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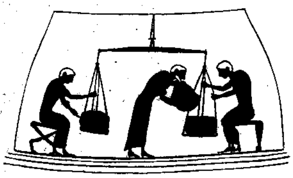

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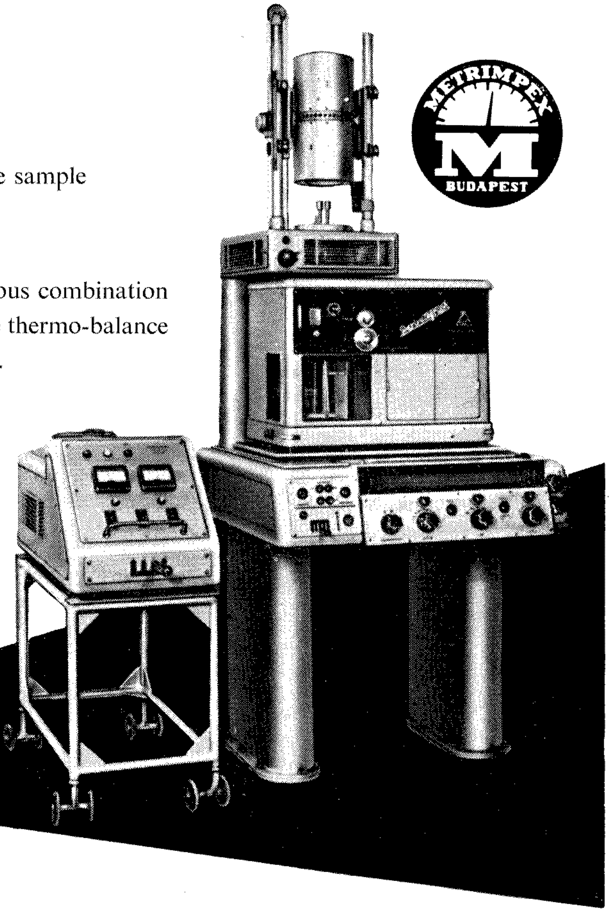

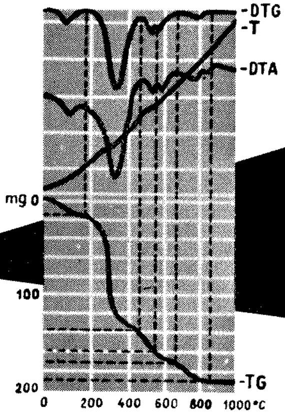
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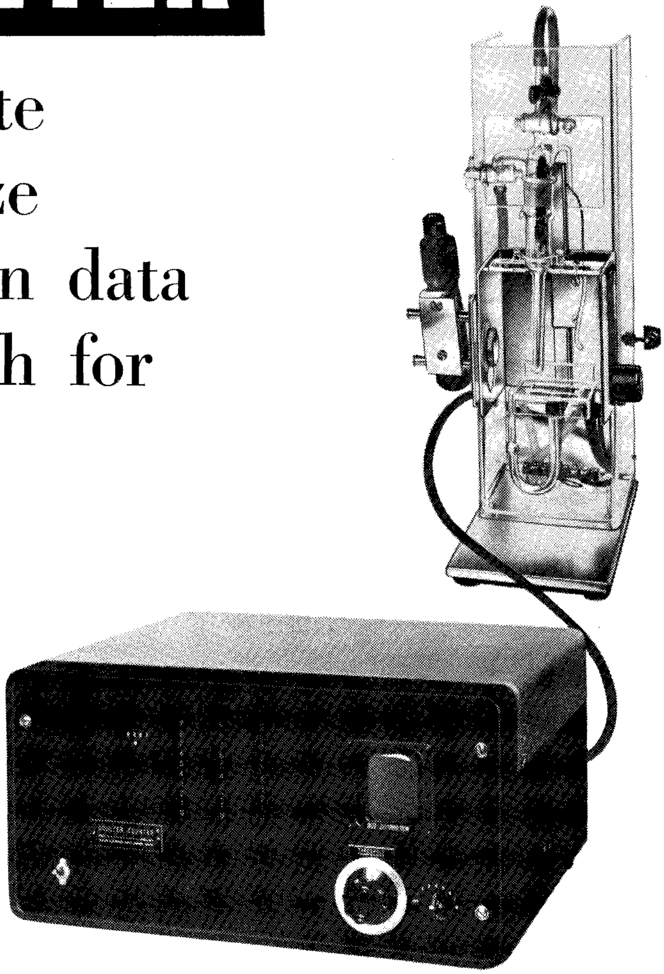

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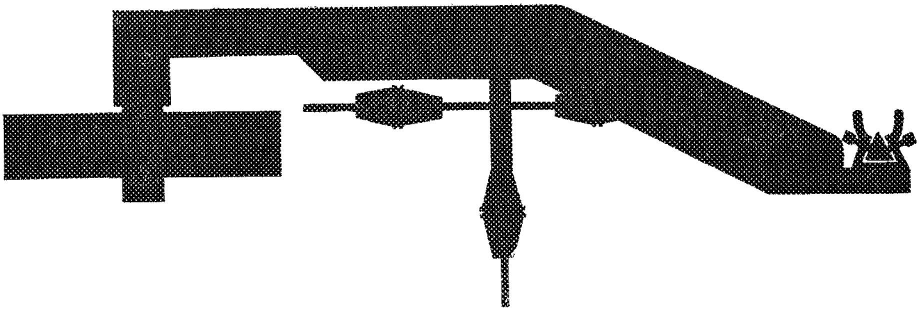

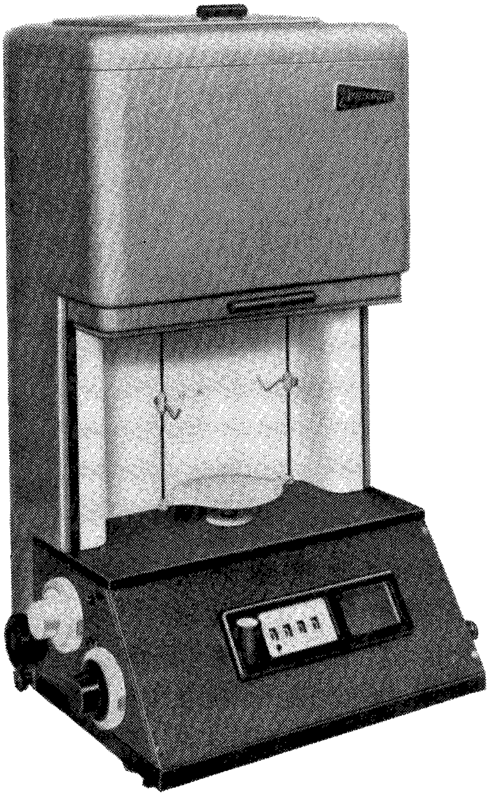

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THE TALANTA MEDAL, 1961

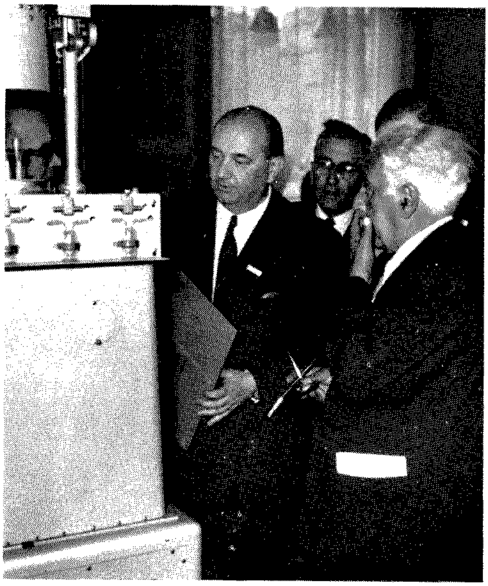
Professor R. Belcher (U.K.) Chairman of the Advisory Board of Talanta and President of the Analytical Chemistry Section of I.U.P.A.C., delivers the citation preceding the presentation of the Talanta Medal to Professor Fritz Feigl (Brazil). The presentation took place in the Ceremonial Hall of the Hungarian Academy of Sciences during the opening of the Analytical Chemistry Congress of the Hungarian Chemical Society. The Congress was held in Budapest on 24–29 April 1961. Others, left to right, at the table are Mr. S. Czottner (Hungarian Minister for Heavy Industry), Professor G. Schay (President of the Hungarian Chemical Society) and Professor I. Rusznyak (President of the Hungarian Academy of Sciences).

The conditions of award of the Talanta Medal were set forth in Talanta, 1959, **3**, 217. Announcement of Professor Feigl (Brazil) as the first recipient was made in Talanta, 1961, **8**, 170.

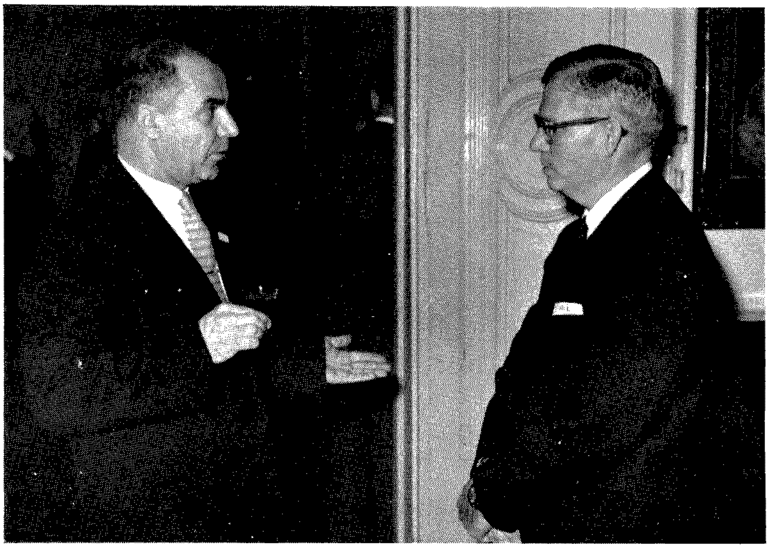
Professor BELCHER (U.K.) presents the Talanta Medal to Professor FEIGL (Brazil) while the President of the Hungarian Academy of Sciences looks

Professor E. SCHULEK (Hungary) extends to Professor FEIGL (Brazil) congratulations from the Analytical Chemistry Congress.

Mrs. SZABÓ (Hungary), Professor L. GORDON (U.S.A.), Regional Editor of Talanta and Secretary of the Analytical Chemistry Section of I.U.P.A.C., and Professor BELCHER (U.K.) examine the Talanta Medal with Professoı FEIGL (Brazil).



Professor L. ERDEY (Hungary) demonstrates the use of the derivative thermogravimetric balance to Professor FEIGL (Brazil).



Professor K. JACIMIRSKIJ (U.S.S.R.) discusses common interests in analytical chemistry with Professor GORDON (U.S.A.). Professor JACIMIRSKIJ will be visiting U.S.A. for the Sixth International Conference on Co-ordination Chemistry at Detroit, Michigan, from 27 August to 2 September, 1961. Both Professors delivered Plenary Lectures at the Congress.

All photographs of the Analytical Chemistry Congress of the Hungarian Chemical Society were taken by JENÖ ICZKOVITS and JOZSEF FARKAS.

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THE DETERMINATION OF TRACES OF IRIDIUM IN SAMPLES OF RHODIUM BY NEUTRON-ACTIVATION AND GAMMA-RAY SPECTROMETRY

D. F. C. MORRIS, D. N. SLATER and R. A. KILLICK
Brunel College of Technology, London, W.3., England

(*Received* 17 *October* 1960. *Accepted* 31 *October* 1960)

Summary—Neutron-activation analysis has been applied to the determination of traces of iridium impurity in specimens of rhodium. The Harwell Pile BEPO has been used as neutron source. The method involved irradiation of samples and standards and their subsequent γ-spectrometric assay; no radiochemical separations were required.

IN a recent paper Morris and Killick[1] have given details of the determination of traces of iridium in palladium and platinum by neutron-activation analysis. The method described involved radiochemical separation of the induced iridium activities using carriers. In the present work, the analysis of traces of iridium in rhodium by neutron-activation, without any chemical processing, is described.

The nuclear characteristics of the isotopes involved when iridium is subjected to bombardment with neutrons of thermal energies are given in Table I.

TABLE I.—NUCLEAR DATA FOR IRIDIUM

Target nuclide	Abundance of nuclide in natural element, %	Isotopic activation cross-section, *barns*	Product of thermal neutron irradiation	Radiation and energy of product nuclide, *MeV*	Half-life of product radionuclide
^{191}Ir	38·5	260	^{192m}Ir	IT e$^-$(γ) 0·056 (^{Q}IT)(99·9%); β^-0·056 (*ca.*0·1%)	1·42 min
		700	^{192}Ir	β^-0·097 (1%), 0·26 (8%), 0·54 (35%), 0·67 (50%); EC (6%); γ0·136, 0·296, 0·308, 0·316, 0·468, 0·604, others.	74 d
^{193}Ir	61·5	130	^{194}Ir	β^- 2·24 (66%), 1·91 (15%), 0·98 (10%), 0·43 (*ca.* 8%); γ 0·329 (others 0·29 to 2·05)	19 hr

EXPERIMENTAL

Specimens of rhodium for analysis were in powder form and *ca.* 0·1-g samples were accurately weighed and sealed in silica irradiation tubes of 4-mm internal diameter. Iridium and rhodium both have large absorption cross sections[2] for thermal neutrons, 440 and 156 barns respectively. To avoid neutron self-shielding differences between samples and standards, therefore, standards were prepared by the admixture of small known quantities of iridium with analytical samples. This was done by adding weighed portions of dilute solutions of iridium [as $(NH_4)_2IrCl_6$ in 3*M* HCl] to *ca.* 0·1-g samples of rhodium in silica tubes of 4-mm internal diameter. The liquid was allowed to soak into the metal powder, and then was carefully evaporated to dryness, after which the tubes were sealed. In the preparation of the standards, weights of iridium added were about 50% of the weights of the element expected to be present in the samples.

Samples, together with standards containing added iridium, were packed with silica wool in standard aluminium screw-top cans and were sent to the Atomic Energy Research Establishment, Harwell, for neutron irradiation. Irradiations were for periods up to 1 week in the Pile BEPO with a thermal neutron flux of 10^{12} neutrons per cm^2 per sec.

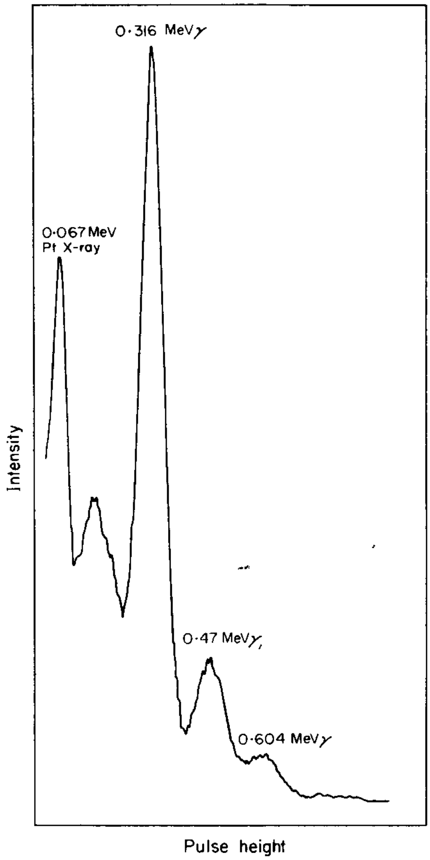

FIG. 1—γ-Ray spectrum of pure iridium-192.

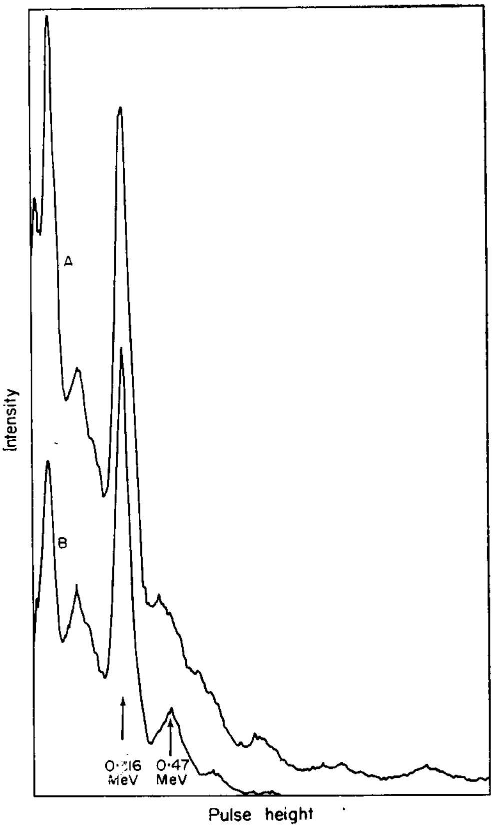

FIG. 2—γ-Ray spectra of a sample of neutron irradiated rhodium:
A—on first day from end of irradiation.
B—on eighth day from end of irradiation.

After irradiation, samples and standards were removed from the silica tubes and distributed uniformly over aluminium counting trays (A.E.R.E. cat. no. 4-3/1068). The silica tubes were rinsed out with hot water, and the resulting slurries on the counting trays were evaporated to dryness under a radiant-heater lamp. (A preliminary experiment with iridium-192 tracer showed that the added iridium in irradiated standards was completely transferred from the silica tubes to the counting trays by this technique). The material on the trays was covered with Sellotape.

After 8 days from the end of neutron-irradiation, the samples and standards were measured at constant geometry with a γ-ray spectrometer. The instrument used consisted of a 1-inch × 1½-inch thallium-activated sodium iodide crystal mounted on a 6097B E.M.I. photomultiplier tube. After amplification, the output pulses from the photomultiplier were passed into a single-channel pulse analyser and thence to a ratemeter. The output was fed into a recording potentiometer ganged to the analyser bias sweep. In this manner it was possible to obtain a γ-ray spectrum as a plot of counting rate *vs.* pulse height.

The intensities of the photo-peaks corresponding to γ-rays of 0·316 and 0·47 MeV were measured in arbitrary units for samples and standards in turn. From the measured peak-heights, and the known weights of samples and standards and the known amounts of added iridium in the standards, the iridium contents of the samples could be calculated.

DISCUSSION AND RESULTS

The γ-ray spectrum of pure iridium-192 is shown in Fig. 1. Spectra of a sample of neutron-irradiated rhodium are shown in Fig. 2.

TABLE II.—RADIONUCLIDES PRODUCED BY (n,γ) OR U(n,f) REACTIONS GIVING γ-RAYS WHICH COULD NOT BE DIFFERENTIATED FROM THE 0·316 MeV IRIDIUM-192 γ-RAY

Nuclide	Half-life	Mode of formation	γ-ray energy, *MeV*
^{160}Tb	73·5 d	^{159}Tb(n,γ)	0·299
^{140}Ba	12·8 d	U(n,f)	0·304
^{233}Pa	27·4 d	^{232}Th(n,γ)^{233}Th(β^-)	0·301, 0·313
^{51}Cr	27·8 d	^{50}Cr(n,γ)	0·320, 0·325
^{105}Rh	36·5 hr	^{104}Ru(n,γ)^{105}Ru(β^-)	0·320
^{193}Os	30·6 hr	^{192}Os(n,γ)	0·321
^{140}La	40·0 hr	^{140}Ba(β^-) ^{139}La(n,γ)	0·3286

Measurements of the decay of the peaks at 0·316 and 0·47 MeV for samples of neutron-irradiated rhodium showed that after 8 days from the end of irradiation only γ-rays from ^{192}Ir were being counted.

Other activities which, after 8 days "cooling", could possibly have interfered with the measurement of the 0·316 MeV and 0·468 MeV γ-rays of ^{192}Ir are shown in Tables II and III.

Some analytical results are shown in Table IV.

