and Leineweber⁶ were observed, using solutions which had not been purified. When the solutions were purified by membrane filtration, critical supersaturation ratios in the range of 40 to 50 were observed. It appears, therefore, that the concentration inhomogeneity resulting from the localised formation of sulphate has a negligible effect on the nucleation process.

Sulphate generated electrolytically by this method is probably of no value in a conventional coulometric titration because of the slowness of the precipitation. The technique is quite satisfactory for nucleation studies, however, and is now being so employed.

Acknowledgements—Some of the experimental work was performed by P. L. Donnelly. Support for the project was furnished by the National Science Foundation under G-22610.

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Summary—Electrolytic generation of sulphate from thiocyanate is found to proceed with 100% current efficiency over a wide range of pH in acid solution. Application of this coulometric technique to precipitation studies is discussed.

Zusammenfassung—Die elektrolytische Bildung von Sulfat aus Rhodanid verläuft in einem großen pH-Bereich in saurer Lösung mit 100-prozentiger Stromausbeute. Die Anwendung dieser coulometrischen Methode auf Fällungsreaktionen wird diskutiert.

Résumé—La production électrolytique du sulfate à partir du thiocyanate s'effectue à 100% dans les solutions acides et dans un large domaine de pH. On présente une discussion des possibilités d'application de cette technique coulométrique aux études de précipitation.

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* Participant in the National Science Foundation Undergraduate Research Participation Programme (G-21893), Summer, 1962.

Spectrophotometric determination of decaborane *via* its β -naphthoquinoline complex

(Received 4 January 1963. Accepted 12 February 1963)

INTRODUCTION

During the development of the coulometric borane monitor reported by Braman *et al.*,¹ the necessity arose for a sensitive method to detect microgram quantities of decaborane. Microgram quantities of boron hydrides can readily be determined by colorimetric procedures after oxidation of

the hydrides to boric acid. They can also be determined by micro-titration with iodine solutions.² These methods are not, however, sufficiently sensitive. The colorimetric method determines total boron, while the micro-titration method does not differentiate between decaborane and other boron hydrides or other reducing agents. A colorimetric method reported by Hill *et al.*³ utilising the *N,N*-diethylnicotinamide complex is likewise not sufficiently sensitive.

The quinoline complex method reported by Hill *et al.*⁴ was considered experimentally. Solutions of the quinoline-decaborane complex were found, however, to exhibit continuous changes in optical density. These changes occurred despite revision of the recommended procedure, such as heating the colour-developing solutions to improve complex formation. Because of the instability of solutions of standard quinoline-decaborane complex with time, it was decided to investigate other amine-type complexing agents to determine whether more stable complexes could be found. Pyridine and β -naphthoquinoline, each of which forms an intense red complex with decaborane and its derivatives in benzene and similar solvents, were subsequently investigated. Pyridine was found to have the disadvantages of quinoline. Preliminary experiments with β -naphthoquinoline (BNQ), however, indicated that this complexing agent forms more colour-stable complexes with decaborane than other amines.

EXPERIMENTAL

Xylene was chosen as the solvent because of its low volatility. Solutions of BNQ-decaborane complex in xylene exhibited an absorption maximum at 490 m μ , and this wavelength was used for the remainder of the experiments.

In a series of experiments, different quantities of BNQ were used with the same amount of decaborane, approximately 11 μ g/ml. The optimum concentration of BNQ was 2.5%. The results of these experiments are shown in Table I. Samples were treated by heating in a water bath for 5 min.

TABLE I.—DETERMINATION OF OPTIMUM BNQ CONCENTRATION

BNQ, %	Absorbancy at 490 m μ
0.5	0.48
1.0	0.522
2.0	0.528
2.5	0.525
3.0	0.530
4.0	0.510
5.0	0.491

TABLE II.—STABILITY OF BNQ COMPLEX IN XYLENE

Boron, μ g	Absorbancy at 490 m μ			
	Immediate	After 18 hr	After 90 hr	After 25 days
20	1.05	1.05	0.79 Red ppt. formed	ppt. formed
10	0.528	0.530	0.528	0.487
5	0.267	0.273	0.270	0.254
2	0.106	0.107	0.107	0.085

* Multiply by 1.18 to obtain μ g of decaborane.

The method of colour development was investigated. Mixtures of BNQ in xylene were added to decaborane and permitted to stand at room temperature. They soon started to form the characteristic red-coloured complex, but the absorbancy changed over a 2-hr period. A change in absorbancy also occurred upon standing overnight. However, when the samples were heated in a boiling water bath for a few min, comparatively constant absorbancy readings were obtained. The optimum heating time was 5 min. The complex was stable for at least 90 hr but for less than 25 days, as indicated by the data in Table II. The sensitivity of the method is estimated to be ± 0.1 μ g of decaborane/ml.

Procedure

Dissolve the sample in xylene. The sample should contain no more than 20 μg of decaborane/ml of final solution. The complex is developed by adding a sufficient amount of 5% BNQ in xylene to give a concentration of 2.5% BNQ in xylene. The procedure is the same for ethyl- and diethyl-decaborane. Standards should be prepared from the pure compounds being determined. No solvents reactive with boron hydrides or coloured materials should be present.

Absorption spectra of decaborane and its alkyl derivatives complexed with BNQ

In order to find the absorption peak maxima and the approximate extinction coefficients of the BNQ complexes with decaborane, ethyldecaborane and diethyldecaborane, their absorption spectra were determined. Samples of the pure alkyl decaborane compounds were obtained by preparative-scale gas chromatography of alkylated decaborane mixtures. The sample of decaborane was purified by recrystallisation from a laboratory sample. The spectra were obtained on a Beckman DK spectrophotometer; 1-cm quartz cells were used.

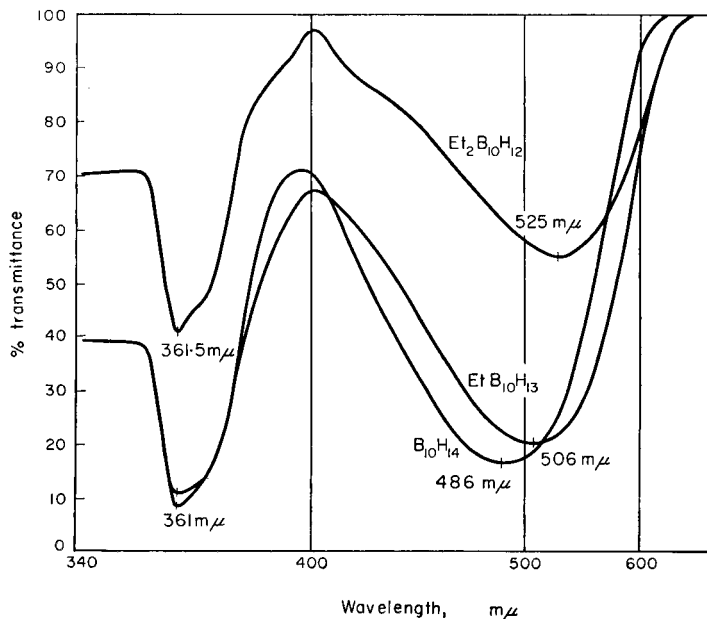


FIG. 1

The absorption spectra are shown in Fig. 1. The addition of ethyl groups to the decaborane central unit produced a shift to the red for the absorption peak in the visible region. The characteristic decaborane peak at 361 mμ in the ultraviolet was apparently not affected. The ultraviolet peak of uncomplexed decaborane occurs at 374 mμ and is a few more mμ towards the red for uncomplexed ethyldecaborane and diethyldecaborane. This may indicate that the BNQ complex shifts the usual decaborane peak from 374 mμ to near 500 mμ and that the 361 mμ peak may be some other absorption peak shifted to 361 mμ from an even shorter wavelength.