TABLE III.—RADIONUCLIDES PRODUCED BY (n,γ) OR U(n,f) REACTIONS GIVING γ-RAYS WHICH COULD NOT BE DIFFERENTIATED FROM THE 0·468 MeV IRIDIUM-192 γ-RAY

Nuclide	Half-life	Mode of formation	γ-ray energy, *MeV*
^{110m}Ag	270 d	^{109}Ag(n,γ)	0·446
^{131}Te	24·8 min	^{130}Te(n,γ) ^{131m}Te(IT)	0·45
^{193}Os	30·6 hr	^{192}Os(n,γ)	0·46
^{187}W	24·0 hr	^{186}W(n,γ)	0·4795
^{131}Ba	11·5 d	^{130}Ba(n,γ)	0·498
^{140}La	40·0 hr	^{140}Ba(β^-), ^{139}La(n,γ)	0·487
^{103}Ru	39·8 d	U(n,f)	0·498

TABLE IV.—IRIDIUM CONTENTS OF SOME SPECIMENS OF RHODIUM DETERMINED BY NEUTRON-ACTIVATION AND γ-SPECTROMETRIC ANALYSIS

Specimen	Iridium content found from 0·316-MeV photopeak, *ppm*	Iridium content found from 0·468-MeV photopeak, *ppm*
Rh 1	172	171
	173	174
	168	169
	168	166
Rh 2	137	135
	146	145
	141	136
	136	134
Rh 10 (very high purity)	3·36	3·6
	3·93	4·2
	3·13	3·6

Acknowledgements—Grateful acknowledgement is made to The Mond Nickel Company Ltd for the loan of specimens of rhodium, for financial support, and for a Research Fellowship to one of us (R. A. K.).

We are indebted to Dr. G. L. Reed for making some valuable modifications to the γ-ray spectrometer.

Zusammenfassung—Neutronenaktivierungsanalyse wurde zur Bestimmung von Iridiumspuren in Rhodiumproben herangezogen. Der Harwellofen BEPO wurde als Strahlenquelle verwendet. Die Methode beschränkt sich auf Bestrahlung von Probe und Standard und anschliessender Zählung der Gammastrahlen; keine radiochemische Trennung ist nötig.

Résumé—L'analyse par activation de neutrons a été appliquée au dosage de traces d'impureté d'iridium dans des échantillons de rhodium. La pile BEPO de Harwell a été utilisée comme source de neutrons. La méthode fait intervenir l'irradiation des échantillons et des témoins puis leur dosage par spectrométrie γ; aucune séparation radiochimique n'a été nécessaire.

REFERENCES

[1] D. F. C. Morris and R. A. Killick, *Talanta*, 1961, **8**, 129.

[2] D. J. Hughes and R. B. Schwartz, *Neutron cross sections*, U.S. Atomic Energy Comm. compilation. BNL 325, 2nd edn. (1958).

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THERMOGRAVIMETRIC DECOMPOSITION OF THORIUM 8-HYDROXYQUINOLATE*

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(*Received* 29 *November* 1960. *Accepted* 30 *January* 1961)

Summary—The thermogravimetric behaviour of crystalline thorium 8-hydroxyquinolate has been correlated with empirical and molecular formulae. The first of two sharp breaks is shown to be due to both water and oxine, and the second to oxine alone.

INTRODUCTION

THERMOGRAVIMETRIC curves for the decomposition of the 8-hydroxyquinolates of various metals have been reported in a number of investigations. Frere,[1] Dupuis and Duval,[2] Borrell and Pâris,[3] and Wendlandt,[4] in particular, have included the thorium 8-hydroxyquinolate in their studies.

There has been considerable interest in obtaining spherical particles of thorium oxide and mixed thorium-uranium oxides for use as a slurry reactor fuel. In the precipitation of thorium from homogeneous solution with 8-acetoxyquinoline, as reported by Salesin and Gordon[5] and Takiyama, Salesin and Gordon,[6] it was noted that the precipitate obtained appeared in the form of uniformly-sized spherical particles several hundredths of a mm in diameter. The particle geometry was not preserved, however, on heating above the decomposition temperature of the thorium 8-hydroxyquinolate.

Also, because some difficulty had been observed previously in obtaining reproducible breaks in the thermogravimetric curves,[1–4] it was of interest to repeat the pyrolysis on the relatively large crystalline precipitate obtained with the precipitation from homogeneous solution.

EXPERIMENTAL

The 8-acetoxyquinoline was obtained from the Burdick and Jackson Laboratories, 1953 S. Harvey St., Muskegon, Michigan. The melting point was 56°. An infrared spectrum was supplied to demonstrate the absence of 8-hydroxyquinoline with a melting point of 73°. A comparison of the two infrared spectra has been given by Salesin and Gordon.[5]

The precipitation from homogeneous solution of thorium 8-hydroxyquinolate was made in the following manner:

Three g of 8-acetoxyquinoline were dissolved in a mixture of 30 ml of glacial acetic acid and 30 ml of water in a 1-litre breaker; 500 ml of water were added. Then 25 ml of thorium nitrate stock solution, containing 600 mg of thorium, were added, and the pH was adjusted to 5·3 with ammonium hydroxide. The solution was heated to 50° and kept at this temperature for 2 hr. The precipitate appeared in about 10 min and was complete in about 2 hr. The cooled mixture was centrifuged, and washed twice with cold distilled water.

The washed precipitate was dried for several days at room temperature in a vacuum desiccator. Drying was also done on the original precipitate in the balance chamber over-night, with dry argon sweep gas at room temperature; and a third procedure was drying at 50° for up to 24 hr with a sweep gas.

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

The balance used for the thermogravimetric pyrolysis studies was a Sartorius Selecta balance equipped with recording attachment and amplifier. The output of the amplifier was displayed on a Bristol Dynamaster recording potentiometer giving a continuous record of weight change *vs.* time. The sample-pan was suspended by a nickel chain into the reaction furnace, situated directly below the balance. Hot convection currents from the furnace were kept out of the balance by a baffle and gas blanket arrangement. A gas distribution manifold allows a choice of reaction gas. All gases passed through a preheat furnace before entering the main reaction furnace. The sample temperature was measured by a calibrated thermocouple positioned directly beneath the sample-pan.

The temperature rise of the furnace was controlled by a West pyrometer controller. A standard heating rate of 3° per min, and a 300-mg sample were used in all experiments. The 300-mg sample was spread evenly over an area of about 3 cm^2.

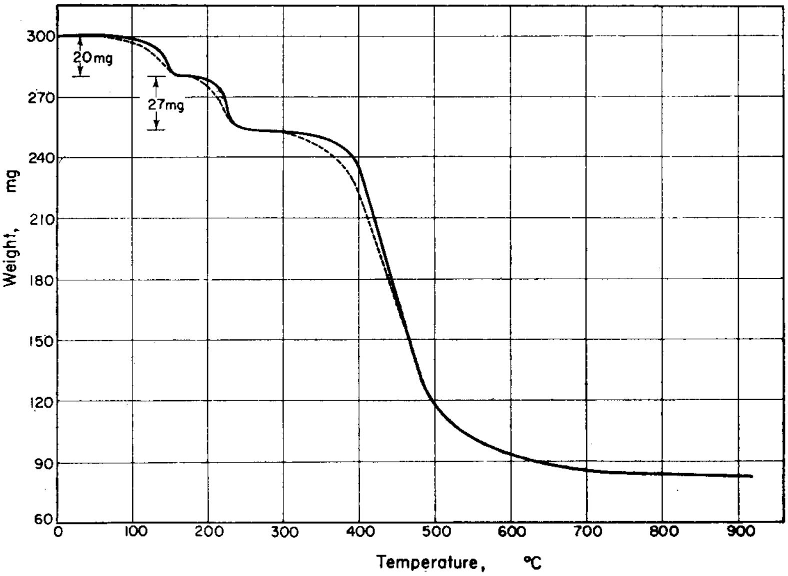

FIG. 1.—Thermal decomposition curve of thorium 8-hydroxyquinolate
——— precipitate from homogeneous solution
– – – – conventional precipitate.

In addition to the thermogravimetric behaviour, the thorium and oxine content of the solid were determined after heating at the plateaus of thermal stability. Analyses were made, both on samples that were removed from the thermobalance by stopping the run at a plateau, and on samples that had been heated in a separate apparatus to the temperature of the plateau on the thermogram.

The thorium content was determined by an air ignition at 950° to yield thorium dioxide. The oxine content was obtained spectrophotometrically. A known quantity of thorium 8-hydroxyquinolate was dissolved in 0·1*N* HCl and diluted to a known volume. The acid decomposes the thorium complex, but yields a solution of the 8-hydroxyquinoline which is stable for days. At lower acid concentration the presence of the thorium in solution may enhance the absorbance due to oxine alone. At the low thorium concentrations involved here, however, and in 0·1*N* HCl, no effect was observed. Crystals of the pure 8-hydroxyquinoline were dissolved in 0·1*N* HCl and diluted to a known volume for use as standards. A Model 11 Cary recording spectrophotometer was employed to record the oxine spectrum in the region of 400 to 290 mμ.

A vertical furnace equipped with a large Pyrex tube was employed, so that material which sublimed or vaporised, in the heating of weighed samples of thorium 8-hydroxyquinolate at a given temperature, could be condensed on a cold section and removed for analysis. The breaks shown in Fig. 1 were easily associated with the appearance of a ring of condensed water vapour and/or 8-hydroxyquinoline crystals on the wall of the cold section of the Pyrex tube. The temperature rise was arrested at about the point of the maximum slope (Fig. 1), and the condensate was collected for a few additional min.

DISCUSSION

The analysis of the condensate on the Pyrex tube walls, summarised in Table I, demonstrated very clearly that the first break yielded two products, water and crystalline 8-hydroxyquinoline. This result was obtained on material that had been dried at 50° for up to 24 hr, and also on material dried at room temperature (25°) in a vacuum for 24 hr. The droplets of water vapour condensate were easily distinguished from the sharp needle-like crystals of oxine on the Pyrex tube wall. In slow heating, it was observed that some oxine crystals formed on the cold wall before the appearance of water droplets, but it was not possible to obtain a clearly observable thermal plateau for each product lost in the first thermal break.

Only the needle-like crystals of oxine were observed to condense on the tube wall at the second break in the curve. Analysis of the condensate substantiated the view that the total weight loss at this temperature was due solely to oxine. At both temperatures, the visible and ultraviolet spectra of the condensate indicated no evidence of degradation of the oxine.

TABLE I.—SUMMARY OF THE ANALYSIS OF THORIUM 8-HYDROXYQUINOLATE SOLIDS AND THEIR FURNACE CONDENSATES AFTER HEATING AT THE THERMAL PLATEAUS

Empirical formulae	Numerical results given for analysis of 300-mg samples	
	Analytical results[d] with standard deviation	Weight losses calculated from postulated formulae
$Th(Ox)_{4\cdot8}\cdot2H_2O$ M.W. = 960 (yellow)	Analysis of the oxine and thorium content gave 4·80 ± 0·03[a]	Precipitates dried below 50° in air or vacuum for 24 hr.
$Th(Ox)_{4\cdot6}$ M.W. = 895 (yellow-green)	H_2O[c] 11·4 ± 0·3 mg *Oxine*[b] 8·9 ± 0·15 mg *Thermograv. loss* 20·0 ± 0·2 mg $\frac{\mathit{Oxine}}{\mathit{Th}} = 4{\cdot}60 \pm 0{\cdot}05$	H_2O 11·2 mg *Oxine* 9·00 mg *Thermograv. loss* = 20·2 mg *Max. temperature employed* 165°
$Th(Ox)_{4\cdot0}$ M.W. = 809 (green)	*Thermograv. loss* 27·0 ± 0·3 mg *Oxine*[b] 27·3 ± 0·4 mg $\frac{\mathit{Oxine}}{\mathit{Th}} = 4{\cdot}00 \pm 0{\cdot}05$	H_2O 0·0 *Oxine* 27·0 mg *Thermograv. loss* = 27·0 mg *Max. temperature employed* 230°

[a] Takiyama, Salesin and Gordon[6] have also obtained a value of 4·8 on crystalline material formed by precipitation from homogeneous solution.

[b] Oxine on furnace walls determined spectrophotometrically.

[c] Mg of water obtained by the difference of losses observed in the thermogravimetric analysis at the first break shown in Fig. 1 and the oxine loss obtained by analysis of the Pyrex tube wall deposits.

[d] Analytical results are summarised from 5 experiments using 3 different samples each precipitated from homogeneous solution. One sample was furnished by Louis Gordon, Case Institute of Technology, Cleveland, Ohio.

It was also observed that the original material $[Th(OX)_{4\cdot8}\cdot2H_2O]$ was quite soluble in dry methyl alcohol, yielding a yellow solution. However, the same rearrangement, or a very similar rearrangement to that which had occurred on heating, took place rapidly in solution. Shortly a new precipitate appeared which, when analysed, indicated a mole ratio of oxine to thorium of 4:1. Large amounts (1·0 g) of the hydrated thorium oxine, when stirred with approximately 100 ml of dry methyl alcohol for about one hour, were converted completely to $Th(Ox)_4$ by a continuous dissolution and re-precipitation. This may offer a precise method of adjusting the thorium oxine stoichiometry, since the released excess oxine and water appear to be more easily volatilised with the alcohol at 100° or less.

No effort has been made to make detailed comparisons of various thermogravimetric values. Borrell and Pâris[3] and Wendlandt[4] and this work are all in general agreement that the normal thorium oxinate, $Th(Ox)_4$, is obtained by heating at or slightly above 275°, 250° and 225° respectively. Takiyama, Salesin and Gordon,[6] however, with conventional drying for 10 hours at 180°, also have obtained the normal thorium oxinate. The rate of decomposition of a solid, and in turn the effect as reflected in thermogravimetric curves, has been neglected in many studies. This has led to difficulties in relating thermogravimetric behaviour to conventional gravimetric analysis. It is appropriate to point out that precise designation of reaction temperatures by thermogravimetric analysis is problematical, and is dependent on the experimental conditions used. This point is discussed by Markowitz and Boryta.[8]

The lack of agreement in attaining the thorium oxide level has been pointed out by Wendlandt.[4] In this work we have not been able to obtain a stable thorium oxide level in the thermogravimetric balance in the 600–700° range, as reported by both Wendlandt,[4] and Borrell and Pâris.[3] Dupuis and Duval[2] found that a stable oxide level was not obtained at 945°. A similar problem in the minimum ignition temperature of aluminium oxide has been studied by Milner and Gordon.[7]

Zusammenfassung—Die thermogravimetrische Zersetzung von kristallinem Thoriumoxinat wurde mit empirischen und Molekularformeln korreliert. Der erste von zwei scharfen Knicken wird durch Wasser und Oxin, der zweite durch Oxin allein verursacht.

Résumé—Les auteurs ont relié la décomposition thermogravimétrique du composé cristallin thorium-8 hydroxyquinoléine aux formules empirique et moléculaire. On montre que la première des deux cassures nettes est due à l'eau et à l'oxine, et la sedonde à l'oxine seule.

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PHOTOMETRISCHE TITRATIONEN—I

ALLGEMEINE BETRACHTUNGEN UND DIE THEORIE CHELOMETRISCHER TITRATIONEN OHNE ANWENDUNG EINES INDICATORS

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Zusammenfassung—Es werden Besonderheiten von chelometrischen Titrationen mit photometrischem Endpunkt ohne Indicator aufgezeigt. Formeln zur Berechnung der Titrationskurven werden abgeleitet. Es wird gezeigt, dass im Falle der Titration eines einzelnen Metalles eine wesentlich geringere Stabilität des Titrationskomplexes toleriert werden kann, als bei anderen Endpunktsmethoden, die nicht auf Extrapolation beruhen. Für die Titration zweier Metalle hintereinander in ein und derselben Lösung ist ein Unterschied (Quotient) in den Stabilitätskonstanten von etwa 100–200 ausreichend. Möglichkeiten der photometrischen Indication ohne Indicator in Kombination mit anderen Endpunktsmethoden werden diskutiert und vom Standpunkt des Selektivitätsproblemes aus betrachtet.

In einer seinerzeit erschienenen Arbeit hat der Autor die Endpunktstheorie chelometrischer Titrationen behandelt.[1] Formeln wurden abgeleitet, anhand derer man die Titrationsbedingungen, Genauigkeit usw. errechnen kann. Die Behandlung des Stoffes wurde aufgrund der Beziehungen zwischen Volum an Masslösung und pM($= -\log M$) durchgeführt. Es war eindringlich darauf verwiesen worden, dass die Verhältnisse eine einschneidende Änderung erfahren, wenn der Endpunkt ohne einen visuellen Indicator ermittelt wird und dass im besooderen die Anwendung graphischer Methoden dazu führt, dass weniger strikte Bedingungen für die Durchführung der Titration toleriert werden können.

Grundsätzlich muss zwischen zwei verschiedenen graphischen Methoden unterschieden werden. Die eine Gruppe von Methoden umfasst solche, die "im Endpunkte" arbeiten, wie z.B. potentiometrische Titrationen. Hier wird der Wendepunkt in der Titrationskurve ermittelt und zwar aus dem Kurventeil nahe vor und nach dem Endpunkt. Unter diesen Bedingungen wird jener Teil der Kurve verwendet, wo das Gleichgewicht des zu messenden Systems in einem ungünstigen Mittelstadium schwebt und den höchsten Grad der Dissoziation des Titrationskomplexes aufweist. Die zweite Gruppe von Methoden verwendet zur Ermittlung des Endpunktes eine Extrapolation. Der eine Kurvenast, der zur Extrapolation herangezogen wird, liegt im Bereich, wo Metallionen im Überschuss vorhanden sind und somit das Gleichgewicht nach der Seite geringerer Dissoziation des Titrationskomplexes verschoben ist. Der zweite Ast liegt im Bereich, wo Titrationsmittel im Überschuss vorhanden ist und auch hier ist das Gleichgewicht in günstigem Sinne nach der Richtung geringerer Dissoziation des Titrationskomplexes verschoben. Methoden, die nach diesem Gesichtspunkte arbeiten, sind z.B. Leitfähigkeits-, amperometrische und photometrische Titrationen.

Soweit es photometrische Titrationen schwacher Säuren und Basen betrifft, sind zahlreiche Beispiele in der Literatur vorhanden, die eindeutig den enormen Vorteil dieser Methode demonstrieren. Auch die theoretischen Grundlagen solcher Titrationen sind bearbeitet worden. Ein ausgezeichneter Artikel von Goddu und Hume[2] behandelt diese Art von Titrationen eingehend. Andere Autoren haben wesentlich zu diesem Gebiete beigetragen.[3,4] Eine letztlich erschienene Zusammenfassung von Headridge[5] bringt ein bis auf die jüngste Zeit vollständiges Literaturverzeichnis.

Goddu und Hume[2] haben darauf verwiesen, dass eine ähnliche Behandlung, wie sie für Säure-Basentitrationen gegeben wurde, auch für komplexometrische Titrationen möglich ist. Es wurde jedoch bislang die Theorie komplexometrischer Titrationen ohne Indicator nicht im Detail durchgearbeitet. Wohl aber existiert eine Behandlung für Titrationen mit einem Indicator.[6]

Bereits nur anfänglich angestellte Berechnungen zeigten sehr rasch, dass die Möglichkeiten komplexometrischer Titrationen ohne Indicator und mit photometrischem Endpunke sehr unterschätzt worden sind. Photometrische Endpunktsanzeige *mit* einem Indicator wurden häufig verwendet und zwar immer dann, wenn es sich um einen für das Auge schleppenden Umschlag handelt oder aber, wenn kleine Stoffmengen zu titrieren waren, so dass Indicator und zu titrierendes Metall bereits in vergleichbaren Mengen vorlagen. Auch zur Erzielung höherer Genauigkeit, bei an sich recht gut arbeitenden Indicatoren, wurden solche Titrationen herangezogen.[7–13]

Im Hinblick auf zwei wichtige Punkte jedoch sind Untersuchungen vernachlässigt worden. Einmal sollte es möglich sein, aus der Extrapolationsmethode Kapital zu schlagen und Komplexbildner zur Titration heranziehen, die so schwache Komplexe bilden, dass mit visueller Indication kein befriedigendes Resultat zu erhalten ist. Zweitens aber sollte es möglich sein, dem Selektivitätsprobleme näher zu treten, wie aufgrund der in der oben erwähnten, früheren Arbeit vorauszusehen war. Im Falle einer Titration ohne Indicator ist der zur Titration von zwei Metallen (in derselben Lösung) nötige Unterschied in den beiden Stabilitätskonstanten wesentlich geringer. Beide Möglichkeiten liessen sich aus einigen Beispielen in den Arbeiten erkennen, die über photometrische Titrationen ohne Indicator veröffentlicht wurden.[14–17]

In welchem diese Möglichkeiten praktische Anwendung finden können und was zu ihrer Abschätzung an theoretischem Rüstzeug benötigt wird, soll hier nunmehr behandelt werden.

(A) *Chelometrische Titration eines Metalles ohne Indicator*

Es sei angenommen, dass ein Metall M mit einem Komplexbildner Y titriert wird, wobei ein 1:1 Komplex nach der Gleichung

$$\mathrm{M} + \mathrm{Y} \rightleftharpoons \mathrm{MY} \tag{I}$$

gebildet wird. Ladungszeichen, weil für den Prozess der Komplexbildung unwesentlich, sind weggelassen.

Im allgemeinsten Falle muss angenommen werden, dass alle drei vorhandenen Teilchenarten bei der gewählten Wellenlänge absorbieren. Wird die Gültigkeit von Beer's Gesetz vorausgesetzt, dann ist die gemessene Gesamtabsorption gleich der Summe der Teilabsorptionen, was mathematisch wie folgt ausgedrückt werden kann:

$$\mathrm{A} = \sum_{i} \epsilon_i [\mathrm{i}]\, \mathrm{l} \tag{1}$$

Hier bedeuten A die Totalabsorption, ϵ den molaren Extinktionskoeffizienten, [i] die Konzentration der Spezie *i* in Mol per Liter und l die Länge des Lichtweges. Da während einer Titration die Länge des Lichtweges konstant ist, kann Gleichung (1) für alle weiteren Zwecke vereinfacht werden, indem man $\varepsilon_i \times 1 = k_i$ zusammenfasst, womit sich ergibt:

$$A = \sum_i k_i[\mathrm{i}] \tag{2}$$

In jeder Phase der Titration müssen die folgenden beiden Gleichungen erfüllt sein:

$$C_M = [M] + [MY] \tag{3}$$

$$C_Y = [Y] + [MY] \tag{4}$$

Als weitere Gleichung kommt noch die Definition der Stabilitätskonstante des Komplexes hinzu, nämlich

$$K = \frac{[MY]}{[M][Y]} \tag{5}$$

Es sei ausdrücklich darauf verwiesen, dass es sich hier um die *scheinbare* Stabilitätskonstante handelt, die aus der absoluten Konstante durch einbezug des α- und β-Faktors errechnet werden kann, um dem Einfluss des pH der Lösung sowie der Anwesenheit allenfalls vorhandener, weiterer Komplexbildner Rechnung zu tragen. Über Berechnungen dieser Art siehe.[18,19]

Die bisher gegebenen Gleichungen genügen um eine photometrische Titrationskurve zu berechnen. Im einzelnen verläuft die Ableitung wie folgt. Gemäss (2) gilt für den in (I) dargelegten Fall

$$A = [M]k_M + [MY]k_{MY} + [Y]k_Y \tag{6}$$

Für theoretische Studien ist es vorteilhaft, anstatt Milliliter Masslösung auf der Abszisse den Komplexationgrad “a” aufzutragen, der gemäss folgender Gleichung definiert ist:

$$\mathrm{a} = \frac{C_Y}{C_M} \tag{7}$$

Kombination von (7) mit (3), (4) und (6) ergibt

$$A = C_M[k_{MY} + k_Y(\mathrm{a} - 1)] + (k_M + k_Y - k_{MY})[M] \tag{8}$$

worin nunmehr auch [M] als Funktion von a auszudrücken ist. Dies geschieht, indem man in (5) durch Heranziehen von (3) und (4) [MY] und [Y] eliminiert und nach [M] auflöst, was folgenden Ausdruck liefert

$$[M] = \frac{[KC_M(1 - \mathrm{a}) - 1] + \sqrt{[KC_M(1 - \mathrm{a}) - 1]^2 + 4KC_M}}{2K} \tag{9}$$

Nur das positive Zeichen der Wurzel hat physikalische Bedeutung, was man leicht zeigen kann, da für a = 0 die Lösung der Gleichung sein muss $[M] = C_M$. Kombination von (8) und (9) ergibt den endgültigen Ausdruck zur Berechnung der Titrationskurve

$$\begin{aligned} A = \frac{1}{2K}\Big\{2KC_M[k_{MY} + k_Y(\mathrm{a} - 1)] + (k_M + k_Y - k_{MY})\Big[KC_M(1 - \mathrm{a}) - \\ - 1 + \sqrt{[kC_M(1 - \mathrm{a}) - 1]^2 + 4KC_M}\Big]\Big\} \end{aligned} \tag{10}$$

Die Anordnung der Glieder in (10) ist so bewerkstelligt, dass man leicht erkennt, dass bei gegebenen Absorptionkoeffizienten der Verlauf der Kurve in der Hauptsache vom Parameter KC_M abhängt.

In vielen praktischen Fällen wird der Komplexbildner farblos sein und u.U. auch das Metallion, oder aber man kann die Wellenlänge des eingestrahlten Lichtes so wählen, dass diese beiden Teilchenarten nicht absorbieren. Dann vereinfacht sich Gleichung (10) wegen $k_M = k_Y = 0$ zu

$$A = k_{MY}(C_M - [M]) \tag{11}$$

worin [M] nach (9) zu berechnen ist.

Einige Titrationskurven für wechselnde Werte von KC_M sind in Abbildung 1, 2 u. 3 gezeigt. Je niederer der Wert von KC_M desto eher weicht die Titrationskurve am Anfang von einer Geraden ab und desto später nach dem Endpunkt geht sie in eine Horizontale über. Theoretisch können äusserst geringe Werte von KC_M toleriert und immer noch brauchbare Resultate erhalten werden, wenn man die Extrapolation mit Teilen der Kurve genügend nahe dem Anfangspunkt und weit genug nach dem Endpunkte durchführt. Soweit es das Anfangsstück betrifft treten in der Praxis jedoch Schwierigkeiten auf, da die Absorptionsmessungen sehr kleine oder sehr grosse Werte aufweisen und wenig präzise sind. Für das Endstück ist zu bedenken, dass der Weg, mit a zu operierem, gleichbedeutend ist mit einer Vernachlässigung der durch den Reagenszusatz bedingten Verdünnung (siehe später).

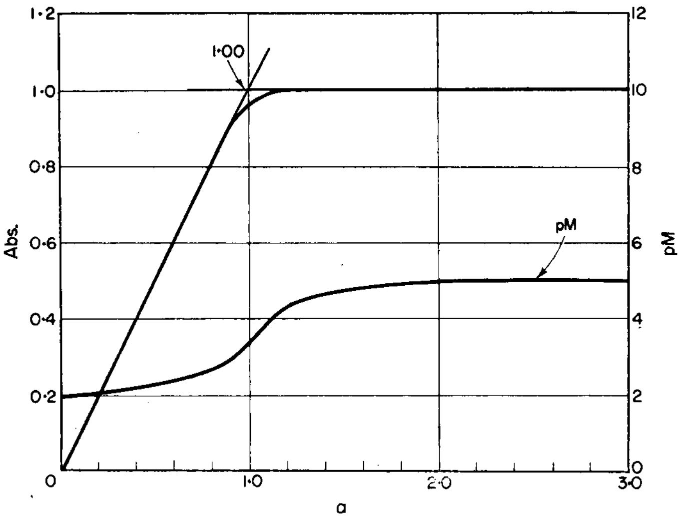

ABBILDUNG 1.—Titrationskurve für die Bestimmung eines einzelnen Metalles. $K = 10^5$, $C_M = 10^{-2}$, $k_{MY} = 100$, $KC_M = 1000$.

Formel (11) gestattet es, unter Annahme plausibler Bedingungen, für KC_M eine rohen Grenzwert zu berechnen, mit dem ein noch brauchbares Resultat erhalten werden kann.

Es sei angenommen, dass die Kurvatur am Beginn so gering ist, dass zwischen dem Punkte a = 0 und a = 0,5 die Annäherung an eine Gerade praktisch hinreichend gegeben ist. Nach dem Äquivalenzpunkt sei die Kurve als horizontal angesehen, wenn der Anstieg zwischen a = 2 und a = 2,5 nur mehr 1 % beträgt.

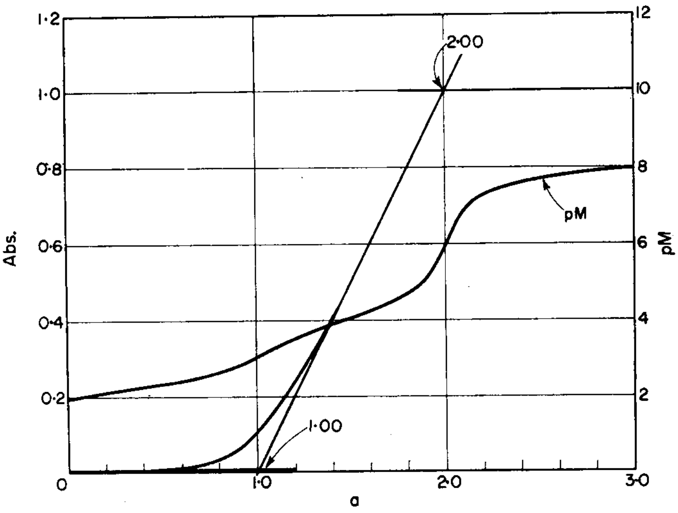

Abbildung 2.—Titrationskurve für die Bestimmung eines einzelnen Metalles. $K = 10^4$, $C_M = 10^{-2}$, $k_{MY} = 100$, $KC_M = 100$.

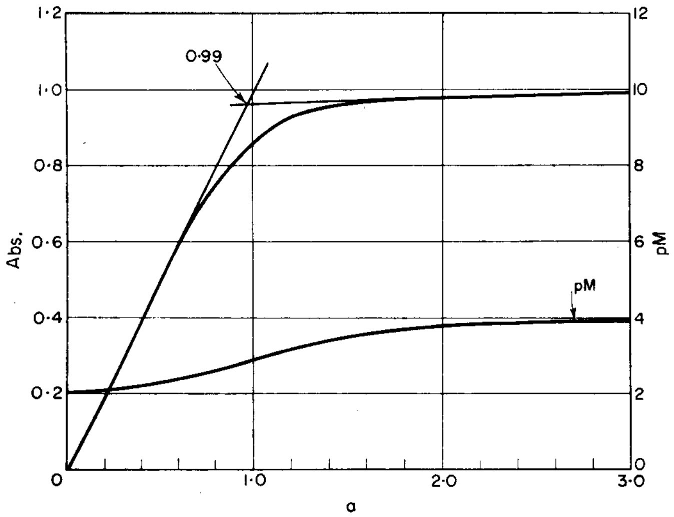

Abbildung 3.—Titrationskurve für die Bestimmung eines einzelnen Metalles. $K = 5 \times 10^3$, $C_M = 10^{-2}$, $k_{MY} = 100$, $KC_M = 50$.

Werden diese Annahmen auf den verinfachten Fall der Gleichung (11) angewandt, ergibt sich folgendes. Die erste Gerade ist gegeben durch zwei Punkte mit den Koordinaten $a = 0$, $A = 0$ und $a = 0{,}5$, $A = A_{0,5}$ Hierbei ist $A_{0,5}$ die Absorption im Punkte $a = 0{,}5$; sie kann nach (11) berechnet werden. Die zweite Gerade ist gegeben durch die beiden Punkte $a = 2$, $A = A_2$ und $a = 2{,}5$, $A = A_{2,5}$. Zusätzlich muss die Bedingung erfüllt sein, dass sich die beiden Geraden im Punkte mit den Koordinaten $a = 1$ und $A = A_1$ schneiden. Es muss nun gefunden werden, für welchen Wert von KC_M diese Bedingung erfüllt ist.

Die erste Gerade wird durch die Gleichung wiedergegeben

$$A = 2A_{0,5}a \tag{12}$$

die zweite durch

$$A = A_2 (0,96 + 0,02a) \qquad (13)$$

da ja $A_{2,5} = 1,01\ A_2$ ist, gemäss der Annahme, dass die Zunahme der Absorption zwischen den beiden Punkten nur 1 % beträgt.

Wird (12) gleich (13) und in dem resultierenden Ausdruck a = 1 gesetzt, so erhält man die Bedingungsgleichung

$$2A_{0,5} = 0,98\ A_2 \qquad (14)$$

Errechnet man aus (11) die entsprechenden Werte für $A_{0,5}$ und A_2, setzt sie in (14) ein und löst nach KC_M auf, so erhält man den Wert $KC_M \simeq 50$.

Dies ist ein erstaunlich niederer Wert. Demnach kann z.B. eine 0,01 molare Metallionenlösung erfolgreich titriert werden, wenn die Stabilitätskonstante des gebildeten Komplexes nur 5 000 beträgt. Eine Kurve mit diesem Werte wurde berechnet und ist in Abbildung 3 dargestellt. Die Abbildung enhält auch die entsprechende pM-Kurve [berechnet mittels (9)]. Es ist klar zu erkennen, dass eine derartige pM-Kurve keinerlei Hoffnung auf einen auch nur einigermassen brauchbaren Endpunkt offen lässt, was immer auch die Methode seiner Festlegung sei.

Natürlich ist das durchgerechnete Beispiel nur ein Idealfall. Es wurde angenommen, dass k_{MY} genügend hoch liegt. Der Einfluss dieses Parameters spielt in der Praxis eine erhebliche Rolle. Man kann jedoch durch geeignete Wahl der Lichweglänge diese Grösse in ziemlich weiten Grenzen variieren. Wesentlich schwerwiegender ist die Idealisierung, die sich durch Verwendung von a als Abszissengrösse ergibt. In der Praxis kann a nicht verwendet werden, da ja zu seiner Berechnung die Kenntnis von C_M benötigt wird; die Ermittlung dieser Grösse jedoch ist zweck der ganzen Analyse. Für den Fall einer tatsächlichen Titration können nur Milliliter Masslösung auf der Abszisse aufgetragen werden. Um dieser Sachlage gerecht zu werden, müssen die Formeln modifiziert werden. Dies geschieht auf folgendem Wege.

C_M ist nicht mehr länger konstant, sondern ändert sich im Verlauf der Titration und muss für jede Zugabe von Masslösung gemäss folgendem Ausdruck berechnet werden:

$$C_M = \frac{C_M{}^0 V}{V + b} \qquad (15)$$

Worin $C_M{}^0$ die Anfangskonzentration, V das Anfangsvolum und b das Volum an Millilitern zugesetzter Masslösung bedeuten.

C_Y lässt sich wie folgt ausdrücken

$$C_Y = \frac{mb}{V + b} \qquad (16)$$

worin ausser den schon oben beschriebenen Symbolen noch m aufscheint, welches die Molarität der Masslösung bedeutet.

Die Kombination von (7), (15) und (16) ergibt nun den Ausdruck

$$a = \frac{mb}{C_M{}^0 V} \qquad (17)$$

der in allen zuständigen Gleichungen einzusetzen ist. Geschieht dies, so erhält man für die Berechnung der Titrationskurve folgende Gleichung

$$A = \frac{C_M{}^0 V}{V + b}\left[k_{MY} + k_Y\left(\frac{mb}{C_M{}^0 V} - 1\right)\right] + (k_M + k_Y - k_{MY})[M] \tag{18}$$

woring [M] nach folgender Formel zu berechnen ist:

$$[M] = \frac{-\left[KC_M{}^0 \frac{V}{V+b}\left(\frac{mb}{C_M{}^0 V} - 1\right) + 1\right] + \sqrt{\left[KC_M{}^0 \frac{V}{V+b}\left(\frac{mb}{C_M{}^0 V} - 1\right) + 1\right]^2 + 4KC_M{}^0 \frac{V}{V+b}}}{2K} \tag{19}$$

Für den vereinfachten Fall, dass nur die Spezie MY absorbiert ergibt sich

$$A = k_{MY}\left(\frac{C_M{}^0 V}{V + b} - [M]\right) \tag{20}$$

worin [M] ebenfalls durch (19) ausgedrückt werden muss.

Die Gleichung ist ungleich komplizierter als (11); sie geht für die Bedingung $V \gg b$ in (11) über.

Ein Versuch, einen Mindestwert für $KC_M{}^0$ zu berechnen, scheitert daran, dass im Zuge der Rechnung Gleichungen von so hoher Ordnung auftreten, dass ihre Lösung algebraisch nicht mehr möglich ist. Es ist daher einfacher vom Falle der vernachlässigten Verdünnung (operieren mit a) einen plausiblen Schluss zu ziehen und anzunehmen, dass ein $KC_M{}^0$-Wert von etwa 200–500 noch gute Resultate liefern wird und diesen Schluss dann experimentell zu prüfen.

Wie schon oben dargelegt, wird es mit fallendem KC_M-Wert nötig, die Extrapolation der ersten Geraden so nahe am Anfangspunkte zu beginnen als nur möglich. Für die zweite Linie wird man recht weit hinter den Äquivalenzpunkt gehen. Letzteres jedoch bedeutet Zugabe einer beträchtlichen Menge an Masslösung, selbst wenn diese in recht hoher Konzentration vorliegt. Im allgemeinen kann man bei diesen Arten von Titrationen der Verdünnung Rechnung tragen, indem man eine Korrektur anbringt. Dies geschieht durch Multiplizieren von A mit dem Faktor $(V + b)/V$. Wird jedoch ein sehr schwacher Komplex als Grundlage der Titration herangezogen, so muss bedacht werden, dass die Verdünnung in zwei verschiedenen Richtungen wirkt. Einmal wird die abgelesene Absorption geringer sein als Folge einer lediglichen Verdünnung der "Farbe" der Lösung. Anbringen der Korrektur trägt diesem Umstande völlig Rechnung. Zum anderen wird jedoch in der verdünnteren Lösung der Komplex stärker dissoziieren. Diese Verschiebung des Gleichgewichtes wird natürlich nicht korrigiert.

Ausser in einer sehr ungünstigen Situation ist jedoch dieser Faktor nicht von zu grossem Einfluss, wie man aus Abbildung 4 erkennen kann. Ohne Korrektur für die Verdünnung ist der gefundene Wert wesentlich zu nieder (9,25 statt 10,00). Nach Korrektur der Kurve ergibt sich 10,19 was nur um 2% zu hoch ist. Die pM-Kurve ist für eine Endpunktsfestlegung, nach welcher Methode auch immer vorgegangen wird, absolut unbrauchbar.

Deshalb ergibt sich hier also im allgemeinen die Forderung, mit möglichst konzentrierten Masslösungen zu arbeiten, nicht nur aus dem sonst üblichen Grunde, dass das Anbringen der Korrektur zeitraubend und umständlich ist, sondern vielmehr, weil die Korrektur die Verzerrung der Kurve einfach nicht völlig beheben kann. Doch kann diese Kompensation nicht beliebig weit getrieben werden. Einmal gebietet die Löslichkeit des Titrationsmittels ein Halt, zum anderen benötigt man feiner geteilte Büretten mit kleinerem Fassungsraum, was ebenfalls begrenzt ist.

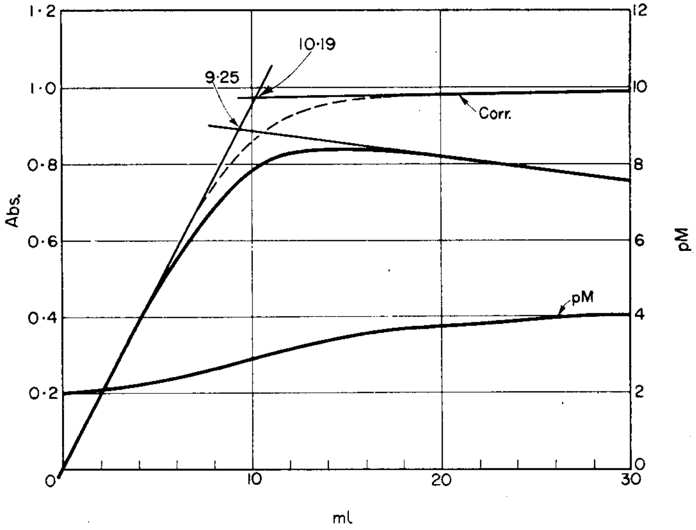

ABBILDUNG 4.—Titrationskurve für die Bestimmung eines einzelnen Metalles ohne und mit Berücksichtigung der Verdünnung durch das Titrationsmittel.
$K = 5 \times 10^3$, $C_M^0 = 10^{-2}$, $k_{MY} = 100$, $KC_M = 50$, V = 100 ml, m = 10^{-1}.

(B) *Chelometrische Titration von zwei Metallen nacheinander in derselben Lösung, ohne Verwendung eines Indikators*

Wenn zwei Metalle zu titrieren sind, werden die mathematischen Ableitungen wesentlich komplizierter, weshalb hier nur auf die Behandlung des Falles eingegangen wird, wo die Verdünnung vernachlässigt werden kann.