The absorbancy indices for the complexes, calculated from the absorption spectra, are given in Table III.

TABLE III.—APPROXIMATE ABSORBANCY INDICES FOR BNQ COMPLEXES OF DECABORANE, ETHYLDECABORANE AND DIETHYLDECABORANE

Complex	Borane, $\text{moles} \times 10^{-4}$	Absorbancy index, m			
		Visible region		Ultraviolet region	
BNQ-decaborane	1.44	5360	486	6700	361
BNQ-ethyldecaborane	1.75	3970	506	6100	361
BNQ-diethyldecaborane	1.74	1500	525	2250	361

DISCUSSION

A comparatively rapid, sensitive ($\pm 0.1 \mu\text{g}$ of decaborane/ml) method has been developed for quantitative determination of decaborane and its derivatives. The absorption spectra of ethyl- and diethyldecaborane were found to be similar to that of decaborane. The derivatives can, therefore, be determined by the method, but they will also constitute interferences because the separation of the absorption maxima is insufficient.

Pentaborane and diborane did not interfere in the formation of coloured complexes, and it is assumed that other lower boron hydrides will not interfere. The method is therefore comparatively specific for uncomplexed decaborane and its derivatives.

Polymeric boron hydrides form coloured complexes with amines and will interfere if present. Boron oxide, boric acid and borate esters do not interfere, but protonic solvents interfere by hydrolysis reaction with the decaborane or with the BNQ-decaborane complex.

The BNQ method worked well for the determination of decaborane in air at concentrations of 0.1 to 0.3 ppm.

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Summary—An improved spectrophotometric method has been developed for the determination of decaborane and its alkyl derivatives. Based upon the β -naphthoquinoline complex of these boranes in xylene, it has a sensitivity of $0.1 \mu\text{g}$ of decaborane/ml.

Zusammenfassung—Eine verbesserte spektralphotometrische Methode für die Bestimmung von Dekaboran und seiner Alkylderivate wurde entwickelt. Sie beruht auf der Komplexbildung dieser Borane mit β -Naphthochinolin in Xylol und gestattet, $0,3 \mu\text{g}$ Dekaboran im Milliliter zu erfassen.

Résumé—Une nouvelle méthode spectrophotométrique a été développée pour le dosage du décarbore et de ses dérivés alcoylés. Cette méthode est basée sur la formation d'un complexe de ces boranes avec la β -naphthoquinoléine dans le xylène, et la sensibilité est de $0,1 \mu\text{g}$ de décarbore/ml.

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Analysis of aqueous mixtures of ϵ -aminocaproic acid and α, ϵ -diaminocaproic acid using ninhydrin

(Received 31 January 1963. Accepted 3 March 1963)

THE analysis of solutions containing ϵ -aminocaproic acid and α, ϵ -diaminocaproic acid (lysine) has previously required a preliminary separation of these components.

Ninhydrin with ϵ -aminocaproic acid and lysine gives, at a pH above 4.7, a characteristic violet colour, the optimum pH of the reaction of each amino acid being different. Moreover, the behaviour of both amino acids is quite different if a ninhydrin reaction at pH 1.0 is applied. ϵ -Aminocaproic acid does not produce any coloured product of reaction at pH 1.0, but α, ϵ -diaminocaproic acid, according to Van Slyke,¹ Chinard,² Work³ and Reifer and Buraczewska,⁴ reacts with ninhydrin under such conditions and it can be determined quantitatively.

On the basis of these data a relatively simple and easy method of quantitative colorimetric analysis of an aqueous mixture of ϵ -aminocaproic acid and lysine has been elaborated.

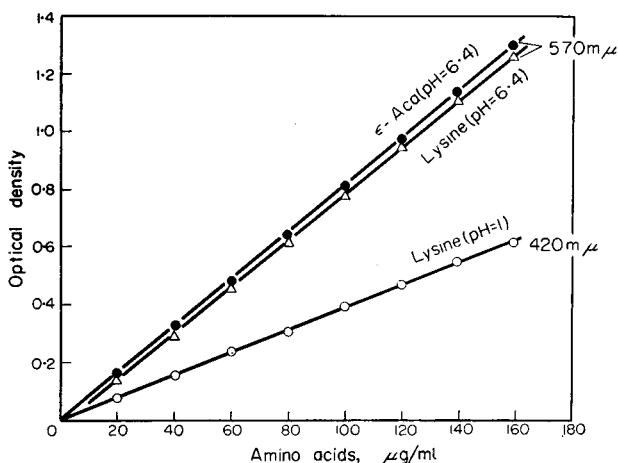


FIG. 2.—Applicability of Beer's law

Standard curve for lysine solutions at pH 1.0³

One ml of glacial acid and 1 ml of 2.5% ninhydrin reagent were added to 1 ml of α, ϵ -diaminocaproic acid solution. The mixture was heated in a boiling water bath for 1 hr, cooled and made up to 5 ml with glacial acetic acid. The optical density was determined in relation to a control sample treated in a similar way, in a 1-cm cuvette at 420 m μ . The colour lasted for over 1 hr and Beer's law was obeyed for concentrations of 10 to 200 μg of lysine (Fig. 2).

From the results obtained above, the following method of analysing an aqueous mixture of ϵ -aminocaproic acid and lysine was elaborated:

(i) Determine the optical density of the mixture at pH 6.4 (as above for ϵ -aminocaproic acid solutions).

(ii) Determine the optical density of the mixture at pH 1.0 (as above for lysine solutions).

(iii) Evaluate the lysine content of the mixture from the standard curve for lysine at pH 1.0 (Fig. 2).

(iv) Read off the optical density appropriate for that concentration of lysine found in (iii) from the lysine standard curve for pH 6.4.

(v) Subtract the optical density found in (iv) for the lysine content at pH 6.4 from the optical density obtained for the mixture at pH 6.4, and from the resulting optical density read off the concentration of ϵ -aminocaproic acid from its standard curve at pH 6.4.

Table I shows the results of several determinations.