Die Stabilitätskonstanten der Komplexe der beiden zu titrierenden Metalle M und N sind gegeben durch

$$K_M = \frac{[MY]}{[M][Y]} \tag{21}$$

$$K_N = \frac{[NY]}{[N][Y]} \tag{22}$$

In jeder Phase der Titration müssend die folgenden drei Gleichungen erfüllt sein

$$C_M = [M] + [MY] \tag{23}$$

$$C_N = [N] + [NY] \tag{24}$$

$$C_Y = [Y] + [MY] + [NY] \tag{25}$$

Es ist offenkundig, dass die Möglichkeit, beide Metall in derselben Lösung *hintereinander* zu titrieren, einmal vom Unterschied in den Stabilitätskonstanten der

Komplexe abhängt. Um diesem Umstande Rechnung zu tragen, wird der Quotient "Q" eingeführt, definiert gemäss

$$Q = \frac{K_M}{K_N} \tag{26}$$

Zum anderen wird die Titration beider Metalle nur möglich sein, wenn die zu titrierenden Spezies und/oder die gebildeten Komplexe optisch differenziert werden können, sodass zwei klar unterscheidbare Knicke in der Titrationskurve (die nun drei Äste aufweisen muss) auftreten. Ob und in welchem Masse dies der Fall ist, hängt von den k-Werten der beteiligten Teilchenarten ab, denn Gleichung (2) ist ja auch für diesen Fall gültig.

Unter Verwendung der einschlägigen Gleichungen lässt sich der Ausdruck zur Berechnung der Titrationskurve wie folgt ableiten.

In Gleichung (26) werden alle Ausdrücke so ersetzt, dass nur mehr [M] als Variable aufscheint. Hierzu erhält man aus (23) $[MY] = C_M - [M]$. Aus (21) errechnet sich $[Y] = (C_M - [M])/[M]K_M$. Dies in Kombination mit (24) und (25) ergibt $[NY] = C_Y - (C_M - [M]) - (C_M - [M])/[M]K_M$, beziehungsweise $[N] = C_N - C_Y + (C_M - [M]) + (C_M - [M])/[M]K_M$ Einsetzen in (26) führt schliesslich zu

$$Q = \frac{C_M - [M]}{[M]} \times \frac{C_N - C_Y + (C_M - [M]) + \dfrac{C_M - [M]}{[M]K_M}}{C_Y - (C_M - [M]) - \dfrac{C_M - [M]}{[M]K_M}} \tag{27}$$

Ein Versuch, [M] als Funktion von C_Y auszudrücken, führt zu einer Gleichung dritten Grades in [M], was für praktisches Arbeiten unbrauchbar ist. Um die Titrationskurve zu berechnen löst man daher nach C_Y auf und berechnet umgekehrt den für verschiedene [M]-Werte sich ergebenden Betrag an Titrationsmittel und gelangt so zum gewünschten Ziele. Die so erhaltene Formel lautet

$$C_Y = \frac{C_M - [M]}{[M]} \left(\frac{C_N}{Q + \dfrac{C_M - [M]}{[M]}} + [M] + \frac{1}{K_M} \right) \tag{28}$$

Führt man weiters noch den Titrationsgrad "a" gemäss (7) definiert ein, so resultiert

$$a = \frac{1}{C_M} \frac{C_M - [M]}{[M]} \left(\frac{C_N}{Q + \dfrac{C_M - [M]}{[M]}} + [M] + \frac{1}{K_M} \right). \tag{29}$$

Zur Berechnung der Absorption seien die folgenden, zum Teil vereinfachenden Annahmen gemacht. Metall M bilde den stabileren Komplex, d.h. es wird also zuerst titriert. Die einzige, bei der gewählten Wellenlänge absorbierende Spezie ist NY. Dann ergibt sich unter Anwendung von (2) und entsprechendem Ersatz von [NY]

$$A = k_{NY}[NY] = k_{NY}\left[QC_M - (C_M - [M]) - \frac{C_M - [M]}{[M]K_M} \right] \tag{30}$$

Verschiedene [M]-Werte werden angenommen und mittels (29) wird a berechnet; die so erhaltenen Werte für a sowie die korrespondierenden [M]-Werte werden in (30) eingesetzt und liefern die Absorptionen, sodass die Titrationskurve konstruiert werden kann. Kurven für verschiedene Werte von Q und K_M sind für äquimolare Mischungen der beiden Metalle berechnet worden und in den Abbildungen 5–9 dargestellt.

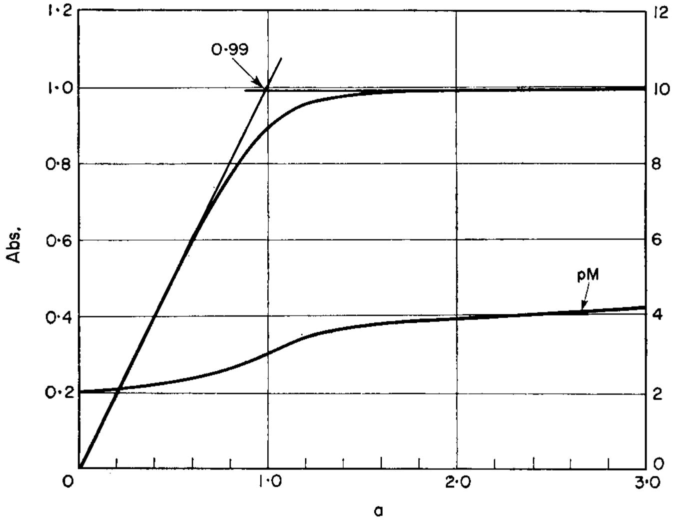

ABBILDUNG 5.—Titrationskurve zur Bestimmung von zwei Metallen. $K_M = 10^{10}$, $K_N = 10^7$, $Q = 1000$, $C_M = C_N = 10^{-2}$, $k_M = k_N = k_{MY} = 0$, $k_{NY} = 100$.

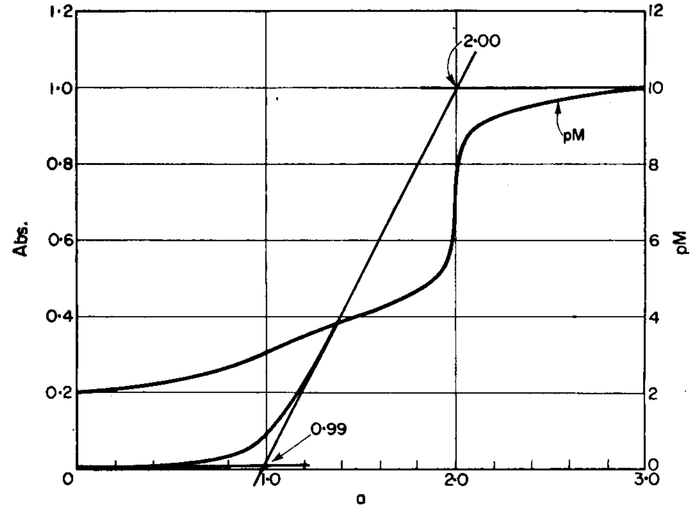

ABBILDUNG 6.—Titrationskurve zur Bestimmung von zwei Metallen. $K_M = 10^{10}$, $K_N = 10^8$, $Q = 100$, $C_M = C_N = 10^{-2}$, $k_M = k_N = k_{MY} = 0$, $k_{NY} = 100$.

Zum Vergleich sind auch die entsprechenden pM-Kurven eingezeichnet. Auch hier zeigt sich wieder deutlich die Überlegenheit der photometrischen Titration.

Die Verhältnisse liegen hier jedoch wesentlich komplizierter. Der Kurvenverlauf ist einmal abhängig von Q. Das heisst, je grösser Q ist, desto besser lassen sich die beiden Metall getrennt erfassen. Zum anderen spielt aber auch die Grösse von K_M

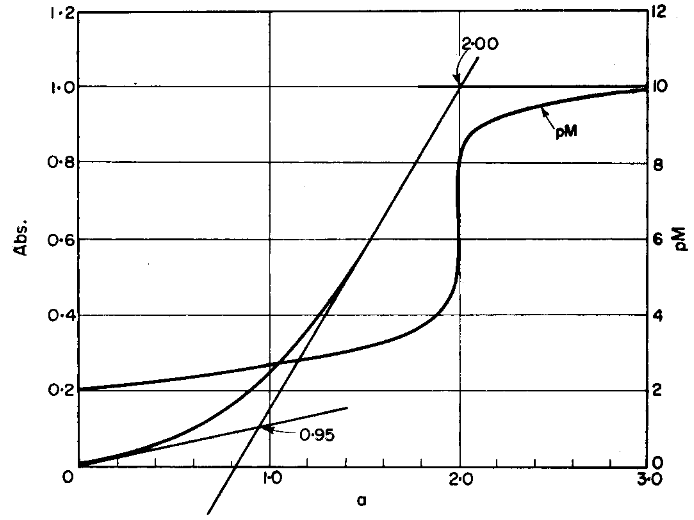

Abbildung 7.—Titrationskurve zur Bestimmung von zwei Metallen. $K_M = 10^{10}$, $K_N = 10^9$, $Q = 10$, $C_M = C_N = 10^{-2}$, $k_M = k_N = k_{MY} = 0$, $k_{NY} = 100$.

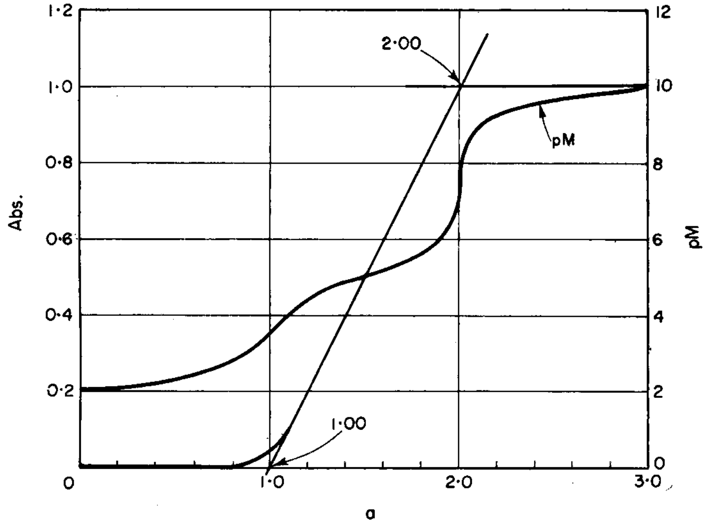

Abbildung 8.—Titrationskurve zur Bestimmung von zwei Metallen. $K_M = 10^8$, $K_N = 10^6$ $Q = 100$, $C_M = C_N = 10^{-2}$ $k_M = k_N = k_{MY} = 0$, $k_{NY} = 100$.

eine entscheidende Rolle. Ist der Wert dieses Parameters klein (absolut und noch wesentlicher im Vergleich zu C_M) so wird, wie zu erwarten, die Lokalisierung des ersten Endpunktes schwierig.

Es ergibt sich für äquimolare Gemische der immerhin erstaunlich niedere, ungefähre Mindestwert für Q (bei annehmbar hohem K_M) von etwa 100. Auch dies ist ein unter Idealbedingungen abgeleiteter Wert und entsprechende Modifikationen sind nötig, wenn die Konzentrations-verhältnisse der beiden Metalle und die k-Werte ungünstig liegen. Aber auch dann ist die photometrische Titration der visuellen oder anderen, ohne Extrapolation arbeitenden Titrationen deutlich überlegen.

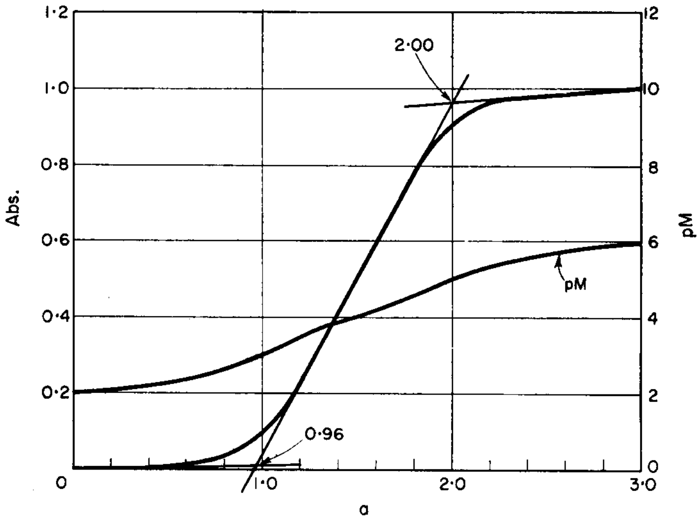

ABBILDUNG 9.—Titrationskurve zur Bestimmung von zwei Metallen. $K_M = 10^6$, $K_N = 10^4$ $Q = 100$. $C_M = C_N = 10^{-2}$ $k_M = k_N = k_{MY} = 0$, $k_{NY} = 100$.

Wird die Verdünnung nicht vernachlässigt, so müssen wie im einfachen Falle der Titration eines einzelnen Metalles die Konzentrationen der drei Reaktanten durch Ausdrücke gemäss (15) und (16) ersetzt werden. Dies führt zu einer Gleichung, die zwar algebraisch gehandhabt werden kann, wobei aber der Rechenaufwand so gross ist, dass der Wert der gewonnenen Erkenntnisse mit der hineingesteckten Arbeit kaum mehr vergleichbar ist. Man muss bedenken, dass die interessantesten Fälle jene sind, bei denen man sich nahe den tolerierbaren Grenzen befindet. Unter diesen Umständen spielen kleine Änderungen in der Konzentration und vor allem in den scheinbaren Stabilitätskonstanten eine recht grosse Rolle. Die scheinbaren Stabilitätskonstanten können in vielen Fällen nicht berechnet werden. In einem tatsächlichen Titrationsgemisch ist die ionale Stärke kaum gleich der, für welche die absoluten Konstanten bekannt sind. Anwesenheit zusätzlicher auch nur schwacher Komplexbildner verursacht weitere Änderungen, die oftmals mangels der nötigen Daten nicht rechnerisch erfasst werden können. Alle Parameter unterliegen während der Titration kleinen Änderungen. Diese und noch andere Einflüsse, wie z.B. das auch nur teilweise Auftreten von sauren und Hydroxokomplexen, machen eine exakte Berechnung schwierigm, wenn nicht überhaupt unmöglich. Es ist wesentlich einfacher für ein im fraglichen Bereich liegendes System, anstatt es durchzurechnen, die Prüfung im Experiment heranzuziehen.

Nichtsdestoweniger aber sind die abgeleiteten Formel für rohe Abschätzungen von grossem Wert. Vor allem aber ermutigen sie Systeme zu untersuchen, die man ansonsten als aussichtslos nie in näheren Betracht gezogen hätte.

(C) *Betrachtungen über einige weitere Möglichkeiten*

Die sich aus den obigen, theoretischen Betrachtungen ergebenden Möglichkeiten können, soweit es praktische Anwendungen betrifft, noch vorteilhaft erweitert werden, indem man die beschriebenen Methoden mit anderen kombiniert. Das lässt sich z.B. am System Kupfer-Nickel zeigen. Wie schon in früher erschienenen Arbeiten gezeigt wurde,[20,21] kann Kupfer sehr leicht und störungsfrei neben Nickel (und anderen Metallionen) bestimmt werden, wenn man mit Trien bei pH 5–6 photometrisch ohne Indicator titriert. Nickel anschliessend durch weitere Zugabe von Trien zu erfassen ist nicht gut möglich, da die durch das Nickel hervorgerufenen Absorptionsänderungen (auch in anderen pH-Bereichen) zu gering sind. Wohl aber kann man durch einfache Zugabe von Ammoniak und Murexid Bedingungen schaffen, unter denen photometrisch ein scharfer Endpunkt resultiert. Dergestalt können Kupfer und Nickel in derselben Lösung hintereinander titriert werden. Ähnliche Möglichkeiten sind für weitere Systeme in Ausarbeitung und über die Resultate wird später berichtet werden.

Man kann weiters zwei Metalle mit zwei verschiedenen Indicatoren und wenn nötig zwei verschiedenen Masslösungen hintereinander titrieren, was visuell praktisch unmöglich ist, da in fast allen Fällen der erste Indicator das Erkennen des zweiten Umschlages für das menschliche Auge unmöglich macht. Die Photozelle des Titrationsgerätes jedoch kann sehr wohl die verschiedenen Änderungen auseinanderhalten.

Die oben abgeleitete Tatsache, dass man zwei Metalle getrennt titrieren kann, auch wenn der Unterschied in den Stabilitätskonstanten nur relativ gering ist, öffnet die Möglichkeit zum Einsatz neuer Maskierungsmittel. Es können nämlich nunmehr als Maskierungsmittel Komplexbildner herangezogen werden, bei denen die Stabilität des Maskierungskomplexes zu gering ist, um eine visuelle Titration zu ermöglichen, da der erzielten Unterschied in der Stabilität der Titrationskomplexe nicht genügend gross wird.

Die bisher genannten Möglichkeiten, sowie deren Kombination und noch weitere mehr können nutzbringend verwendet werden, um dem Selektivitätsproblem chelometrischer Titrationen erfolgreich näher zu treten. Über ihre praktische Anwendung wird beim Studium verschiedener Systeme in folgenden Mitteilungen dieser Reihe berichtet werden.

Die vorliegende Arbeit wurde mit Unterstützung der National Science Foundation durchgeführt.

Summary—The characteristics of chelatometric titrations with a photometric end-point without an indicator are discussed, and formulae are derived for the calculation of the titration curves. It is shown that in titrating a single metal a considerably smaller stability of the titration complex can be tolerated than in other methods of fixing the end-point which do not depend on extrapolation. For the titration of two metals in the same solution, in succession, a difference in the stability constants of a factor of about 100 to 200 is sufficient. The possibilities of using the method in combination with other end-point methods are discussed, and problems of selectivity are considered.

Résumé—L'auteur discute des caractéristiques des titrages complexométriques avec point équivalent déterminé par photométrie, sans indicateur; les formules des courbes de titrages sont établies L'auteur montre que, pour titrer un métal seul, une faible stabilité du complexe de titrage peut être tolérée, de même que dans d'autres méthodes de fixation du point équivalent qui ne dépendent pas de l'extrapolation. Pour le titrage successif de deux métaux dans la même solution, une différence des constantes de stabilité d'un facteur 100 à 200 environ est suffisante. Les possibilités d'utiliser cette méthode combinée avec d'autres méthodes de détection du point équivalent sont discutées, les problèmes de sélectivité sont considérés.

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THE ANION-EXCHANGE SEPARATION OF TECHNETIUM, RHENIUM AND MANGANESE

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Summary—An anion-exchange method for the separation of technetium, rhenium and manganese is outlined. After sorption on the resin column, manganese is first eluted with hydrochloric acid, rhenium with ammonium thiocyanate in hydrochloric acid, and technetium by means of nitric acid. In the eluates rhenium is determined colorimetrically and technetium radiochemically. As little as 10 μg of technetium in the form of potassium pertechnetate can be separated from 15 mg of manganese as potassium permanganate and 0·8 mg of rhenium in the form of potassium perrhenate.

IN 1955, Gerlit,[1] discussing the chemical properties of technetium, remarked on the lack of analytical procedures for the element. Since that date the position has improved somewhat and publications have appeared dealing with a number of aspects of the analytical chemistry of the element.[2] One aspect of the analytical chemistry which, however, appears to have had scant attention is that associated with the ion-exchange behaviour of the element, particularly in relation to the other elements of Group VIIa of the Periodic Classification, *i.e.* manganese and rhenium.

The first ion-exchange study of technetium and rhenium was carried out by Atteberry and Boyd[3] using ion-exchange resin Dowex 2. Both elements in this work were sorbed on a resin column 0·72 cm^2 × 51 cm and eluted at a flow rate of 1·7 ml/min with ammonium sulphate and thiocyanate at pH 8·3–8·5. By this procedure a clear separation of rhenium and technetium was not obtained. The authors further state that as manganese in the form of permanganate reacts with the resin, no experiments were carried out with all three elements.

The ion-exchange separation of technetium and molybdenum has also been investigated by Huffman, Oswalt and Williams,[4] and the separation of technetium and rhenium on resin Dowex 1, using perchloric acid as eluent was studied by Sen Sarma *et al.*[5] These latter workers found that the separation was not clean and showed a residual tailing effect which could not be eliminated. Other attempts at the separation of technetium and rhenium have been carried out,[6] but as pointed out,[7] they suffer from shortcomings such as low separation factors, low yields and failure at trace levels.

This paper describes the results of investigations carried out on the anion-exchange separation of manganese, technetium and rhenium.