TABLE I.—DETERMINATION OF ϵ -AMINOCAPROIC ACID (ϵ -ACA) AND LYSINE IN AQUEOUS SOLUTIONS.

Amino acid	Taken, $\mu\text{g/ml}$	E_{lys} (pH 1)	E_{lys} (pH 6.4)	E_{mixt} (pH 6.4)	$E_{\epsilon\text{ACA}}$ (pH 6.4)	Found, $\mu\text{g/ml}$	Error, %
Lysine	15					15	± 0.0
ϵ -ACA	50	0.06	0.095	0.52	0.425	52	+4.0
Lysine	40					40	± 0.0
ϵ -ACA	60	0.16	0.29	0.78	0.49	60	± 0.0
Lysine	65					66	+1.5
ϵ -ACA	67	0.26	0.505	1.08	0.575	70	+4.3
Lysine	30					31.5	+5.0
ϵ -ACA	20	0.125	0.225	0.38	0.155	19	-5.0
Lysine	80					80	± 0.0
ϵ -ACA	40	0.31	0.615	0.96	0.345	42	+5.0
Lysine	150					151	± 0.7
ϵ -ACA	50	0.69	1.19	1.60	0.41	50	± 0.0

RESULTS AND DISCUSSION

Two values of pH, 1.0 and 6.4, were used for the determinations. Lysine was determined at pH 1.0, and the optical density of the sum of the amino acids was determined at pH 6.4. The maximum absorption of lysine appeared at pH 5.7, but ϵ -aminocaproic acid showed its maximum absorption at pH 6.4, when the solution was violet in colour. At this pH the colour of the lysine solution was nearest to that of the colour of the ϵ -aminocaproic acid solution. The choice of pH 6.4 for the determinations made it possible to avoid serious errors in measurement resulting from differences in absorption. At pH 5.7 the colour of the two amino acids differed considerably.

By means of the ninhydrin method ϵ -aminocaproic acid can be determined in the range of 5 to 250 μg . Lysine may be determined at pH 1.0 in the range of 10 to 200 μg (according to Chinard² from 15 to 70 μg). However, in our method the concentration of both amino acids was limited to 160 μg and the mixture did not contain more than 200 μg altogether.

The method is simple and it may be used for serial determinations of aqueous mixtures of ϵ -aminocaproic acid and lysine, as well as for determining caprolactam in the presence of both amino acids.⁶ The error is $\pm 5\%$.

Acknowledgement—The authors wish to thank Professor S. Niewiarowski for his interest in this work and helpful discussions.

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Summary—A simple method for the simultaneous determination of ϵ -aminocaproic acid and α,ϵ -diaminocaproic acid (lysine) in aqueous solution is based on the differential colorimetric reactions given with ninhydrin at pH 1 and pH 6.4.

Zusammenfassung—Es wurde eine einfache kolorimetrische Methode zur Bestimmung der ϵ -Aminocapronsäure und Lysin in Wasserlösungen ausgearbeitet. Die Bestimmung erfolgt durch Photometrierung des mit Ninhydrin unter bestimmten Bedingungen (pH 1.0 und 6.4) gebildeten Farbstoffs.

Résumé—Nous avons élaboré une simple technique quantitative de dosage de l'acide ϵ -aminocaproïque, en présence de lysine, en solutions aqueuses. Cette technique est basée sur la réaction colorimétrique avec ninhydrine que nous avons effectuée au même temps à pH 1.0 et pH 6.4.

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Destructive chlorination of organic compounds—I: General observations

(Received 5 February 1963. Accepted 18 February 1963)

IN 1867, Mitscherlich¹ described an original method for the analysis of organic substances which involved combustion in a stream of chlorine, using a contact layer of carbon, kept at approximately 700°–800°, in the combustion tube. The organic compound was chlorinated in such a way that only some carbon and exhaustively chlorinated hydrocarbons remained, the former where the substance was originally, the latter in the cold parts of the apparatus; all hydrogen was converted into hydrogen chloride, and all oxygen into carbon monoxide and dioxide. Using this method Mitscherlich determined hydrogen and oxygen in a series of organic and inorganic compounds.

This method for the determination of hydrogen and oxygen appears to merit further study. Potentially, the smooth conversion of hydrogen to hydrogen chloride might be one of the most sensitive and accurate means of determination of this element, because, as is known, titration of a strong acid with even so dilute a solution as 0.001*N* alkali still gives a very sharp end-point, and 1 ml of 0.001*N* alkali is equivalent to 1 μg of hydrogen. The conversion of oxygen to a mixture of carbon monoxide and dioxide is, of course, less promising. In this connection one should recall the importance of maintaining the carbon contact-layer within a certain temperature range in the Schütze and Unterzaucher oxygen determination, to ensure that all oxygen has been converted only to carbon monoxide. These facts were not known to Mitscherlich. Moreover, if suitable conditions can be found, the formation of phosgene from carbon monoxide and chlorine might be achieved; this formation, if quantitative, might lead to possible new ways of determining the oxygen. Determination of some other elements commonly found in organic compounds may also be possible. In consequence, the analytical use of the destructive chlorination of organic compounds has been studied in more detail. Preliminary results are reported here.

The first step was to elucidate the behaviour of the elements occurring more commonly in organic compounds during destructive chlorination, and in the absence of a catalyst. The apparatus (Fig. 1)

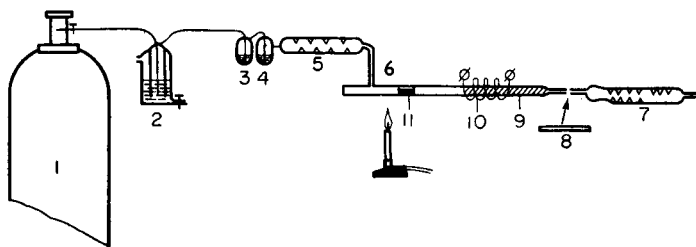


FIG. 1.—Apparatus.
 1—steel flask
 2—wash bottle and pressure regulator
 3, 4—bubble counters
 5—phosphorus pentoxide tube
 6—combustion tube
 7—absorber
 8—trap
 9—quartz wool layer
 10—electrical oven
 11—quartz boat

was a simple quartz combustion tube (6) 40 cm long, fitted with a side inlet tube. This tube was filled for the first quarter of its length with quartz wool (9), the second half of this (10) being heated to red heat. Chlorine taken from a steel cylinder (1) was washed with concentrated aqueous sodium chloride solution in a wash bottle (2), passed through two bubble counters (3, 4), and then dried in a tube containing phosphorus pentoxide (5), connected to the inlet of the combustion tube. An absorber (7), of the same type as that used by Unterzaucher,² wetted inside with concentrated sodium chloride solution, was connected to the constricted outlet of the combustion tube. In some experiments a 10-cm long glass tube (8) (as a trap) was placed between the absorber and the combustion tube. A flow-rate of about 10 ml of chlorine per min was normally used. After the experiment, chlorine was expelled from the disconnected absorber by a stream of air. The absorber was rinsed with water into a titration flask, and the solution was titrated with standard sodium hydroxide using bromocresol green-methyl red as indicator. The blank (25 min) usually amounted to about 0.1–0.2 ml of 0.04*N* NaOH, (equivalent to 4–8 μg of hydrogen). The test substance was placed in the combustion tube in a quartz boat (11). The “combustion” procedure was similar to that in the normal carbon and hydrogen determination.