EXPERIMENTAL

Reagents and apparatus

Amberlite IRA 400 *resin* was used. After grinding in a mortar and sieving, particles in the range 72–100 B.S.S. mesh were washed thoroughly with 2*N* nitric acid and then converted into the chloride form.

Potassium pertechnetate: An aqueous solution containing 10 μg/0·1 ml was used.

Potassium perrhenate: An aqueous solution containing 2·5 mg/ml. was used.

Potassium permanganate: An aqueous solution containing 10 mg/ml. was used.

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4π Gas flow counter: For counting the soft β particles (0·29 MeV) emitted by ^{99}Tc, a 4π Gas Flow Counter (Labgear Type D4126) was used. As a check, some experiments were carried out with a Scintillation Counter (Ekco Ltd., Type N664A).

INVESTIGATIONS

Numerous attempts were made to separate rhenium and technetium by sorbing them on the resin as pertechnetate and perrhenate and eluting with different eluents. Elution with 0·1*N* perchloric acid[5] showed some success, but elution curves overlapped. Attempts using mixed solvents such as alcohol–water and perchloric acid or acetone–water and perchloric acid gave elution curves inferior to water and perchloric acid alone. In the report to the International Conference on the Peaceful Uses of Atomic Energy,[1] Gerlit states that pertechnetate in strong hydrochloric acid is reduced to the 4-valent state. An attempt was made to use this as a basis of separation of technetium and rhenium, but without success. Complexing eluents were next investigated, and of these the most successful were potassium xanthate and ammonium thiocyanate. The former appeared to separate the two elements, but as the reagent exerts a very strong quenching effect radiochemically, measurement of technetium was never certain and the method was abandoned. The most satisfactory separation was achieved with ammonium thiocyanate.

Separation of Mn, Tc and Re using ammonium thiocyanate

(*a*) *Preparation of the test sample.* Prepare the elements for separation by dissolving them, in the permanganate, pertechnetate and perrhenate forms, in 5 ml of water. Acidify with hydrochloric acid until the normality is 0·1–0·3 in hydrochloric acid. Add Perhydrol to reduce permanganate to manganese chloride and remove excess Perhydrol by heating. The test sample is now ready for transference to the ion-exchange column.

(*b*) *Operation of the column.* Transfer the prepared test sample to a column of Amberlite IRA 400 resin of dimensions 0·2 cm^2 × 2·5–3 cm. Wash out the vessel containing the test sample with approximately 3 ml of 0·1–0·2*N* hydrochloric acid. When the level of the liquid reaches the top of the resin, using a flow rate of 1 ml/15 min, wash with 0·1–0·2*N* hydrochloric acid at a rate of 1 ml/6 min to elute manganese. Manganese in the reduced form is not sorbed on the resin, and complete removal is effected in 20 ml of eluate.

To separate rhenium and technetium, add 5% ammonium thiocyanate in 0·1–0·2*N* hydrochloric acid to the column and elute at a rate of 1 ml/15 min. Under the conditions outlined all of the rhenium is eluted in 15–20 ml of solution (Fig. 1).

Wash the column with 10 ml of water to remove ammonium thiocyanate and follow with 20 ml of 0·1*N* nitric acid at a flow rate of 1 ml/10 min to remove the CNS$^-$ remaining in the column (*cf.* Note 4). Change the concentration of nitric acid to 4*N* and elute at a flow rate of 1 ml/15 min to remove technetium from the column (Fig. 1).

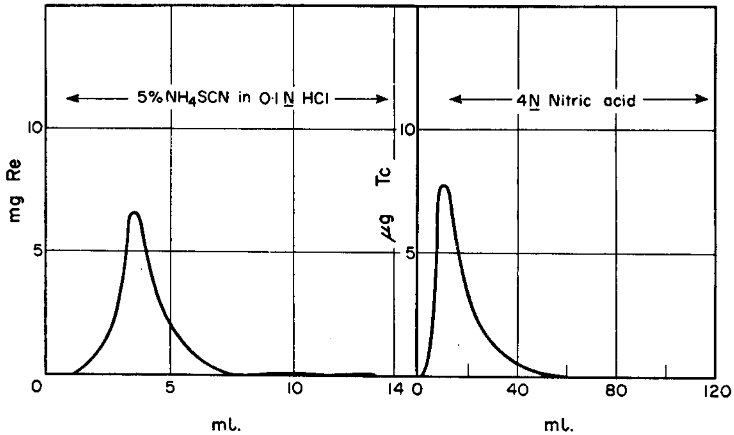

Fig. 1.—Separation of rhenium and technetium. Column: 2·5 cm × 0·2 cm^2. Amberlite IRA 400, mesh 72-100. Flow rate: 1 ml/15 min.

Notes

1. After 20 ml of 0·1–0·2N hydrochloric acid had passed through the column to elute manganese, no positive test for the element was ever found in subsequent eluates.
2. Technetium was never detected in the manganese or rhenium eluates.
3. When technetium is sorbed on the column as pertechnetate, a small fraction (0·1–0·2 %) always passes through. This has also been observed by other workers.[4]
4. When 0·1N nitric acid is used to elute technetium, it reacts with the CNS^- remaining in the column, and a ring of NO_2 moves down the column. If the nitric acid is passed down the column at a fast rate, the reaction is vigorous and bubbles are produced. With this treatment usually no technetium is eluted, but on occasions 0·05–0·1 % was washed out.
5. With 40 ml of 4N nitric acid, more than 90 % of technetium is removed from the column (Fig. 1). For complete removal 200 ml of eluent is required.
6. The resin particle size has an effect on the elution rate of technetium. For resin particle sizes in the range 52–72 B.S.S., extraction was slower and incomplete. At particle size below 52 B.S.S. very large amounts of nitric acid were required to remove technetium, and removal was incomplete. Retention of technetium by the column was also observed if the same resin column was used too often.
7. Elution of the three elements requires a total time of about 24 hr.

DETERMINATION OF TECHNETIUM AND RHENIUM

1. *Technetium*

Numerous experiments were carried out to investigate possible ways of determining technetium after its removal form the ion-exchange column. A difficulty in the determination is that the element is volatile in solutions of sulphuric and perchloric acid. Chloride is also a strong quenching agent in scintillation counting. Mounting of the sample for counting was also found important, if reproducible results were to be obtained. The most satisfactory procedure using the proportional counter is outlined below.

Procedure: Evaporate the nitric acid solution from the column, containing technetium, under an infrared lamp until the volume is about 0·5 ml. The temperature of the solution should always be less than 90°.

Dilute the volume to 1 ml in a graduated flask and deliver 0·05 ml of this solution to a piece of filter paper, ensuring that the diameter of the spot is never greater than about 1 cm.

Place in the proportional counter and measure.

Notes

1. Under the conditions outlined reproducibility was good.
2. With the proportional counter a background of 90–100 counts/100 sec was usually obtained and 0·5 μg Tc in 0·05 ml gave a count of around 4000/100 sec.
3. Many salts quench counting, and their presence must be avoided. In the procedure above a little quenching is observed by, it is thought, solubles extracted from the resin by the nitric acid. This was determined and found to be less than 10 %.

An attempt was made to determine technetium spectrophotometrically in the nitric acid eluate. Technetium as pertechnetate absorbs at very short wavelength. Rulfs and Meinke[8] determined the absorption spectrum of pertechnetate in hydrochloric acid and found two absorption peaks at 290 mμ and 247 mμ. This was later confirmed.[9] In the present work, since it was found that nitric acid absorbs in the same region of the ultraviolet as pertechnetate, it was the intention to expel nitric acid and re-dissolve in hydrochloric acid. The absorption spectrum of potassium pertechnetate in 0·1N hydrochloric against a 0·1N hydrochloric acid blank was determined. This shows a clear absorption peak at 206 mμ. No peaks at 247 or 290 mμ were obtained. When, however, attempts were made to use this method for the determination of technetium, difficulties were encountered. On evaporation of nitric acid, traces always remained which caused fluctuations in the results. Stronger heating to remove the traces of nitric acid led to the danger of loss of some technetium. Using this method, the error was around 20 %. The thiocyanate method recommended by Crouthamel[10] was also investigated, but for the small quantities of technetium involved was found to be unsatisfactory.

TABLE 1.

No.	Rhenium		Technetium		Manganese	
	Given	Found	Given	Found	Given	Found
1	1·25	1·00	0·01	0·01		
2	2·5	2·25	0·02	0·02		
3	2·5	2·38	0·015	0·013(6)		
4	1·25	1·4	0·02	0·017		
5	1·25	1·25	0·01	0·009(2)		
6	0·125	0·125	0·03	0·028(5)		
7	0·125	0·15	0·15	0·13		
8	2·5	2·88	0·2	0·22		
9	1·25	1·25	0·01	0·01	15·0	Not Determined
10	1·25	1·25	0·01	0·009(5)	15·0	

2. *Rhenium*

Rhenium is eluted from the ion-exchanger with 5 % ammonium thiocyanate in hydrochloric acid. It was found to be a simple matter to determine the rhenium in this eluate colorimetrically using the method of Geilmann *et al.*[11] In this method, an acid solution of perrhenate, on treatment with thiocyanate and stannous chloride, exhibits a yellowish colour which has been attributed to the formation of $ReO(CNS)_4^-$. At room temperature, maximum colour development takes place within 10 min, and there is no significant change in 30 min. Employing standard conditions, results were found to be reproducible.

Synthetic mixtures

As a final test on the proposed method, some "unknown" mixtures were analysed by one of us (M.P.). The results are shown in Table I. All quantities are expressed in mg.

Samples 9 and 10 contained 15 mg of manganese, which was removed according to the proposed scheme, but not determined.

In all the samples rhenium was present as perrhenate and technetium as pertechnetate.

In samples 3 and 4 an "aged" resin which had been used many times was employed. (*cf.* Note 6 under *Operation of the Column*). To achieve the values, No. 3–0·013(6) mg (error −9 %), No. 4–0·017 mg error −15 %), 60 ml of 4*N* nitric acid were required. With 20 ml of 4*N* nitric acid a considerable quantity of technetium was retained by the column.

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Zusammenfassung—Eine Ionenaustauscher-Methode zur Trennung von Technetium, Rhenium und Mangan wird beschrieben. Nach Sorption an der Säule wird zuerst Mangan mit verdünnter Salzsäure eluiert, dann Rhenium mit Ammoniumthiocyanat in Salzsäure und zuletzt Technetium mit Salpetersäure. In den Eluaten werden Rhenium photometrisch und Technetium radiochemisch bestimmt. 10 μg Technetium als Kaliumpertechnatat können von 15 mg Mangan (als Kaliumpermanganat) und 0·8 mg Rhenium (als Kaliumperrhenat) getrennt werden.

Résumé—Les auteurs donnent un aperçu d'une méthode de séparation du technétium, du rhénium et du manganèse per échange d'ions. Après fixation sur une colonne de résine, le manganèse est élué

en premier par de l'acide chlorhydrique, le rhénium par du thiocyanate d'ammonium dans l'acide chlorhydrique et le technétium par de l'acide nitrique. Dans les solutions éluées, le rhénium est dosé par colorimétrie, et le technétium par radiochimie. 10 μg de technétium sous forme de pertechnétate de potassium peuvent être séparés de 15 mg de manganèse à l'état de permanganate de potassium et de 0·8 mg de rhénium à l'état de perrhénate de potassium.

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APPLICATIONS OF COMPLEMENTARY TRI-STIMULUS COLORIMETRY—IV

INVESTIGATION OF A TARTRATE COMPLEX CONTAINING BOTH COPPER AND ALUMINIUM

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Summary—The theory of complementary tri-stimulus colorimetry has been extended and applied to the study of equilibria. A mixed complex containing copper, aluminium and tartrate has been studied. The mixed complex is more stable than the tartrate complexes of the individual metals and is even formed in solutions containing more tartrate than is necessary to form the single complexes. Formation of the mixed complex is slow, as is its reaction with other complex-forming substances, and it is accompanied by the release of hydroxyl ions. The pH range of existence of the mixed complex has been determined and its composition has been investigated.

SEVERAL years ago triethylenetetramine (trien) was studied as a chelating titrant in the photometric titration of copper^{II}.[1,2] In the course of this investigation an unexpected time effect was observed when copper was titrated at pH 8 in tartrate solution in the presence of aluminium ion. The concentration of tartrate was maintained sufficiently high to assure its complexation with both copper and aluminium separately. The inference from that effect (which is most pronounced at about pH 8 and which vanishes gradually when the pH is either lowered or raised) was that a complex species is formed which contains tartrate and both metal ions. This mixed complex must have a higher stability than the individual tartrate complexes of aluminium and of copper. Some changes in the absorbance curve of a copper tartrate solution after the addition of aluminium ion were observed, thus providing further evidence for the existence of such a mixed complex.

Both the formation of the mixed complex and its reaction with other complex forming agents are slow. If a copper tartrate solution is mixed with an aluminium tartrate solution, both buffered to about pH 8, the photometric titration of copper with trien is possible if it is started immediately and performed quickly. If the mixed solution is allowed to stand overnight or if it is heated to boiling and cooled, the galvanometer needle creeps after each addition of trien and the titration is rendered practically impossible. The rate at which the copper is transferred from the mixed copper–aluminium–tartrate complex to the trien complex can be followed by adding an excess of trien and observing the absorbance as a function of time. A plot of such time curves is shown in Fig. 11.

It has been found that citrate behaves in a similar fashion. Further investigation has shown that chromium^{III} also behaves in the same manner as aluminium. In this case, the time effect is even more pronounced and it seems that only a portion of the copper is ever released from the mixed complex; some is held permanently and it is not transferred to the trien complex even after standing for several hr. More research is needed in this direction. An analogous mixed complex, containing uranium^{VI}, aluminium and citrate in a molar ratio of 1:1:2 has been described by Booman and Holbroock.[3]

Complementary tri-stimulus colorimetry has been developed and several publications[4–8] have shown the value of this approach in the investigation of equilibria. One of the main advantages lies in the possibility of utilising many wavelengths in a particular region rather than one, as is usual in other approaches where, generally, only the absorption maxima are employed to derive conclusions. Furthermore, some of the parameters in complementary tri-stimulus colorimetry are independent of the analytical concentration of the colorant species involved, thus offering distinct advantages. It seemed worthwhile, therefore, to apply this approach to the investigation of the mixed copper–aluminium–tartrate complex. No references could be found in the literature to the existence of such a complex other than the two mentioned above.[2,3] Of course, a great number of mixed complexes are known in which more than one metal is co-ordinated with a multidentate ligand but the co-ordination of two metals within one complex species, in the presence of a ligand concentration which is more than sufficient to complex both metals separately, appears quite unusual.

From the viewpoint of analytical chemistry, the investigation seems important because of the interferences caused by aluminium in the above mentioned determination of copper. Furthermore, this time effect may offer possibilities for a kinetic masking of copper, provided, of course, that analogous complexes with other metals such as nickel or cobalt do not exhibit the same behaviour.

Such mixed complex formation was probably not discovered earlier because it does not manifest itself strongly in the visible region of the spectrum. Only a very slight change in colour occurs when moderate amounts of aluminium tartrate are added to a copper tartrate solution. Furthermore, this change occurs slowly and then only within a limited pH range.

The main purpose of the present paper is to extend the theoretical background of complementary tri-stimulus colorimetry in its application without relation to the human eye, and to establish unambiguously the existence of the peculiar mixed complex. To reach definite conclusions about composition, mechanism of formation, stability, *etc.* of the mixed complex is difficult because so little is known about the tartrate complexes of copper and even less about those of aluminium. The existing literature is frequently contradictory and many of the relevant papers are available as abstracts only. Hence, some investigations of the copper tartrate complex alone have been included.

In the preceding paper of this series,[8] it was stated that the occurrence of a straight line in a u–v plot is a necessary but insufficient condition for the presence of an equilibrium which involves only two absorbing species (*i.e.* absorbing in the selected region of the spectrum); this is the case with most acid-base indicators. From an understanding of the basis of complementary tri-stimulus colorimetry, this statement might be treated as self-evident. Nevertheless, in the following paragraph, a mathematical proof will be given because it is important for the appreciation of an inverse form of that statement.

According to the general procedure of complementary tri-stimulus colorimetry, several ranges (in general, three) are selected to cover the desired part (or even whole) of the absorbance curve and several wavelengths (ordinates) in each range are selected.

The absorbance values are read at each ordinate in each range and their sum is taken. The sum, R, in the r^{th} range for all ordinates up to and including the i^{th} is then given by

$$R_{\mathrm{r}} = \sum_{\mathrm{i}}^{\mathrm{n}} A_{\mathrm{r,i}} \tag{1}$$

where A is the absorbance. The complementary colour co-ordinates can then be calculated from

$$Q_{\mathrm{r}} = \frac{R_{\mathrm{r}}}{\sum\limits_{\mathrm{r}} R_{\mathrm{r}}} \tag{2}$$

In the usual procedure, equation (2) is equivalent to the three equations:

$$u = \frac{U}{U + V + W} \tag{3a}$$

$$v = \frac{V}{U + V + W} \tag{3b}$$

$$w = \frac{W}{U + V + W} \tag{3c}$$

where for r = 1, 2 and 3, R_{r} becomes U, V and W, and Q_{r} becomes u, v and w, respectively. As can be seen, the complementary colour co-ordinates (u, v and w) are concentration independent. The sum $U + V + W$ is denoted as J and may be called the "optical concentration". It is related to the analytical concentration C by the relation

$$J = E \times C \times l \tag{4}$$

where E is the overall absorptivity and l is the length of the light path through the absorbing solution.

The complementary colour co-ordinates of a mixture of any number of colorants are given by the equation

$$Q_{\mathrm{r,m}} = \frac{\sum\limits_{\mathrm{i}} C_{\mathrm{i}} \times Q_{\mathrm{r,i}} \times E_{\mathrm{i}}}{\sum\limits_{\mathrm{i}} C_{\mathrm{i}} \times E_{\mathrm{i}}} \tag{5}$$

provided that Beer's law is obeyed by each colorant at each of the selected ordinates and that there is no interaction between the colorants.

In the case of an equilibrium of the type

$$\mathrm{M} + \mathrm{Y} \rightleftarrows \mathrm{MY}$$

where, disregarding charges, M represents a metal ion, Y a complexing agent and MY the 1:1 complex of the two, the treatment takes the following form.

The following equations are given and hold for every state of the equilibrium:

$$K = \frac{[\mathrm{MY}]}{[\mathrm{M}][\mathrm{Y}]} \tag{6}$$

$$C_{\mathrm{M}} = [\mathrm{M}] + [\mathrm{MY}] \tag{7}$$

$$C_{\mathrm{Y}} = [\mathrm{Y}] + [\mathrm{MY}] \tag{8}$$

where K is the stability constant of the complex, and C_{M} and C_{Y} are the total (analytical) concentrations of the metal and the complex-forming reagent. Charges have been omitted because they are irrelevant to the present discussion and would only serve to confuse the presentation. It may be emphasised that it is the *apparent* (sometimes also called effective or conditional) stability constant which is involved in this equation. This can be calculated from the absolute constant by taking α and β factors into account in order to correct, respectively, for any influence due to pH and the presence of any other complexing agent. For this calculation see, for example, references 9, 10.

In general, it must be assumed that all three species exhibit colour *i.e.* absorb light. In that case, the complementary colour point of the system in any state of equilibrium is given according to (5), by

$$Q_{\mathrm{r,m}} = \frac{[\mathrm{M}]Q_{\mathrm{r,M}}E_{\mathrm{M}} + [\mathrm{Y}]Q_{\mathrm{r,Y}}E_{\mathrm{Y}} + [\mathrm{MY}]Q_{\mathrm{r,MY}}E_{\mathrm{MY}}}{[\mathrm{M}]E_{\mathrm{M}} + [\mathrm{Y}]E_{\mathrm{Y}} + [\mathrm{MY}]E_{\mathrm{MY}}} \tag{9}$$

By combining (9) with (7) and (8), so as to eliminate [Y] and [MY], the following is obtained

$$Q_{\mathrm{r,m}} = \frac{\begin{array}{l}[\mathrm{M}](Q_{\mathrm{r,M}}E_{\mathrm{M}} + Q_{\mathrm{r,Y}}E_{\mathrm{Y}} - Q_{\mathrm{r,MY}}E_{\mathrm{MY}}) \\ \qquad + C_{\mathrm{M}}(Q_{\mathrm{r,MY}}E_{\mathrm{MY}} - Q_{\mathrm{r,Y}}E_{\mathrm{Y}}) + C_{\mathrm{Y}}Q_{\mathrm{r,Y}}E_{\mathrm{Y}}\end{array}}{[\mathrm{M}](E_{\mathrm{M}} + E_{\mathrm{Y}} - E_{\mathrm{MY}}) + C_{\mathrm{M}}(E_{\mathrm{MY}} - E_{\mathrm{Y}}) + C_{\mathrm{Y}}E_{\mathrm{Y}}} \tag{10}$$

[M] in equation (10) is expressed by

$$[\mathrm{M}] = \frac{1}{2K}\{[K(C_{\mathrm{M}} - C_{\mathrm{Y}}) - 1] + \sqrt{[K(C_{\mathrm{M}} - C_{\mathrm{Y}}) - 1]^2 + 4KC_{\mathrm{M}}}\} \tag{11}$$

which is readily obtained from a combination of equations (6)–(8).

Inspection of (10), with [M] replaced according to (11), reveals that a plot of Q_{r} versus C_{M} or C_{Y} yields a rather complicated curve which would be difficult to treat.

Differentiation of $Q_{\mathrm{r,m}}$ in the combination (10)–(11) with respect to C_{Y} in order to locate any possible relative maxima and/or minima yields a higher order equation which cannot be interpreted. Some interesting information can, however, be obtained from a u–v, u–w or v–w plot, whichever is most suitable.

Equation (10) is actually equivalent to three equations (with r = 1, 2 and 3) and can readily be solved for [M] yielding:

$$[\mathrm{M}] = \frac{\begin{array}{l}[C_{\mathrm{M}}(Q_{\mathrm{r,MY}}E_{\mathrm{MY}} - Q_{\mathrm{r,Y}}E_{\mathrm{Y}}) + C_{\mathrm{Y}}Q_{\mathrm{r,Y}}E_{\mathrm{Y}}] \\ \qquad\qquad - Q_{\mathrm{r,m}}[C_{\mathrm{M}}(E_{\mathrm{MY}} - E_{\mathrm{Y}}) + C_{\mathrm{Y}}E_{\mathrm{Y}}]\end{array}}{Q_{\mathrm{r,m}}(E_{\mathrm{M}} + E_{\mathrm{Y}} - E_{\mathrm{MY}}) - (Q_{\mathrm{r,M}}E_{\mathrm{M}} + Q_{\mathrm{r,Y}}E_{\mathrm{Y}} - Q_{\mathrm{r,MY}}E_{\mathrm{MY}})} \tag{12}$$

By inserting $Q_{1,\mathrm{m}}$ ($= u_{\mathrm{m}}$) and $Q_{2,\mathrm{m}}$ ($= v_{\mathrm{m}}$) for r = 1 and 2, respectively, and equating the expressions obtained in order to eliminate [M], the desired relationship between u_{m} and v_{m} is obtained:

$$\begin{aligned}&\frac{C_{\mathrm{M}}(u_{\mathrm{MY}}E_{\mathrm{MY}} - u_{\mathrm{Y}}E_{\mathrm{Y}}) + C_{\mathrm{Y}}u_{\mathrm{Y}}E_{\mathrm{Y}} - u_{\mathrm{m}}[C_{\mathrm{M}}(E_{\mathrm{MY}} - E_{\mathrm{Y}}) + C_{\mathrm{Y}}E_{\mathrm{Y}}]}{u_{\mathrm{m}}(E_{\mathrm{M}} + E_{\mathrm{Y}} - E_{\mathrm{MY}}) - (u_{\mathrm{M}}E_{\mathrm{M}} + u_{\mathrm{Y}}E_{\mathrm{Y}} - u_{\mathrm{MY}}E_{\mathrm{MY}})} \\ &\qquad = \frac{C_{\mathrm{M}}(v_{\mathrm{MY}}E_{\mathrm{MY}} - v_{\mathrm{m}}E_{\mathrm{Y}}) + C_{\mathrm{Y}}v_{\mathrm{Y}}E_{\mathrm{Y}} - v_{\mathrm{m}}[C_{\mathrm{M}}(E_{\mathrm{MY}} - E_{\mathrm{Y}}) + C_{\mathrm{Y}}E_{\mathrm{Y}}]}{v_{\mathrm{m}}(E_{\mathrm{M}} + E_{\mathrm{Y}} + E_{\mathrm{MY}}) - (v_{\mathrm{M}}E_{\mathrm{M}} + v_{\mathrm{Y}}E_{\mathrm{Y}} - v_{\mathrm{MY}}E_{\mathrm{MY}})}\end{aligned} \tag{13}$$

Solution for v_m yields

$$v_m = \frac{\begin{aligned} &u_m\{[C_M(E_{MY} - E_Y) + C_Y E_Y](v_M E_M + v_Y E_Y - v_{MY} E_{MY}) \\ &- [C_M(v_{MY} E_{MY} - v_Y E_Y) + C_Y v_Y E_Y](E_M + E_Y - E_{MY}) \\ &+ [C_M(v_{MY} E_{MY} - v_Y E_Y) + C_Y v_Y E_Y](u_M E_M + u_Y E_Y - u_{MY} E_{MY}) \\ &- [C_M(u_{MY} E_{MY} - u_Y E_Y) + C_Y u_Y E_Y](v_M E_M + v_Y E_Y - v_{MY} E_{MY}) \end{aligned}}{\begin{aligned} &[C_M(E_{MY} - E_Y) + C_Y E_Y](u_M E_M + u_Y E_Y - u_{MY} E_{MY}) \\ &\qquad - [C_M(u_{MY} E_{MY} - u_Y E_Y) + C_Y u_Y E_Y](E_M + E_Y - E_{MY}) \end{aligned}} \tag{14}$$

Since v_m is a function of C_M and C_Y as well as of u_m, there is no simple relationship between u_m and v_m even when C_M or C_Y or their sum is held constant. Frequently, however, the complexing agent is colourless, or at least a range can be chosen in which it does not absorb. In that case, $E_Y = 0$ and equation (14) collapses to the simple straight line relationship:

$$v_m = \frac{u_m(v_M - v_{MY}) + u_M v_{MY} - u_{MY} v_M}{u_M - u_{MY}} \tag{15}$$

Analogous expressions of equal simplicity are obtained for cases with E_M or E_{MY} = zero.

Hence, the important conclusion is obtained that *more than two colorants must be present if the u–v (or u–w or v–w) plot is not a straight line.* It should be emphasised that a colorant in this respect is a species which absorbs in any or all of the ranges selected. It is, however, of utmost importance to appreciate that the inverse of the above conclusion is *not* valid: that is, the occurrence of a straight line in a *u–v* plot does not necessarily indicate the presence of a simple equilibrium. It may, however, strongly support any evidence to that effect derived from other measurements.

It is also possible to study the dependence of an equilibrium upon variation of the pH or of the concentration of one of the reactants. A *u*–pH or a *u–C* plot will yield a straight line, parallel to the pH or *C* axis (usually plotted as the abscissa), if these factors do not affect the equilibrium. A horizontal line will also be obtained during the range where a complex is formed gradually, since the value of *u* is concentration independent. Thus, for example, a *u*–pH plot will reveal the existence and pH range of each colorimetrically unique complex in a system, and over each range in which a stable form occurs the line will be parallel to the abscissa, provided, of course, that there is no overlapping of consecutive steps. The non parallel portions of such a plot indicate the ranges of transition from one form to another.

With this information at hand, the results of several series of experiments, performed in connection with the investigation of the mixed copper aluminium tartrate complex, can be discussed.

EXPERIMENTAL

All reagents used in this investigation were of analytical grade. d-Tartaric acid was used in all experiments. The absorbance curves were obtained with a Cary 14 recording spectrophotometer. The photometric time studies were performed employing a Bausch and Lomb Spectronic 20 photometer. The time effect on pH was studied employing a Leeds and Northrup pH-meter and a Sargent recorder.

RESULTS AND DISCUSSION

A typical absorbance curve for the copper tartrate complex in the region 350–900 mμ shows a very strong absorbance up to about 400 mμ. The curve then drops sharply, almost to zero, and rises slowly to a maximum in the nearest infrared. The location and, to some extent, the height of the latter maximum are dependent upon the pH. For this reason, the region from 600–900 mμ was utilised for further investigations. In order to obtain thorough coverage of this region the following ranges were selected: *u*-range, 600–690 mμ; *v*-range, 700–790 mμ; *w*-range, 800–890 mμ.

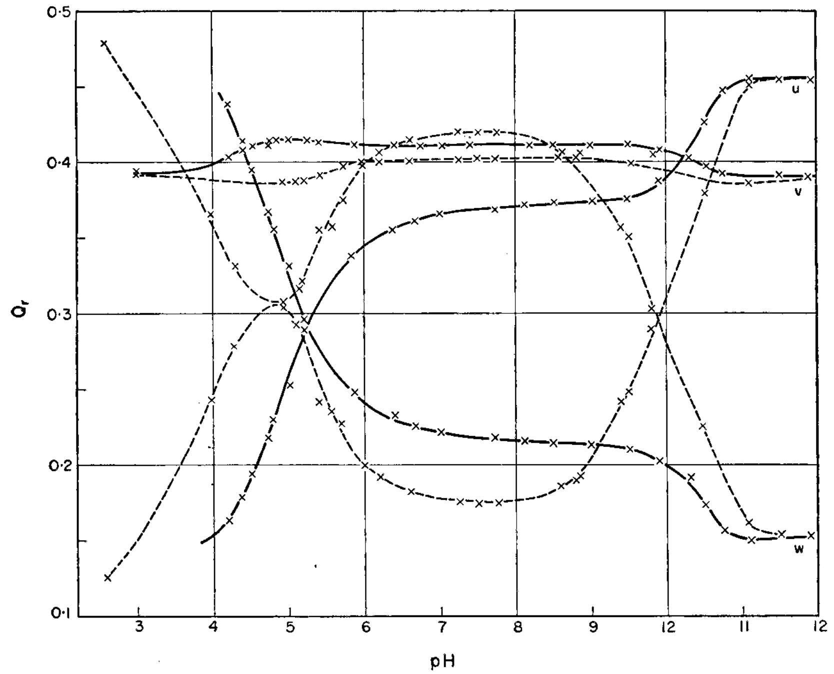

FIG. 1.—Dependence of Q_r on pH.

Solid curves: solution 0·02*M* in copper and 0·05*M* in tartrate.
Broken curves: copper and tartrate concentrations as above and 0·0385*M* in aluminium

Each range contained ten ordinates at 10-mμ intervals. The *u*, *v* and *w* values were computed in the manner previously described.[6]

The solid curves in Fig. 1 show the variation of *u*, *v* and *w* values with the pH of a solution 0·02 *M* in copper nitrate and 0·05 *M* in tartrate. These values were computed from absorbance curves obtained at various pH values; some of those curves are shown in Fig. 2. Below pH 4, the *u*–pH curves approach the horizontal. It was difficult to obtain reliable results in this region because precipitation occurred, especially at the higher tartrate concentration used in later experiments. No effort has been made to obtain complete information below pH 4 since it is not relevant to the present investigations. It is possible, to a certain degree, to reconcile this curve with some of the data reported in the literature. Fronaeus[11] reported the following stability constants of copper tartrate complexes: $\log K_1 = 3{\cdot}20$; $\log K_2 = 1{\cdot}91$; $\log K_3 = -0{\cdot}34$ and $\log K_4 = 1{\cdot}73$. The values are for *d*-tartaric acid, which has also been used in the experiments reported in the present paper. These data explain the contention of Sen Sarma[12] that only a 1:1 complex exists in very dilute acid solutions. In the pH range with which the present study is concerned, hydroxo complexes clearly must be taken into consideration. Various types have been reported.

Tikhonov and Belskaya[13] reported the existence of the following species, where T stands for the tartrate ion: CuT in the range pH 2–5; $Cu(OH)T^-$ at pH 5·3–9, and $Cu(OH)_2T^{2-}$ at pH 9–13.5. This would agree with the trend of the curves in Fig. 1.

Souchay and Lefebre[14] reported the equilibrium:

$$Cu_3(OH)_6T_3{}^{6-} \rightleftarrows Cu(OH)_2T_2{}^{4-} + \text{excess } T^{2-},$$

the species on the left side being present at pH 8 when tartrate and copper are present in a molar ratio of 2:1. Ablov and Popovich[15] assumed a molar ratio for Cu:T of 4:3 in higher tartrate concentrations at about pH 7. They included no hydroxo ligands in their formulation.

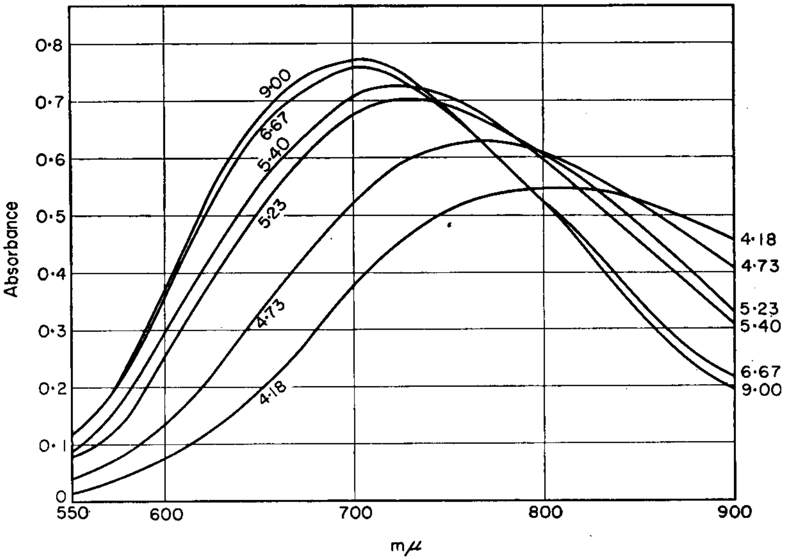

FIG. 2.—Absorbance curves of solutions 0·02*M* in copper and 0·05*M* in tartrate at various pH values

Curves similar to Fig. 1 have been obtained for the system with increasing tartrate concentrations and are presented as solid curves in Figs. 3, 4 and 5. Since no additional information can be obtained from *v* and *w* curves only the *u* curves are shown.

All curves approach the horizontal at about pH 4; this may be attributed to the formation of the species CuT or at even lower pH values of $CuHT^+$. All curves approach the horizontal at pH values higher than 10, though at a slightly different level. At very high pH values (not shown because it is not pertinent to the present study), a further change in equilibrium is indicated which can be attributed to the formation of the cuprate ion.[14]

At low tartrate concentrations, the middle part of the curves in the pH range 5–10 may be related to the existence of the complex $Cu(OH)T^-$ according to Tikhonov and Belskaya.[13] At higher tartrate concentrations the co-ordination requirements of

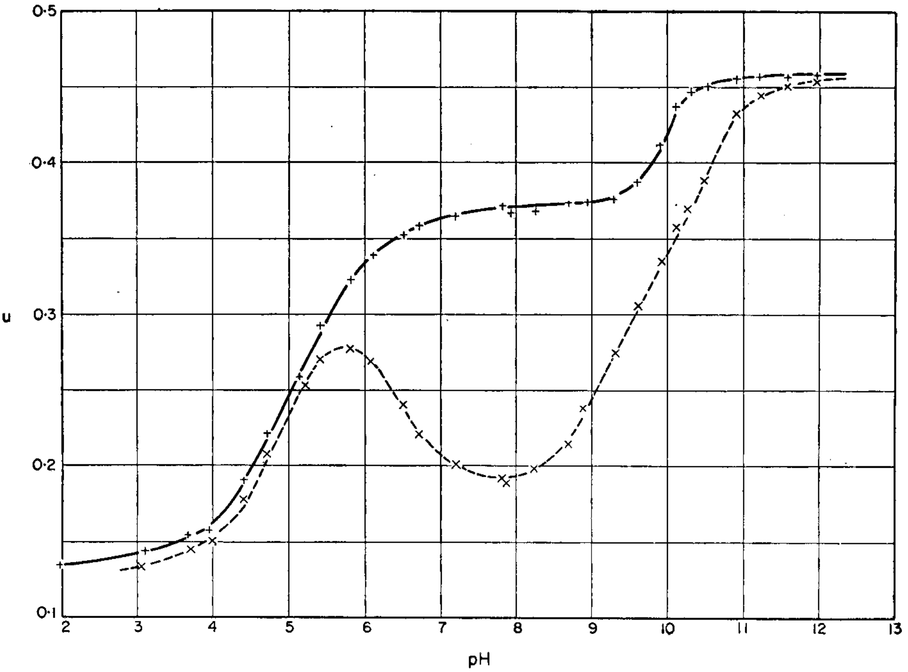

FIG. 3.—Dependence of *u* on pH.
Solid curve: solution 0·02*M* in copper and 0·1*M* in tartrate.
Broken curve: copper and tartrate concentrations as above and 0·0385*M* in aluminium.

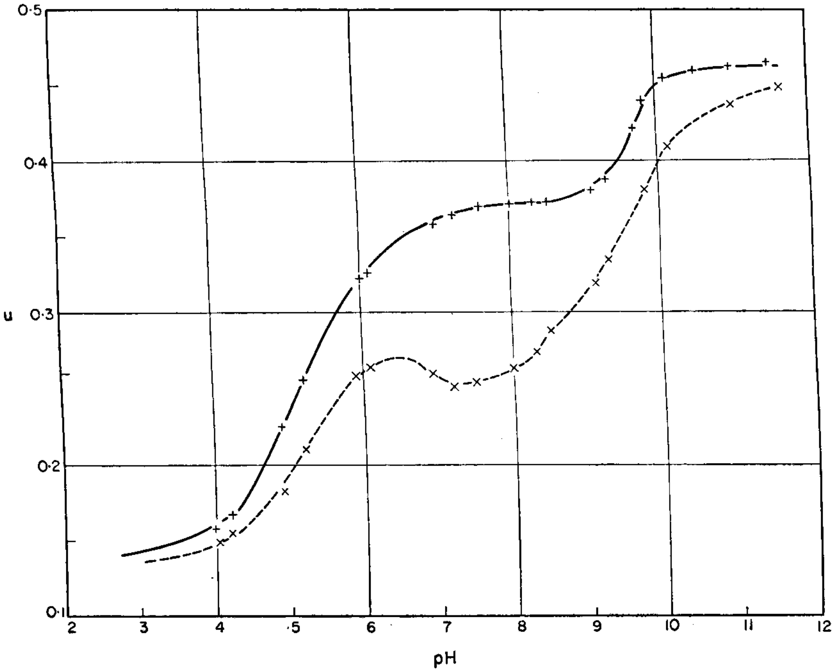

FIG. 4.—Dependence of *u* on pH.
Solid curve: solution 0·02*M* in copper and 0·2*M* in tartrate.
Broken curve: copper and tartrate concentrations as above and 0·0385*M* in aluminium.

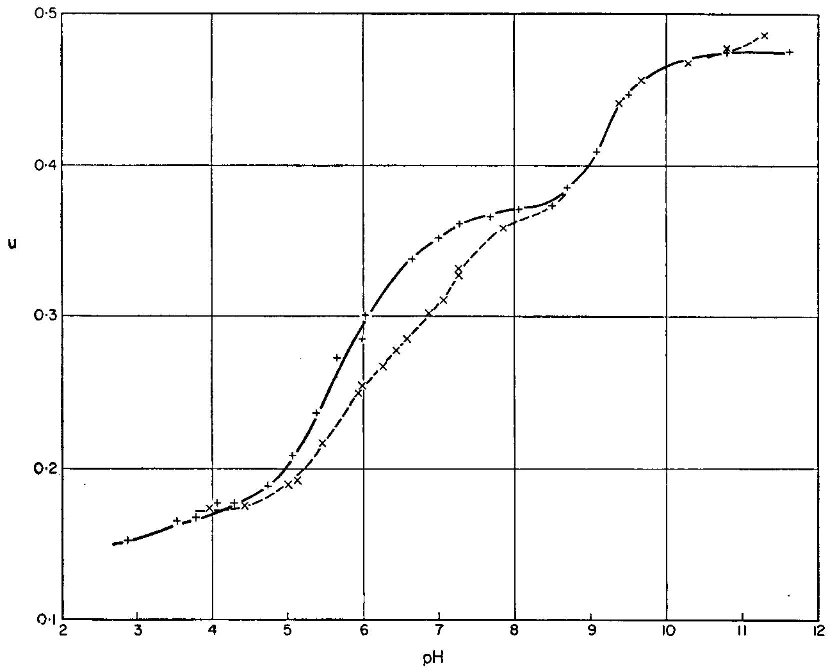

FIG. 5.—Dependence of *u* on pH.
Solid curve: solution 0·02*M* in copper and 0·5*M* in tartrate.
Broken curve: copper and tartrate concentration as above and 0·0385*M* in aluminium.

copper seem to be more and more satisfied by tartrate as opposed to the hydroxo ligand. Hence, overlapping equilibria occur and the length of the horizontal part (related to the monohydroxotartrate) shrinks, degenerating to an inflection point at a tartrate concentration of 1 M. The corresponding curves for copper tartrate from Figs. 1, 3, 4, 5 and an additional curve measured at a tartrate concentration of 1 M are collected in Fig. 6 in order to facilitate comparison.