BEHAVIOUR OF SOME ELEMENTS

Hydrogen

The hydrogen of water (test substance $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$) is converted to hydrogen chloride quantitatively only at a temperature of about 1000° or higher.

The hydrogen of organic compounds gives amounts of hydrogen chloride approaching the theoretical values (Table I). Many elements interfere, however, causing high results.

Nitrogen

If oxygen is also present, either in the nitrogenous compound, or in the stream of chlorine, some nitrogen oxides are formed, and are retained in the absorber, being oxidised by the chlorine to produce nitric acid.

TABLE I.—DETERMINATION OF HYDROGEN

Compound	Hydrogen, %					
	Calculated	Found				
Benzoic acid	4.95	5.09,	5.01,	5.03,	4.90,	4.92
Oxalic acid	4.79	4.67,	4.73,	4.67,	4.62,	4.92
Stearic acid	12.76	12.43,	13.10,	12.45,	13.00,	13.05

Sulphur

Sulphuric and hydrochloric acids were found in the absorber if either a compound containing sulphur or elemental sulphur was combusted. The same applied if dry potassium sulphate or barium sulphate was heated in a stream of chlorine, although the destruction, especially of the latter compound, was not quantitative.

If a cooled trap was placed before the absorber a condensate containing sulphur and chlorine was sometimes observed during the combustion of the sulphur-containing organic compound.

Bromine

Elemental bromine, or perhaps bromine chloride, was observed in the case of bromine-containing compounds; this dissolved temporarily in the absorber liquid, but escaped before the end of analysis. No interference with the hydrogen determination was noted.

Iodine

Iodine trichloride deposited quantitatively in a tube placed before the absorber if cooled with solid carbon dioxide. Under these conditions iodine did not interfere with the hydrogen determination.

Phosphorus

Phosphoric and hydrochloric acids were formed in the absorber during the combustion of a compound containing phosphorus. Even phosphorus pentoxide behaved at least partially in this way, if heated in a stream of chlorine.

In the combustion of elemental phosphorus, the pentachloride was formed; this could be retained in a cooled tube placed between the combustion and absorption tubes.

Carbon

According to the nature of the organic compound, a variable amount of carbon might remain in the boat after pyrolysis in the chlorine stream. Sometimes carbon deposits were observed in the hot part of the quartz wool; and tar condensates appeared in the colder part, which, in some cases (*e.g.*, benzoic acid) were found to consist mainly of hexachlorbenzene.

Oxygen

The determination of oxygen in the presence of other elements has not, as yet, been studied very thoroughly. In some cases high results for hydrogen determinations were obtained with compounds containing only carbon, hydrogen and oxygen, and even with compounds containing only carbon and hydrogen (*e.g.*, anthracene, naphthalene). Phosgene was found in the combustion gases in such cases. The necessary oxygen might have originated from impurities in the chlorine stream, if the substance itself did not contain oxygen. The high results were caused by the hydrolysis of a part of the phosgene passing through the absorber.

The study of the analytical use of destructive chlorination will be continued, investigating contact materials for the chlorination, further reactions, absorption systems for the reaction products, and further identification and determination of the reaction products. A detailed account of all experiments will be published later.

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Summary—Destructive chlorination at high temperature in the determination of some elements, particularly of hydrogen and oxygen, is discussed. Basic observations concerning the behaviour, in the course of the exhaustive chlorination, of some elements usually present in the organic compounds described.

Zusammenfassung—Der chlorierende Abbau bei hoher Temperatur zur Bestimmung einiger Elemente, besonders Wasserstoff und Sauerstoff, wurde diskutiert. Grundlegende Beobachtungen über das Verhalten einiger Elemente, die gewöhnlich in organischen Verbindungen vorkommen, beim chlorierenden Abbau wurden mitgeteilt.

Résumé—On présente une discussion sur la minéralisation à haute température utilisée dans la détermination de quelques éléments (hydrogène et oxygène en particulier). On décrit les observations fondamentales concernant le comportement de quelques éléments habituellement présents dans les composés organiques analysés par ce procédé de dégradation.

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NOTICES

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

AUSTRALIA

Tuesday–Friday 20–23 August 1963: Fourth Australian Spectroscopy Conference: Spectroscopy Committee of Australian Academy of Sciences: Australian National University, Canberra (see Talanta, 1962, 9, 1071).

DEUTSCHE DEMOKRATISCHE REPUBLIK

24. und 25. Oktober 1963—Merseburger Hochschultagung über **Moderne Methoden der analytischen Chemie**. (Die Einzelheiten sind in *Talanta*, 1963, 10, Juni iii zu finden.)

FRANCE

La 8^{ème} réunion de la **Commission Internationale de Terminologie "C.I.T."** du **Comité Internationale de la Détergence "C.I.D."** a eu lieu à Milan, les 28 et 29 Mars 1963, sur invitation du Comité Italien de la Détergence et sous la présidence de M. JACQUES COMBETTE (France).

Au cours de ces deux journées de travail, la Commission a adopté en seconde lecture, des définitions de termes généraux des agents de sufrace, et beaucoup d'autres ont été étudiées en première lecture. Selon la procédure adoptée par la Commission, les premiers de ces termes seront prochainement communiqués à l'I.S.O., pour servir de bases ultérieurement à des projets de recommandations internationales.

Par ailleurs, la Commission a longuement discuté de termes physicochimiques et a entendu des exposés qui pourront par la suite aboutir à des conceptions nouvelles dans ce domaine.

Enfin, la C.I.T. a adopté, en première lecture, un projet de classement simplifié des agents de surface, basé sur le système décimal et dérivé du classement scientifique précédemment établi.

En fin de séance, les membres de la Commission se sont mis d'accord sur des communications à présenter au 4^{ème} Congrès International de la Détergence, qui aura lieu à Bruxelles en Septembre 1964.

La **Commission Internationale d'Essais "C.I.E."** du **Comité International de la Détergence "C.I.D."** s'est réunie pour la 6^{ème} fois à Paris, les 8 et 9 Avril 1963, sous la présidence de M. de LAUNOIT (Belgique) et sur invitation du Comité Français de la Détergence. La Commission a été reçue par M. GLENARD, Président du Comité Français de la Détergence.

La C.I.E. décida que ses travaux étaient suffisamment avancés pour procéder à la rédaction de plusieurs projets de normes, en particulier sur la préparation de l'eau distillée, la préparation de eau dure, la stabilité des agents de surface en eau dure, etc.

Par ailleurs, elle constitua un groupe de travail pour étudier les méthodes d'essais relatives au lessivage (méthode des bandes-témoins). Elle confia le soin à certain de ses membres de publier des articles dans la presse technique relatifs à la masse volumique apparente des agents de surface en pâte et en poudre, et au point de trouble des éthers polyglycoliques.

Il fut décidé de procéder à des études expérimentales interlaboratoires sur des sujets tels que viscosité des agents de surface, pouvoir mouillant surcoton, indice de trouble des éthers polyglycoliques.

Enfin, la Commission mettra en route, au cours de l'année, des études préliminaires sur plusieurs sujets tels que stabilité des agents de surface en solution, coloration des agents de surface, tension d'adhésion, pouvoir détergent, etc.

SWITZERLAND

Tuesday 27 August–Wednesday 4 September 1963: Second World IFAC Congress on Automatic Control: Swiss Federation of Automatic Control: Basle (see Talanta, 1963, 10, June iii).

UNITED KINGDOM

Wednesday–Wednesday 10–17 July 1963: XIXth International Congress of Pure and Applied Chemistry: London.

The programme for the section devoted to **Analytical Chemistry** is as follows:

Plenary Lectures

Friday, 12th July, Morning

Variation of the half-wave potential of organic compounds with pH

P. J. ELVING

Monday, 15th July, Morning

Modern problems in the determination of trace elements in pure compounds.

I. P. ALIMARIN

Masking and promotion of reactions in quantitative analysis.

A. RINGBOM

Section on TRACE ANALYSIS

Monday, 15th July, Afternoon

Determination of traces of osmium in ruthenium sponge by neutron-activation analysis.

R. GIJBELS and J. HOSTE

Determination of very small quantities of tantalum in niobium by using activation by neutrons and gamma spectrometry.

F. DUGAIN and J. LAVERLOCHERE

Germanium, arsenic, antimony, copper, chromium, molybdenum, silver, indium, zinc and palladium content of sixty-seven iron meteorites, as determined by neutron-activation analysis.

A. A. SMALES and D. MAPPER

Determination of trace elements in natural materials by activation analysis.

W. D. EHMANN

Determination of rubidium and caesium in stony meteorites by neutron-activation analysis and by mass spectrometry.

A. A. SMALES, T. C. HUGHES, D. MAPPER, C. A. J. MCINNES and R. K. WEBSTER

Improvements in systematic analysis of high-purity metals by radioactivation.

PH. ALBERT, M. CUYPERS, N. DESCHAMPS, L. FOURNET and A. LESBATS

Neutron-charged particle reactions: the analysis of thin lithium and boron films.

H. L. FINSTON, Y. WELLWART and W. BISHOP

Neutron activation analysis of trace impurities in organic materials.

J. PAULY and F. GIRARDI

Determination of impurities in high-purity beryllium metal by thermal neutron activation and gamma activation.

C. A. BAKER

Tuesday, 16th July, Morning

Determination of small amounts of iron and chromium in sapphire and ruby for maser applications.

R. J. POWELL, P. M. C. PROFFITT
R. C. CHIRNSIDE

Concentration, separation and determination of microgram quantities of certain heavy metals.

D. B. ADAMS

Spectrophotometric determination of iron and uranium with troponoids.

Y. O. OKA, K. YAMAMOTO and M. UMEHARA

Spectrophotometric determination of micro-amounts of nitrogen with organic solvent extraction.

H. GOTÔ, M. NAMIKI and Y. KAKITA

Selective and highly-sensitive photometric determinations by means of boron-containing metal chelates.

F. UMLAND and D. THIERIG

Investigation of N,N,N',N'-tetramethyl-o-tolidene for the determination of small amounts of oxidants; photometric determination of gold.

N. JORDANOV and C. DAIEV

Liquid-liquid extraction of Cu(II), Zu(II) and Mu(II) by 1-(2-pyridylazo)-2-naphthol and 4-(2-phenylazo)1-naphthol.

D. BETTERIDGE, H. FREISER and Q. FERNANDO

Tuesday, 16th July, Afternoon

Mass spectrographic microanalysis of solids with a focussed laser beam.

R. E. HONIG and J. R. WOOLSTON

Surface ionization techniques in isotope analysis by mass spectroscopy.

A. H. TURNBULL

Combined use of mass spectrometry and gas chromatography as a method for analysing complex mixtures and the microscopic amounts of impurities they contain.

X-ray fluorescence analysis by the Filterscan technique.

State analysis of trace impurities by electron paramagnetic resonance and X-ray microanalyser.

Determination of trace amounts of gases in small volumes of steam by gas chromatography.

A membrane-equilibration procedure for overcoming interference in dissolved oxygen microanalysis.

An infrared spectroscopic determination of the oxygen-18 content of minute samples of benzophenone.

The application of the electrolytic hygrometer to the determination of small amounts of moisture and oxygen in tungsten powder.

A method for increasing the sensitivity, accuracy and specificity of kinetic methods of analysis.

V. L. TALROSE

H. J. DOTHE

S. FUJIWARA

J. E. STILL and J. H. KONRATH

E. C. POTTER and G. E. EVERITT

I. LAULICHT and S. PINCHAS

J. E. STILL and A. D. POOLE

K. B. YATSIMIRSKII

Wednesday, 17th July, Morning

Chelate formation of metals with sodium alizarin-3-sulphonate and the analytical applications of the chelates in trace determinations.

Chelometric determination of copper, cobalt and nickel with metal fluorechromic indicator; volumetric determination of traces of copper.

Determination of traces of carbon dioxide by gas-chromatography.

Cyanometric micro- and macro-titrations in non-aqueous media.

Trace analysis by anodic stripping voltammetry: trace metals in Dead Sea brine: lead and copper.

A. K. DEY

F. BERMEJO MARTINEZ and

A. MARGALET-BARRAL

A. LUCCHESI

L. ERDEY, O. GIMESI and G. RADY

M. ARIEL, U. EISNER and

S. GOTTESFELD

Section on SEPARATION METHODS

Thursday, 11th July, Morning

Highly selective separation of metals on redox exchangers.

Possibilities of separation with the Dower A-1 chelating ion-exchange resin.

An improved method for the quantitative determination of amino-acids by ion-exchange chromatography.

Anion-exchange separation of titanium, niobium, tantalum, molybdenum and tungsten.

Separation of the rare earths by partition chromatography with reversed phases.

Application of mixed partition systems in chromato-polarography.

Application of chitin in chromatographic separation of cation UO_2^{2+} from Ca^{2+} , Mg^{2+} and Fe^{2+} .

B. SANSONI

G. SCHMUCKLER and H. FRIEDMANN

S. JACOBS

J. B. HEADRIDGE and E. J. DIXON

T. B. PIERCE, P. F. PECK and

R. S. HOBBS

W. KEMULA and D. SYBILSKA

D. GLOWACKS and J. POPOWICZ

Thursday, 11th July, Afternoon

High-voltage ionophoresis as a method for separation and isolation of compounds of great chemical similarity.