If, indeed, the course of the complex formation is such that $Cu(OH)_2T^{2-}$ is the only species present within the pH range 9–13·5, it must be expected that all curves will return to the same level. This is not, however, the case, as is evident from Fig. 6, and it suggests the presence of a new species at high concentrations of tartrate and hydroxyl ion.

The broken curves in Figs. 1, 3, 4 and 5 represent results obtained when aluminium was present in the solution. Since neither aluminium nor its tartrate complex absorbs in the 600–900 mμ range, it is obvious that there is some reaction between aluminium and copper tartrate.

The deviations of the broken curves from the solid curves are greatest at the lowest tartrate concentration and decrease with increasing concentration of tartrate. This could be interpreted as a competition of copper and aluminium for the limited amount of tartrate and not the formation of a mixed complex. There is, however, still a pronounced deviation at higher tartrate concentrations, even when tartrate is present far in excess of the amount which would be necessary to complex both the copper and the aluminium separately. Further, at the lowest tartrate concentration either copper or aluminium should precipitate as a hydroxide in the higher pH ranges because there

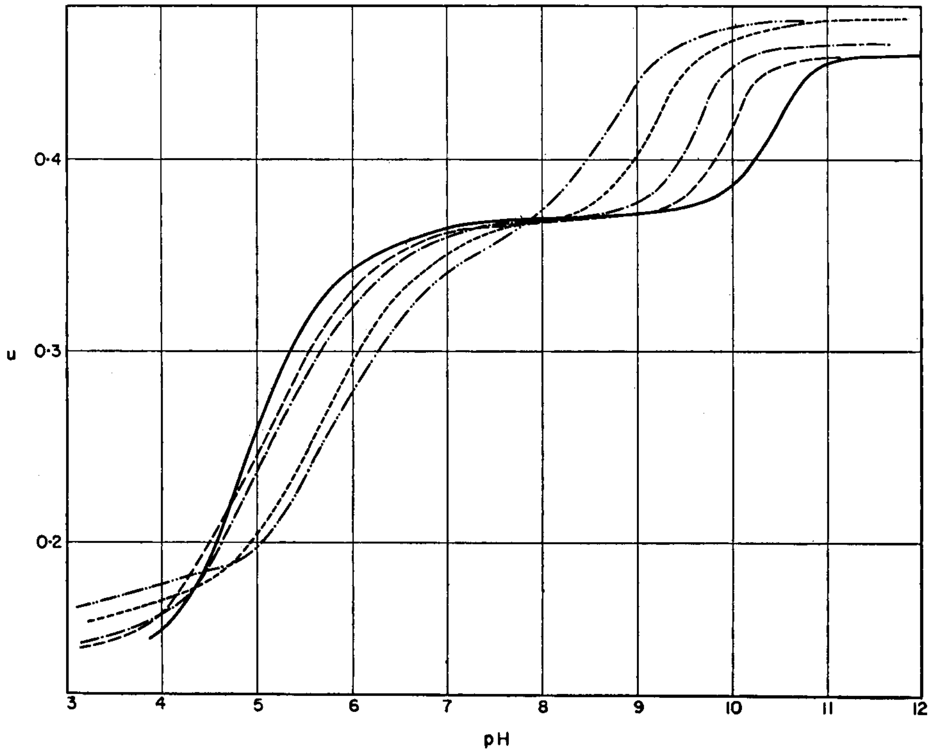

FIG. 6.—Dependence of *u* on pH. All curves for solutions 0·02*M* in copper.

Tartrate concentration ..–..–.. 1*M*

.... 0·5*M*

.–.–.–.– 0·2*M*

– – – – 0·1*M*

——— 0·05*M*

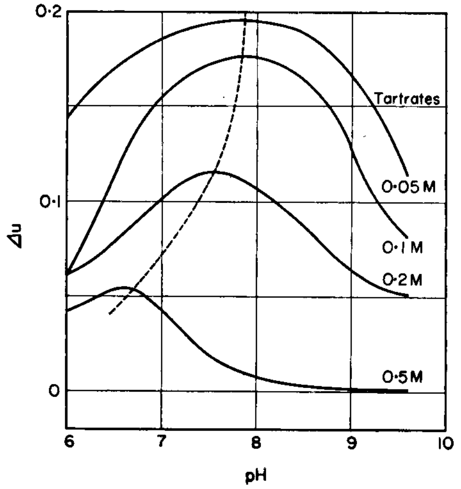

FIG. 7.—Differences in the *u* values of solutions with and without aluminium at different tartrate concentrations as a function of pH.

is not sufficient tartrate present to keep both metal ions complexed independently to a degree sufficient to prevent their precipitation. Hence, the only conclusion is that a complex species is formed which contains all three—copper, aluminium and tartrate. It is important to realise that this mixed complex must have a higher stability than that of the simple tartrate complex of either metal. The optical results, however, do not give any clues to the mechanism of the formation of the mixed complex.

Fig. 7 presents a plot of the differences in the *u*-values of the copper tartrate solutions, with and without aluminium present, versus pH. For low tartrate concentrations, this difference is greatest at about pH 8, which is the region in which aluminium has been found to interfere with the titration of copper with trien.[2] Several time curves were made at various pH values by mixing copper and aluminium tartrate solutions which had been adjusted to exactly the same pH. One of these curves is shown in Fig. 8 as a representative example. Due to the rather small difference in the absorptivities of copper tartrate and the mixed complex, the effect is not very great. Similar time curves can be obtained when the formation of the mixed complex is followed polarographically. The interpretation of the polarographic curves is difficult because the pH of the solution changes during the formation of the mixed complex (see below). The time effect of the degradation of the mixed complex can be studied very effectively when the mixed complex is allowed to react with other complexing agents (see later).

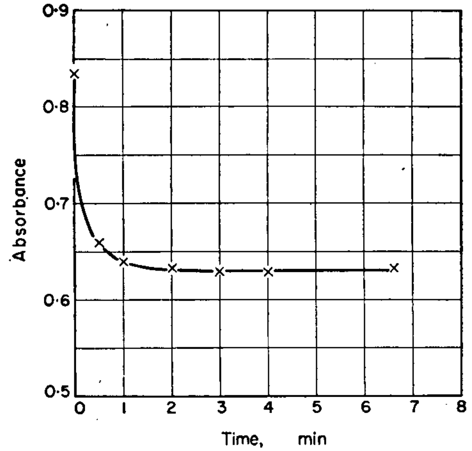

FIG. 8.—Time dependence of the formation of the mixed complex.
Equal volumes of solution A and B were mixed at time zero.
Solution A: 0·04*M* in copper; 0·1*M* in tartrate.
Solution B: 0·09*M* in aluminium; 0·1*M* in tartrate.
Initial pH = 8·00.
Absorbance measured at 700 mμ.

Except at very high tartrate concentrations, the maximum time effect is observed in the pH range 7·5–8·0, which is exactly the range in which hydroxyl ions are part of the copper tartrate complex (see above). It is reasonable, therefore, to assume that hydroxyl ions may be released, causing a rise in pH, when the mixed comple is formed. This pH effect should, of course, also be time dependent, since it would be contingent upon the slow formation of the mixed complex. To investigate this, copper and aluminium tartrate solutions were prepared and adjusted to exactly the same pH. The

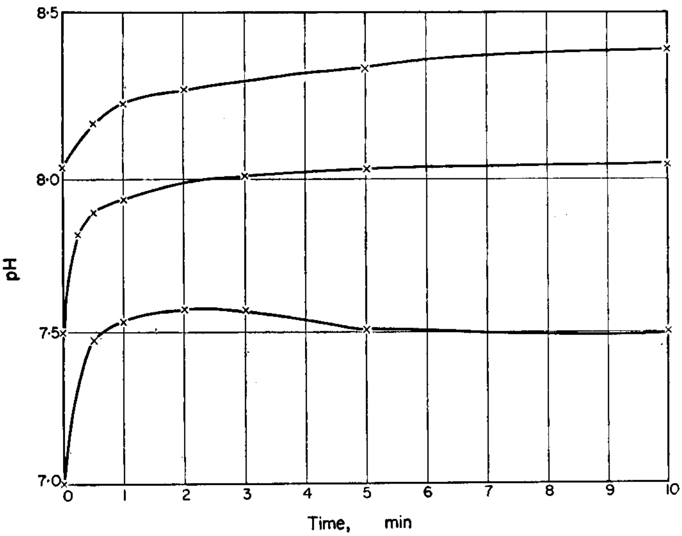

FIG. 9.—Change of pH with time after mixing solutions 0.04M in copper and 0·09M in aluminium, both solutions 0·1M in tartrate.

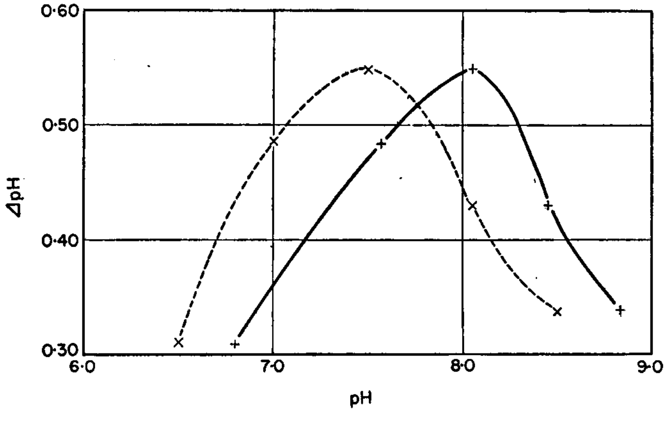

FIG. 10.—Changes in pH as a function of initial pH (dashed curve) and final pH (solid curve), obtained from data in Fig. 9.

solutions were then mixed and the pH changes with time were recorded. Some examples of the curves obtained are presented in Fig. 9. When the differences between the initial and final pH values were plotted versus the initial pH and also against the final pH, the curves in Fig. 10 were obtained.

When the mixed complex is formed with the release of hydroxyl ion, the amount of hydroxyl ion released would appear to be directly related to the copper concentration, where the aluminium concentration is kept constant. Therefore, after a constant pH value had been reached in the series of experiments described in the preceding paragraph, each of the solutions was titrated with hydrochloric acid until the initial pH value was reached again. Of course, after each addition of acid considerable time was allowed to pass in order to assure that equilibrium had definitely been reached. However, when comparing the amount of hydrochloric acid used with the copper concentration present, no obvious relationship could be detected. On reflection, this result is not surprising and there are several possible explanations of the discrepancy.

First, the percentage of copper present initially as hydroxo complex is not known. Furthermore, the ratio of possible mono- and dihydroxo complexes is unknown; then it must be realised that there is definite proof that the formation of the mixed complex does not go to completion. Finally, nothing is known about the aluminium tartrate, which may also be present in a hydroxo complex form and participate in the donation of hydroxyl ions. In every case considered more hydrochloric acid was needed than would correspond to 100% conversion of the copper dihydroxo complex to the mixed complex, which seems to indicate that the aluminium tartrate is indeed involved in the release of hydroxyl ions.

From the optical results secured in the present study, no conclusion can be drawn as to the mechanism involved in the formation of the mixed complex. Copper may transfer to the aluminium tartrate complex or the inverse may occur; further, it may well be that both complexes join together with the expulsion of hydroxyl ions. There are several other possibilities.

The time effect greatly depends on the form in which the aluminium is added to the copper tartrate solution. It is considerable when copper tartrate solution is mixed

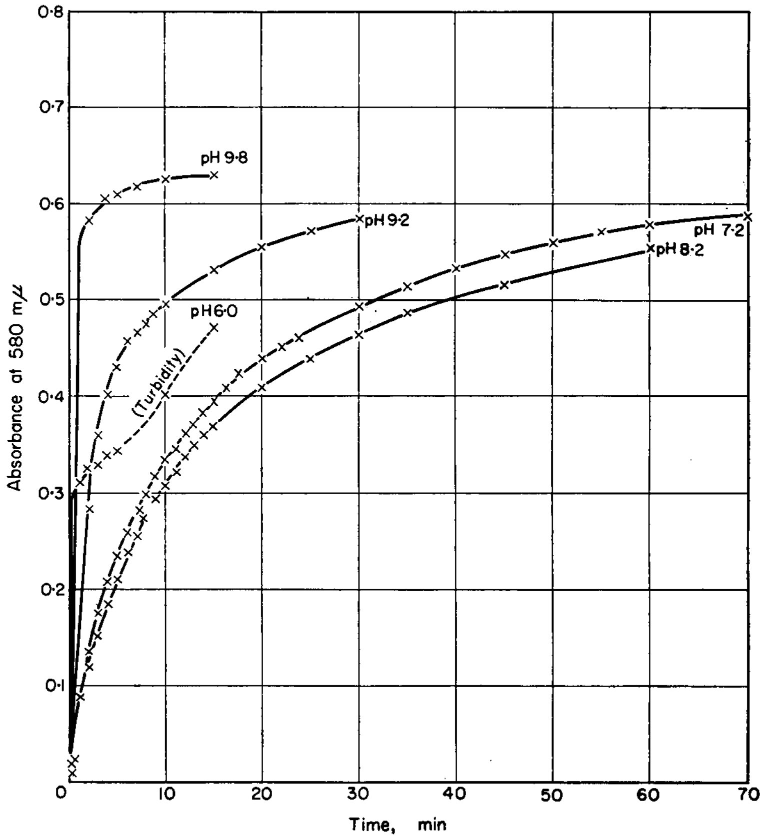

Fig. 11.—Change of absorbance (at 580 mμ) with time after adding trien to a solution 0·02*M* in copper, 0·0385*M* in aluminium and 0·1*M* in tartrate.

with an aluminium tartrate solution, both adjusted to the same pH and having equal tartrate concentration, so that the latter will not change during the mixing. However, when aluminium chloride or sulphate solution is added to the alkaline copper tartrate solution, a far greater time effect is observed. Of course, it is difficult to compare the two cases on the basis of pH effects since it is, for obvious reasons, impossible to bring the aluminium salt solution to the desired pH value. When aluminium chloride or sulphate solution is added, a neutralisation process may take first place, which leads in a first step to the formation of hydroxo compounds of aluminium, which are known to react extremely slowly, then these species react first with tartrate or directly with copper tartrate to give eventually the mixed complex.

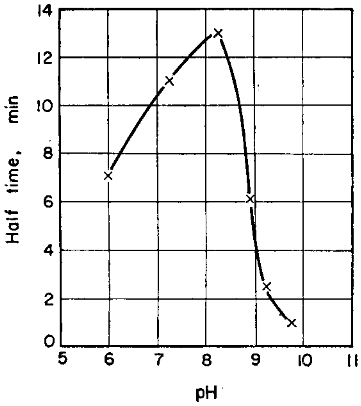

FIG. 12.—Half-time values depending on pH. Data derived from Fig. 11.

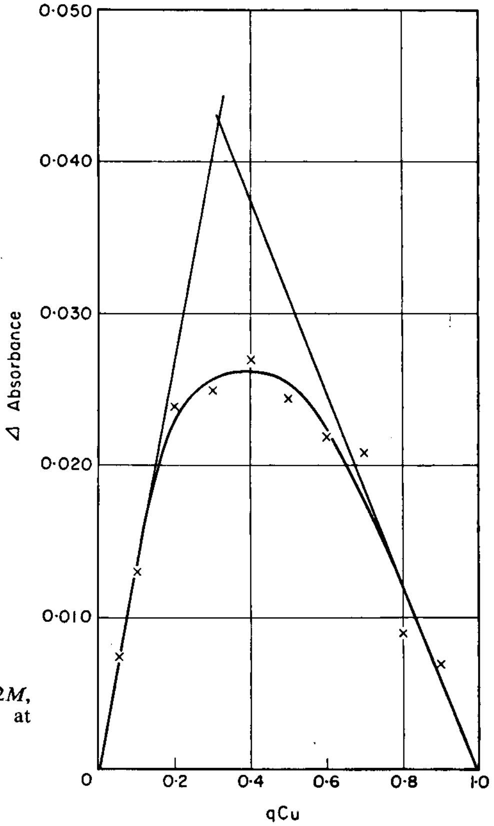

FIG. 13.—Job plot. $C_{Cu} + C_{Al} = 0{\cdot}02M$, tartrate $0{\cdot}5M$; absorbance measured at 700 mμ.

The mixed complex reacts slowly in any type of reaction. This has become evident in the course of the acidimetric titration of the hydroxyl ions as mentioned above. It also reacts slowly with other complexing agents which are sufficiently strong to take copper away from the mixed complex. As an example, the reaction of the mixed complex with excess trien has been studied photometrically. Some time curves obtained at various pH values are presented in Fig. 11. The half-time values (that is the time at which the absorbance reached one-half of its final maximum value) have been plotted against the initial pH and the resulting curve (Fig. 12) shows a maximum near pH 8. Of course, the exact location and also the height of that maximum are dependent on the tartrate concentration. These results are in agreement with those obtained in the pH studies discussed above. Similar curves and identical conclusions were obtained when the replacement study was performed employing EDTA instead of trien.

In an attempt to evaluate the ratio of copper to aluminium in the mixed complex, two Job plots were made. In the first, so as to eliminate any possible effect arising from the removal of tartrate from copper tartrate by aluminium, a rather high tartrate concentration (0·5*M*) was employed, and the sum of the concentrations of aluminium and copper was kept constant at 0·02*M*. The effect, as expected, was very slight at this high tartrate concentration, and did not exceed 0·025 absorbance units. The tangents to the straight portions of the best curve drawn through the rather badly scattered points intersect at a copper mole fraction of about 0·3. Application of the method of least squares, utilising the points q_{Cu} = 0·0, 0·1 and 0·2 for the left branch and 0·6, 0·7, 0·8, 0·9 and 1·0 for the right branch, placed the intersection at $q_{Cu} = 0{\cdot}32_5$ (Fig. 13).

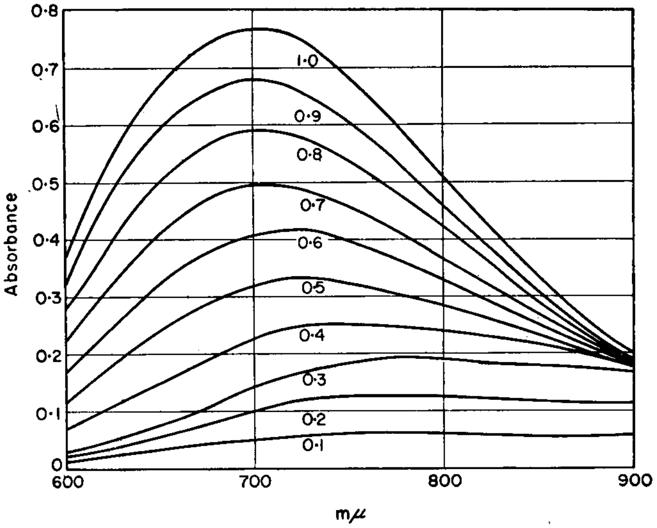

FIG. 14.—Absorbance curves for Job plot. $C_{Cu} + C_{Al}$ = 0·02*M*, tartrate 0·05*M*.

It is, however, very risky to base a definite conclusion on so small an effect, so a second Job plot was made at a tartrate concentration of 0·05 *M*. The absorbance curves obtained are presented in Fig. 14 and the Job curve in Fig. 15. In this case, the intersection is clearly at q_{Cu} = 0·33 (the same value was obtained by the least square method), thus indicating a ratio for Cu: Al of 1: 2. In the light of this result the conclusion obtained from the Job plot at the higher tartrate concentration can be accepted.