Application of different electrophoreses media for resolution of blood proteins and haemoglobins.

Relations between structural elements and the paper-chromatographic R_f values of azo-dyes.

Identification of hydrophilic substituents in organic compounds by chromatography at different pH values.

A study of phingosine partially purified by three-phase countercurrent distribution.

Separations in analytical chemistry with organophosphorous compounds.

E. BLASIUS and PREETZ

M. S. EL RIDI, A. A. HAY, G. KAMEL,

A. ZAKI and S. TOPPOZADA

A. LORINZ and F. PETER

J. EGGERS and F. SCHLEGELMILCH

H. L. MELTZER and B. WEISS

J. C. WHITE

Relations between extracting power and basicity of long-chain aliphatic amines.

Methods for separation of gold and platinum from other transition metals.

Influence of the excess free energy of the mixture of solvents on the partition coefficient-composition curves.

Polarographic determination of dissolved oxygen in hydrazine solutions.

B. TREMILLON and M. RUMEAU

M. ZIEGLER

H. BUCHOWSKI

H. J. CLULEY and J. L. ROBERTS

Friday, 12th July, Afternoon

Chemical separation with ion-exchange resin applied to radioactivation microanalysis.

New chemical separations in the determination of burn-up of nuclear fuel test specimens.

Radiochemical analysis of ^{140}Ba - ^{140}La in freshly irradiated fuel elements; application of the method to the burn-up determination.

Quantitative analysis of plastics and synthetic fibres.

Zone melting in organic chemistry.

Increasing the selectivity of complexans and their application in analytical chemistry.

G. AUBOUIN and L. LAVERLOCHERE

A. J. FUDGE, E. FOSTER and
M. F. BANHAM

A. GUILLON and R. SAUVAGNAC

O. K. DOBOZY and J. NORNING

J. C. MAIRE and J. MORITZ

R. P. LASTOVSKY, N. M. DJATLOVA,

V. J. TJOMKINA and

I. D. KOLPAKOVA

Separation and determination of zirconium, thorium, titanium and rare earths.

Negative peak effect in gas chromatography.

Analysis of ^{14}Co - $^{14}\text{Co}^2$ mixtures by gas-chromatographic separation and aqueous solution counting.

R. PŘIBIL

J. D. WILSON and M. WILKINS

H. J. CLULEY and J. H. KONRATH

Section on ELECTROANALYSIS

Friday, 12th July, Afternoon

Determination of rhodium and its separation from iridium by electrodeposition.

Conductometric titration of natural waters.

A.c. oscillographic investigation of 3-hydroxy-2-naphthanilide derivatives.

Methods of electrochemical analysis of organic compounds in non-aqueous solutions.

Studies of azo-dyes and their metal complexes: the polarography of iron, nickel and chromium in the presence of Solochrome, Violet RS.

W. A. E. MCBRYDE, N. A. GRAHAM

and W. L. OTT

F. H. CONSTABLE

BY. PÁLYI and F. PETER

A. P. KRESHKOV

G. F. REYNOLDS and S. M. PALMER

Monday, 15th July, Afternoon

Electrochemical determination of enzymes.

Differential electrolytic potentiometry-XIII: Absolute DEP as an index of poisoning capacity.

Use of various electrode systems in non-aqueous solvents.

Properties of an electrode glass responsive to potassium and to ammonium ions.

Stability and analytical applications of diethylamino-dithioformates.

Use of electrochemical masking in some voltametric analyses.

Polarography in heterocyclic chemistry: reduction mechanism and analytical applications.

Adsorption phenomena and their influence in inorganic polarography

Quantitative determination of lead, cadmium, indium, copper and bismuth impurities in germanium and gallium by oscillographic polarography.

Polarographic investigation of diesters of the 1-hydroxy-2,2,2-trichloroethylphosphonic acid.

D. N. KRAMER and G. G. GUILBAULT

E. BISHOP and G. D. SHORT

F. PELLERIN and D. DEMAY

G. MATTOCK and R. UNCLES

A. HULANICKI

T. FUJINAGA

P. FOURNARI and M. PERSON

E. LAVIRON and M. PERSON

D. I. RJABCHIKOV, JA. P. GOKHSHEIN
and A. M. DEMKIN

GY. PÁLYI

Tuesday, 16th July, Morning

*A new polarographic linear diffusion electrode.
Polarographic reduction of sample single bonds.*

*Precise determination of oxygen: uranium ratios in uranium dioxide by comparative polarography.
Derivative cathode-ray polarography.*

Polarographic determination of CO_2 , SO_2 , H_2S and HCl .

*Comparative polarography.
Polarographic and oscillographic investigation of surface-active substances.*

Tuesday, 16th July, Afternoon

Electrochemical determination of plutonium.

Differential electrolytic potentiometry-XII: Coulometric determination of nanogram quantities of halides at extreme dilution.

Coulometric titration of phenothiazine with electrogenerated phenazothionium ion in acetonitrile.

An electroanalytical method for the determination of phenols and their rates of halogenation.

Studies on the trace determination of ruthenium and iridium by controlled-potential coulometry.

Analytical study of ruthenium.

Ionophoretic analysis of iron (III) thio-cyanato-complexes and some other complex compounds.

Influence of the formation of intermetallic compounds in the amalgam method for the separation and determinations of metals.

Some differences between results from polarographic investigations and controlled potential reductions.

J. JORDAN and J. H. CLAUSEN
P. ZUMAN, O. MANOUSEK and
V. HORAK

H. I. SHALGOSKY and R. C. SMART
R. C. ROONEY

G. SCHÖBER, H. DEHN,
V. GUTMANN and H. KIRCH
H. M. DAVIS

F. PETER and A. LÖRINCZ

G. W. C. MILNER, G. PHILLIPS
and A. J. WOOD

E. BISHOP and R. G. DHANESHWAR
J. BADOZ-LAMBLING and D.
STOJKOVIC

Q. FERNANDO, H. FREISER,
G. S. KOZAK and C. BOSTIC

G. A. RECHNITZ
J. ZYKA, I. NEMEC and A. BERKA
E. JOZEFOWICZ, T. KWASIK and
J. MASLOWSKA

A. I. ZEBREVE and M. T. KOZLOVSKII

H. LUND

Section on TEACHING OF ANALYTICAL CHEMISTRY

Thursday, 11th July, Morning

Teaching and training of analytical chemists: the industrial viewpoint.

Modern trends in teaching metallurgical and mineral analysis.

Analytical chemistry for students of chemical engineering.

Teaching of analytical chemistry in Colleges of Technology in the United Kingdom.

Suggestions for analytical chemistry courses in English colleges.

C. WHALLEY

D. A. PANTONY

J. A. BARNARD and R. CHAYEN

L. S. BARK

P. J. HENDRA and K. E. JOHNSTON

Friday, 12th July, Afternoon

Analytical chemistry in the M.I.T. plan for chemical education.

Teaching of inorganic analytical chemistry.

Teaching of instrumental methods of analysis.

Teaching methods of instrumental analysis in universities.

D. N. HUME

R. A. CHALMERS

W. A. ALEXANDER

E. PUNGOR

Thursday-Friday 5-6 September 1963: Joint Meeting on Modern Aspects of Chromatography: Institute of Chemistry of Ireland and Society for Analytical Chemistry, Scottish Section, Rupert Guinness Hall, Dublin.

The following papers will be presented:

Chemical structure and partition chromatography.

Thin-layer chromatography of long-chain amines.

J. GREEN

E. S. LANE

Thin-layer chromatography and its applications to dyestuffs and plasticisers.

Thin-layer chromatography: Applications to steroid chemistry.

Some Applications of gel filtration and ion-exchange chromatography to the fractionation of polysaccharides.

Ion exchange in the study of metal complexes in solution.

Chromatography in the identification of plant products.

Some recent applications of paper chromatography in the petroleum industry.

Recent applications of gas chromatography.

A statistical evaluation of gas-liquid partition chromatography as a method of quantitative analysis.

Determination of nitro constituents of explosives by gas chromatography.

Gas chromatographic analysis of beer.

On the Friday evening there will be a symposium Dinner and it is hoped to arrange a tour of the city. Accommodation can be arranged in City Hotels. Further details can be obtained, but not later than 15 July, from Mr. J. W. MURFIN, Boots Pure Drug Co. Ltd., Motherwell Street, Airdrie, Lanarkshire.

Tuesday-Thursday 8-10 September 1963: Fifth International Symposium on Gas Chromatography: Institute of Petroleum Gas Chromatography Discussion Group: Brighton, England.

The main aim of the symposium will be to launch a concentrated attack on the underlying physical processes responsible for separation. To achieve this, the morning sessions will be entirely devoted to this theme, the subjects for the three morning sessions being "Techniques of Separation and Identification", "Column Design" and "Exploitation of Molecular Interactions". Each morning session will be commenced by two papers given by recognised authorities. Informal discussions will be held in the afternoon sessions on a wide range of subjects relevant to the development and application of the technique. As at previous symposia, the technical programme will be accompanied by a full social programme and an instrument exhibition. Intending delegates and those wishing to submit papers should write to: The Organizing Officer, Fifth International Symposium on Gas Chromatography, 61 New Cavendish Street, London W.1, England.

UNITED STATES OF AMERICA

Wednesday-Friday 7-9 August 1963: Twelfth Annual Conference on Applications of X-Ray Analysis: Albany Hotel, Denver, Colo.

Monday-Friday 12-16 August 1963: Gordon Research Conference on Instrumentation: Colby Junior College, New London, New Hampshire (see *Talanta*, 1963, 10, May iii).

Monday-Friday 19-23 August 1963: Fifth International Congress of Clinical Chemistry: Detroit, Mich.

Monday-Friday 19-23 August 1963: Gordon Research Conference on Ion Exchange: Kimball Union Academy, Meriden, New Hampshire (see *Talanta*, 1963, 10, May iv).

Monday-Friday 26-30 August 1963: Gordon Research Conference on Analytical Chemistry: New Hampton School, New Hampton, New Hampshire: (see *Talanta*, 1963, 10, May iv).

Wednesday-Saturday 28-31 August 1963: Twenty-First Annual Meeting of Electron Microscope Society of America: Denver-Hilton Hotel, Denver, Colo.

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

The subject matter for discussion will follow the precedents set at the 1962 meeting which was to discuss those aspects of gas chromatographic technology which directly effect its utility and practical value in research and control applications. The meeting will be divided into sessions devoted to major topics including automatic data handling, selection of detectors for particular applications, the use of capillary columns in standard laboratory practice, and the combination of gas chromatographic with mass spectrometric instrumentation. A general meeting of the Committee will also be scheduled as well as sub-committee meetings on co-ordination and standardisation of methods; definitions, nomenclatures and standard data; and research activities. Sessions will consist of presentations by panels of distinguished practitioners of the particular aspects of chromatography under discussion, followed by general discussion by the audience at large.

Contributing to the usefulness of the meeting to the practicing gas chromatographer will be the summary and discussion of results of the quantitative analyses performed by all participants on a single sample of fatty acid esters to be distributed to all registrants.

G. R. JAMIESON

P. OXLEY

D. M. W. ANDERSON

J. K. FOREMAN

D. M. DONNELLY

R. B. DELVES

B. A. ROSE

C. E. ROLAND JONES and

D. KINSLER

A. F. WILLIAMS

G. A. F. HARRISON

The General Chairman of the meeting is NATHANIAL BRENNER of the Perkin-Elmer Corporation, and meetings arrangements are being supervised by CHARLES H. ORR of the Proctor & Gamble Co.

The latest reference to all standards published by the American Society for Testing and Materials, the 1962 Index to ASTM Standards, has just been issued by the Society. This handy adjunct to the 11 parts comprising the 1961 Book of ASTM Standards, the 1962 Supplements to these parts, and the special volume, 1960 Book of ASTM Methods for Chemical Analysis of Metals, supersedes all previous ASTM Indexes.

It is sent without charge to those receiving the Book of Standards. Single copies are sent on request by ASTM Headquarters, 1916 Race Street, Philadelphia 3, Pa. Additional copies may be obtained at \$1.00 each.

ERRATA

Volume 8, page 803, reference 3: for G. H. Wilkins read C. H. Wilkins.

Volume 10, page 291, line above equation (13): this should refer to equation (11) instead of to equation (12)

Volume 10, page 291, line after equation (13): for T_n read I_n .

Volume 10, page 414, line 8: this should read Trusell and Diehl,⁸

Volume 10, page 416, line 4: for Smith and Goehler⁸ read Smith and Goehler².

Volume 10, page 416, reference 6: this should read F. Trusell and Diehl, *Analyt. Chem.*, 1963, 35, 674.

Volume 10, page 564, line 12 after Table I: this should read *On distilling 10–15 ml of water. . .*

Volume 10, page 691; the reference quoted in full in the middle of the page is meant to be a footnote referring to the asterisk in the title to the Preliminary Communication.

BOOK REVIEWS

Inorganic Chemistry, LOUIS K. SHARP. The Williams and Wilkins Company, Baltimore, 1962. Pp. viii + 339. \$8.00.

In one way this book has a new approach. It has been written with the object of covering the requirements of students reading for degrees or diplomas in pharmacy. In the past the inorganic side of chemistry has been played light for students of this type. This volume is, therefore, to be welcomed because, although inorganic compounds are not widely used by the pharmaceutical chemist, his chemical training is not complete without a study of the fundamental behaviour of all the elements and their interrelationships.

The book is divided into two parts. Part I, under the heading of General Chemistry, is concerned with fundamental material, and discusses in succeeding chapters the discovery of the chemical elements, atomic, molecular and equivalent weights, the structure of the atom, the classification of the chemical elements, the standard electrode potentials and the properties of the elements, valency, co-ordination compounds and inorganic stereochemistry, radio-isotopes, typical elements, transition elements and rare earths, and the purification of inorganic chemicals and tests for purity.

Part II of the book deals with the elements and their compounds, and attention is given to those compounds of each element which are of importance in medicine.

The book is written in a very interesting style. For example, in the first chapter, dealing with the discovery of the chemical elements, the author has gathered together information and put it together in a way which will hold the interest of student or mature chemist.

In those chapters of Part I which deal with fundamentals the stress is on the periodicity of properties. The result is a book which is worthy of study by any student of inorganic chemistry, because the presentation will undoubtedly reduce "fact-cramming" to a minimum.

One minor criticism is that the chapter on the preparation of chemical elements and tests for purity seems out of place in the theoretical part of the book. Several typographical errors are present in the copy reviewed. On p. 10, line 5, "Becquel" is wrongly spelled. Again, where the elements Fermium and Astatine are mentioned, e.g. pp. 10, 13, 56, they are spelled wrongly.

Finally, on p. 103 the formula of nickel dimethylglyoxime is given without hydrogen bonding. In the modern interpretation of this chelate, the hydrogen bond is considered to be an essential part of the structure.

This book can be highly recommended.

R. J. MAGEE

Advances in Inorganic Chemistry and Radiochemistry, Vol. 4. Edited by H. J. EMELEUS and A. G. SHARPE. Academic Press, Inc., New York, U.S.A., 1962. Pp. 344. 88s.

THIS annual review publication has earned top place among the inorganic review journals by reason of the timeliness, broad scope, authoritative character, and thorough documentation of its contributions. The proportion of really well-written and imaginative articles in it has been exceptionally high. In the present volume these standards are maintained.

As the radioactive elements have become available in increasing amounts, their chemistry has become more and more closely identified with conventional inorganic chemistry. In the only "radiochemical" chapter of this volume, *The Chemistry of Polonium*, K. W. Bagnall describes the properties of milligram quantities of the element and its compounds very much as one would describe the chemistry of a non-radioactive element. He interprets the early tracer observations in the light of current work with visible amounts.

Physical methods of structure determination are now indispensable to every inorganic research programme. Unfortunately they often have to be applied semi-empirically, which has tended to encourage wishful thinking and tendentious argument in the interpretation of results. J. R. Miller in *Recent Advances in Stereochemistry of Nickel, Palladium and Platinum*, and E. L. Mutterties and W. D. Phillips in *The Use of Nuclear Magnetic Resonance in Inorganic Chemistry*, are careful to avoid this trap, and these authors deserve praise for their finely critical attitude and good writing.

E. Thilo's *Condensed Phosphates and Arsenates* is a broad, complete survey, in which experimental work on preparation and structure determination is emphasised, and in which Professor Thilo's own considerable achievements are placed in correct perspective.

The chapter by R. G. Guy and B. L. Shaw entitled *Olefin, Acetylene and π -Allylic Complexes of Transition Metals* is the most complete and up-to-date review of this rapidly developing subject now available. It is particularly useful for its description of the novel π -allylic complexes.

J. D. Mackenzie's *Oxide Melts* is not perfectly written, but presents a clear and interesting picture of some unusual liquid structures.

This book is a very good investment for research workers in inorganic chemistry, and for teachers of the subject at advanced levels.

H. G. HEAL

A lángfotometria elméleti alapjai-I (Theoretical Background of Flame Photometry, Vol. I). ERNŐ PUNGOR. Akadémiai Kiadó, Budapest, 1962. pp. 195. 50 Hungarian Forint. In Hungarian.

PROFESSOR Pungor's book represents an entirely new concept among texts on flame photometry. Its aim is to present the physical bases of flame photometric processes as exactly as possible. Because the topics treated are sometimes not closely related, the book itself seems to be somewhat of a mosaic. This is, however, an advantage from some points of view; the reader can select those topics in which he is interested, without the necessity of reading through the whole text.

The text is divided into six parts. Part I deals with theoretical and practical problems of the flame, including flame velocity, its determination and the effect of various factors on it, theory of flame extending, extinction, etc. Part II, entitled *Determination of radical concentrations and radical equilibria in the flame*, treats the subjects mainly on the basis of chemical and spectroscopic phenomena. The hydrogen-oxygen flame is discussed in detail, while other types of flame are mentioned only briefly. A thorough treatment of ionisation and measurement of OH radical concentration is presented. Part III deals with temperature and its measurement in flames, while Part IV describes the various types of flame used in flame photometry. Part V on *Atomic absorption* seems to be too short (only 2 pages), giving a very brief description of the subject. The last part (VI) deals with the theory of atomisation and spray chamber coagulation, summarising the well known results of the author. A very good bibliography (including 199 references) and index complete the book.

The book is to be published also in English, so this very interesting text will become available to chemists all over the world. Further volumes, dealing with the practice of flame photometry, are awaited with interest.

GYULA SVEHLA

PAPERS RECEIVED

- Determination of nitrogen in organic compounds using ion exchange resins:** R. A. SHAH and A. A. QADRI. (3 May 1963).
- The spectrophotometric estimation of indoles using a modification of the Ehrlich colour reaction:** P. BYROM and J. H. TURNBULL. (3 May 1962).
- The dissolution of alunite employing hot concentrated perchloric acid: Determination of silica and aluminium:** G. FREDERICK SMITH and WM. H. TAYLOR. (4 May 1963).
- Thiourea in analysis—I: Estimation of selenium and tellurium:** A. S. R. MURTY. (6 May 1963).
- Thiourea in analysis—II: Colorimetric determination of molybdenum and vanadium:** A. S. R. MURTY. (6 May 1963).
- A solvatochromic chelating agent:** A. MUELLER, J. TRAVIS LEACH and J. P. PHILLIPS (6 May 1963).
- Phase titrations—III: New applications including the assay of water in pyridine:** D. W. ROGERS and A. ÖZSOĞOMONYAN. (7 May 1963).
- Electron microscopy studies of nickel dimethylglyoximate:** KAZUYOSHI TAKIYAMA and LOUIS GORDON. (10 May 1963).
- Polarographic determination of Cu^{II} , As^{III} and As^{V} in copper arsenite:** T. L. HUNTER, J. F. HAZEL and WALLACE M. MCNABB. (13 May 1963).
- Determination of silver in lead by neutron-activation analysis:** F. ADAMS, J. HOSTE and A. SPEECKE. (13 May 1963).
- Non-destructive activation analysis of arsenic and antimony in lead:** F. ADAMS and J. HOSTE. (13 May 1963).
- The determination of thiomalic acid:** V. CHROMÝ and V. SVOBODA. (15 May 1963).
- The determination of ^{226}Ra in human bone:** NAOMI A. HALLDEN, ISABEL M. FISENNE and JOHN H. HARLEY. (15 May 1963).
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