In order to investigate further the situation at higher tartrate concentrations, the mole ratio method was applied. Increasing amounts of aluminium were added to solutions 0·02 *M* in copper and 0·5 *M* in tartrate. The pH of each solution was adjusted to about 6·6 and the solutions were allowed to stand overnight. The pH was then brought to exactly 6·60 and an acetate buffer of that pH was added. After another day the pH was checked again and re-adjusted if necessary. The pH value of 6·60 was chosen because at this pH the difference in absorbance of solutions with and without aluminium is greatest at a tartrate concentration of 0·5 *M* (see Fig. 7).

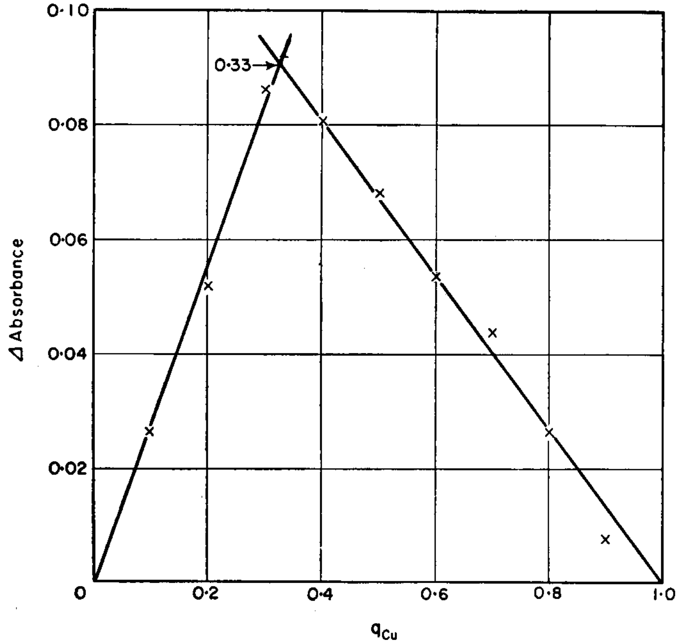

FIG. 15.—Job plot of data in FIG. 14.

Absorbance curves were obtained for all of these solutions and the absorbance at 700 mμ was plotted against the molar ratio of aluminium to copper. The plot is shown in Fig. 16. Amazingly there are three straight branches. The first intersection is at a molar ratio for Al: Cu of about 2:1 which is in agreement with the Job plot. There is,

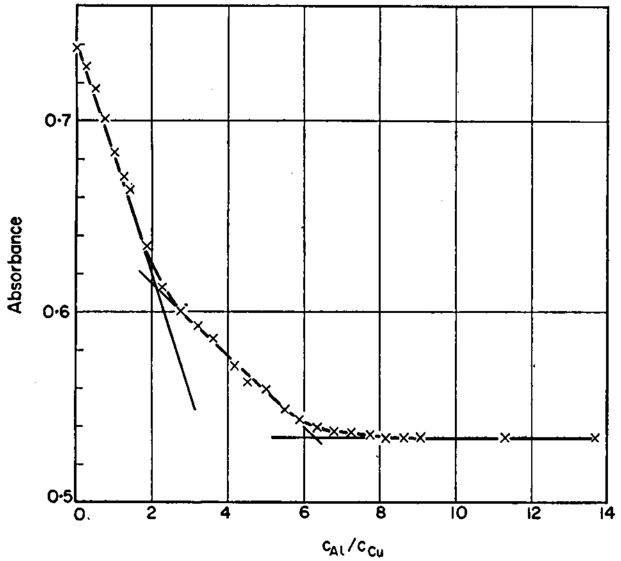

FIG. 16.—Method of constant variation. $C_{Cu} = 0{\cdot}02M$ = constant; tartrate $0{\cdot}5M$; pH 6·60; absorbance readings at 700 mμ.

however, an indication of a second complex with the ratio in the neighbourhood of 6:1, forming at very high aluminium contents. The discrepancy between the results obtained by the two different methods cannot be explained.

Further evidence for the fact that some rather complicated reactions are involved is obtained from a *u–w* plot which is presented in Fig. 17. Some portions of the line are definitely curved, indicating the presence of equilibria involving more than two coloured species.

In order to demonstrate further the pH dependence of the equilibria involved, *u–v* plots of copper tartrate and copper aluminium tartrate solutions were made, two of which are presented in Fig. 18. Only straight line plots were obtained from the aluminium-free solutions, each straight portion corresponding to the transition from one equilibrium to another. The regions in which only one species predominates are represented by a point or by a closely grouped collection of pH points. As shown in the theoretical section of this paper, the straight lines in these *u–v* plots may indicate, but do not prove, the presence of a simple equilibrium. The three branches of the line for 0·05 *M* copper solution (with no aluminium present) may be attributed, respectively, to the transitions:

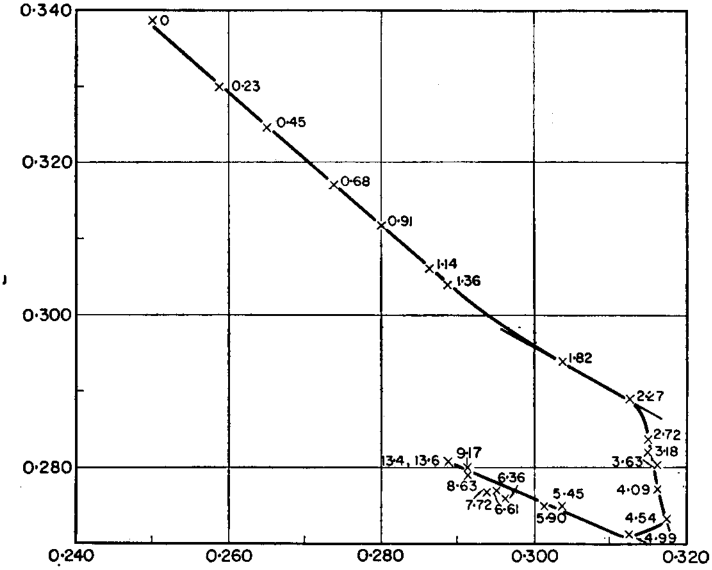

FIG. 17.—*u-w* Plot of the data of method of constant variation. Numbers at the curve relate to the ratio C_{Al}/C_{Cu}.

$$\mathrm{Cu} \rightleftharpoons \mathrm{CuT} \quad \text{or possibly} \quad \mathrm{CuHT} \rightleftharpoons \mathrm{CuT} \qquad \text{(I)}$$

$$\mathrm{CuT} \rightleftharpoons \mathrm{Cu(OH)T} \qquad \text{(II)}$$

$$\mathrm{Cu(OH)T} \rightleftharpoons \mathrm{Cu(OH)_2T} \qquad \text{(III)}$$

Fig. 18 presents *u–v* plots for a solution also containing aluminium (broken curves). Here there are many more transitions and more complicated equilibria are involved. At the present state of development of complementary tri-stimulus colorimetry this is the only conclusion which can be drawn. It is impossible, at present, to relate the different parts of the curve to specific equilibria. In fact, it is doubtful if optical results alone will ever suffice to that end. pH titrations of copper aluminium tartrate solution would provide additional information, but because of the very slow reaction rates, this would be tedious and has not been attempted.

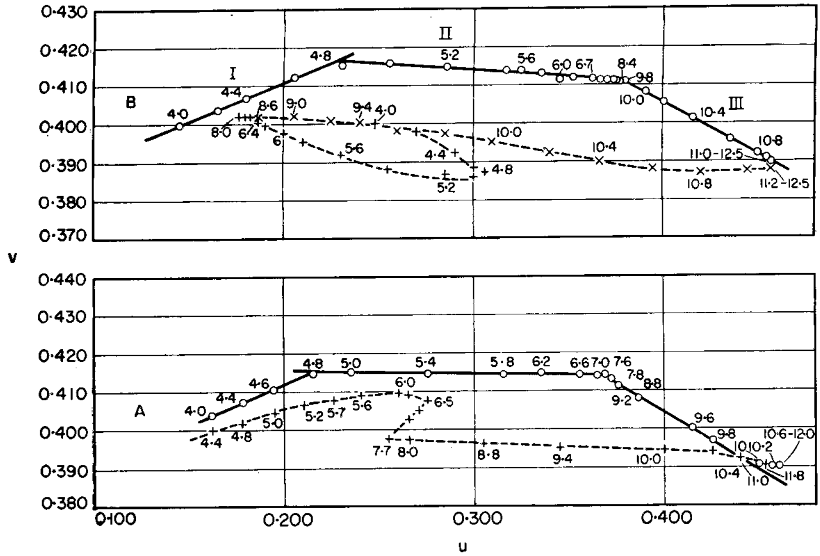

FIG. 18.—*u*-*w* Plots.

A: solid curve: solution 0·02*M* in copper and 0·2*M* in tartrate.
broken curve: copper and tartrate concentrations as above and 0·0385*M* in aluminium.
B: solid curve: solution 0·02*M* in copper and 0·05*M* in tartrate.
broken curve: copper and tartrate concentrations as above and 0·0385*M* in aluminium.
Numbers adjacent to the curves refer to the pH values.

CONCLUSION

When copper, aluminium and tartrate ions are present in a neutral or slightly alkaline solution a mixed complex is formed. This mixed complex may also contain some hydroxo groups. The stability of the mixed complex is greater than that of the tartrate complexes of the two metals, as can be deduced from the fact that the mixed complex forms to an appreciable amount even at tartrate concentrations which are more than sufficient to complex both metals separately. Further corroboration is obtained from the fact that no precipitation of the metal hydroxides is observed in an alkaline solution containing far too little tartrate to complex both metals separately. The formation of the mixed complex is pH dependent and reaches a maximum between pH 6 and 8, depending on the tartrate concentration. The lower the tartrate concentration, the higher the pH at which maximum formation of the mixed complex occurs. Both formation and cleavage of the mixed complex are slow processes which can be followed photometrically. At the pH range in which the mixed complex is stable, hydroxo groups are present in the copper tartrate complex and most probably also in the aluminium tartrate complex. Hydroxyl ions are released during the formation of the mixed complex and hence the formation may be followed via pH measurements. At low tartrate concentrations, the molar ration of Cu : Al in the mixed complex is 1 : 2. At high tartrate and aluminium concentrations this ratio is uncertain and results obtained by the method of constant variation suggests that the ratio has a different value or that at least two different complexes are present.

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Zusammenfassung—Die Theorie der komplementären Tristimuluskolorimetrie wurde erweitert und auf das Studium von Komplexgleichgewichten angewandt. Ein Mischkomplex, der Kupfer, Aluminium und Tartrat enthäl, wurde untersucht. Der Mischkomplex ist stabiler als die einfachen Tartratkomplexe von Kupfer und Aluminium und wird auch gebildet, wenn Tartrat in beträchtlich höherer Konzentration anwesend ist, als zur Bildung der einfachen Metallkomplexe benötigt wird. Die Bildung des Mischkomplexes erfolgt langsam und auch seine Reaktionen mit anderen Komplexbildnern sind verzögert. Die Bildung des Mischkomplexes ist mit Freiwerden von Hydroxylionen gekoppelt. Der pH-Bereich, in dem der Mischkomplex existiert, wurde ermittelt und die Zusammensetzung des Komplexes studiert.

Résumé—La théorie de la colorimétrie trichrome a été étendue et appliquée à l'étude des équilibres. Un complexe mixte contenant du cuivre, de l'aluminium et du tartrate a été étudié. Le complexe mixte est plus stable que les complexes tartriques des métaux individuels, et il se forme même dans des solutions contenant plus de tartrate qu'il n'est nécessaire pour former les complexes simples. La formation du complexe mixte est lente, de même que sa réaction avec d'autres substances formant des des complexes. La formation du complexe mixte est accompagnée de la libération d'ions hydroxyles. Le domaine de pH dans lequel existe le complexe mixte a été déterminé, et sa composition a été étudiée.

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SEPARATION AND COLORIMETRIC DETERMINATION OF TRACE QUANTITIES OF MAGNESIUM IN HIGH-PURITY BERYLLIUM OXIDE*

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Summary—A colorimetric method is described for the determination of trace quantities of magnesium in beryllium metal and its oxide. Beryllium, which is known to interfere with the colorimetric determination of magnesium by the available chromogenic reagents, is separated from the magnesium by forming the beryllium perfluorobutyrate salt at pH 3 to 4, and then extracting it with several portions of diethyl ether. By increasing the number of equilibrations with ether, as much as 1 g of beryllium can be separated from 10 μg of magnesium. The magnesium is then measured spectrophotometrically as the highly coloured complex with Magon, sodium 1-azo-2-hydroxy-3-(2,4-dimethylcarboxanilido) naphthalene-1-(2-hydroxybenzene-5-sulphonate), which exhibits a peak of maximum absorbance at 510 mμ. Over the range of 0·04 to 0·40 μg of magnesium per ml, the absorbance conforms to Beer's law. The method has been applied successfully to the determination of quantities of magnesium as low as 10 μg. The coefficient of variation for samples which contain 200 μg of magnesium is 2%.

METHODS for the determination of trace quantities of magnesium in high-purity beryllium metal and its oxide are generally unsatisfactory. Despite the high order of sensitivity afforded by a number of reagents for magnesium, such as Eriochrome Black T,[3,8,9] Thiazole yellow,[1,2] and Magon,[4,5] suitable precision in the range of 1 to 100 ppm is lacking. This situation is probably because of incomplete separation of beryllium which is known to interfere with the above reagents for magnesium. Mills and Whetsel,[7,8] in their investigation of the extraction properties of perfluorocarboxylic acids, found that beryllium behaved uniquely in that it was extractable, in contrast to the other bivalent cations. By combining this separation technique with the highly sensitive reagent, Magon, sodium 1-azo-2-hydroxy-3-(2,4-dimethylcarboxanilido) naphthalene-1-(2-hydroxybenzene-5 sulphonate), a reliable precise method for the determination of traces of magnesium in beryllium metal and its oxide has been developed and applied successfully.

EXPERIMENTAL

Reagents

Stock solution of magnesium: Prepared by dissolving 3·4 g of $MgCl_2{\cdot}6H_2O$ in 200 ml of 1*M* hydrochloric acid in a polyethylene bottle. This solution was standardised gravimetrically by the di-ammonium phosphate method.

Borax buffer solution, 0·08*M:* Prepared by dissolving 3·05 g of $Na_2B_4O_7{\cdot}10H_2O$ in 100 ml of water.

Ether, anhydrous reagent grade.

Perfluorobutyric acid-sodium salt (*NaPFB*) (Minnesota Mining and Manufacturing Co.), 1*M* solution: Prepared by neutralising 13 ml of the reagent with sodium hydroxide before dilution to 100 ml with water. When stored in a polyethylene container this reagent is stable indefinitely.

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Polyvinyl alcohol (Elvanol, du Pont grade 52–22), 2% solution: Prepared by dissolving 2 g in 100 ml of water. When stored in a refrigerator this reagent is stable for about 1 month.

Reagent solution (*Magon*) (LaMotte Chemical Products Co.,), 0·015%: Prepared by dissolving 30 mg of sodium 1-azo-2-hydroxy-3-(2,4-dimethylcarboxanilido)naphthalene-1-(2-hydroxybenzene-5-sulphonate) in 200 ml of ethanol. This reagent is stable for at least 1 month.

Apparatus

A Cary Model 14-M recording spectrophotometer was used to obtain the spectra reported here. Matched fused 1-cm Corex cells were used.

RESULTS AND DISCUSSION

Effect of polyvinyl alcohol

In their investigation of the determination of magnesium by the Magon method, Mann and Yoe[4] reported that for accurate measurements it was necessary to hold the pH fairly constant. This was done by making the magnesium solution, from which aliquots are taken, just acid to phenolphthalein. Observing these conditions, it was found that 30 μg of beryllium in the test aliquot caused an error of about 5% in the magnesium determination. McCann,[6] in his determination of magnesium by the Thiazole yellow method, added a dispersing agent, polyvinyl alcohol, to the solutions under investigation before adding the chromogenic reagent. When polyvinyl alcohol is added to the magnesium solutions before adjusting the pH in the Magon method, a weight ratio of beryllium to magnesium as great as 200:1 could be tolerated.

Since magnesium is usually contained in beryllium metal and its oxide as a trace quantity, rarely exceeding 200 ppm in any given determination of magnesium, the ratio of beryllium to magnesium contained in the test aliquot would most likely be greater than 200:1. Therefore the excess of beryllium which is known to interfere with the method must be removed in some manner.

Extraction of beryllium

The most logical approach in the determination of traces of impurities in highly purified materials is, when necessary, to separate the minor component from the matrix. Since no suitable method is available for completely separating magnesium from the beryllium matrix, attention was turned to methods for reducing the matrix concentration as much as possible.

Mills and Whetsel,[7] in their investigation of the uses of perfluorocarboxylic acids as separating agents, found that many multivalent and a few bivalent cations, which include beryllium, are separated from univalent and the other bivalent ions using perfluorobutyric acid as the extracting agent and ethyl ether as the second solvent. Their extraction data are based on the fact that the perfluorocarboxylic acids are increasingly more soluble in the organic solvent than in aqueous media. Further, upon evaporation of the ether extracts they found that the extracted species is a basic salt. Utilising the data of Mills and Whetsel,[7] the separation of beryllium from magnesium by extracting the beryllium into perfluorobutyric acid in ether was investigated.

Dilutions of perchloric acid solutions of beryllium were taken to determine the extraction characteristics of beryllium with perfluorobutyric acid in ether. The pH of the solutions was adjusted to the range 1·0 to 5·0. After adding 0·5 mmoles of perfluorobutyric acid for each mg of beryllium present, the solutions were equilibrated for 2 min. As shown in Fig. 1, the extraction is dependent on the pH of the aqueous solution. At a pH of 1·0, little extraction of the beryllium occurs; at a pH of 2·0, the extraction coefficient is about 4. Precipitation occurs when the pH is adjusted to 5·0. When the pH of the aqueous solution is adjusted to 3·0 to 4·0, about 96% of the beryllium is removed by a single extraction. These results agree well with the data of Mills and Whetsel,[8] who stated that extractions using the perfluorocarboxylic acids proceed best at a pH slightly less than that at which the cation would form an insoluble hydroxide. On the basis of these results, when the magnesium is contained in beryllium oxide in the range of 100 to 200 ppm, sufficient quantities of beryllium are removed to permit an accurate measurement of the magnesium by a single extraction. When the magnesium is of the order of 0 to 100 ppm, however, additional extractions with ether are required. Since the maximum quantity of beryllium that can be tolerated in the test aliquot of magnesium has been determined, and since about 96% of the beryllium is removed by each equilibration, the number of ethereal extractions necessary to remove the prescribed amount of beryllium can be calculated. No additional perfluorobutyric acid, however, need be added.

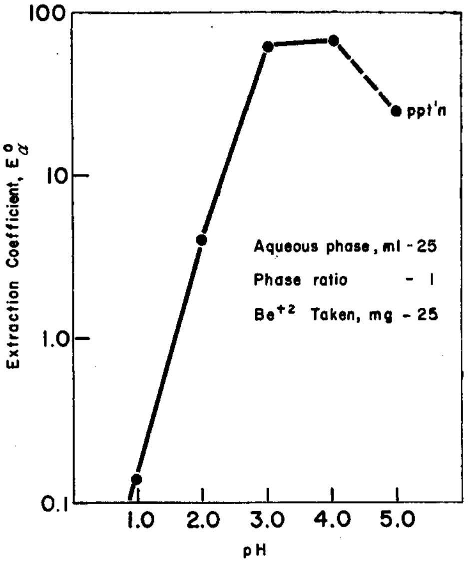

FIG. 1.—Effect of pH on the extraction of Be^{2+} with NaPFB in ether.

Other elements listed by Mann and Yoe[4] as interferences with the method include aluminium, molybdenum, chromium, iron, uranium, thorium, rare earths, and nickel. The normal separation of beryllium from magnesium by extracting the beryllium into perfluorobutyric acid in ether also removes these multivalent cations. The only ion not removed by this extraction is nickel. When present in a concentration level two times that of magnesium, nickel produces a 5% error; at a 5:1 level the error is about 30%. Fortunately, nickel rarely exceeds 100 ppm in these beryllium materials. Nickel does not, therefore, present too difficult a problem in this particular application.

Effect of acid media

Beryllium is extracted equally well from nitric, hydrochloric, or perchloric acid solutions by perfluorobutyric acid in ether; little or no extraction occurs when the beryllium is contained in hydrofluoric or sulphuric acid solutions. This unique property can be made use of in reclaiming the perfluorobutyric acid. The beryllium is back-extracted from the combined ether extracts into 4*M* sulphuric acid, the ether is evaporated, and the reclaimed acid is then ready for future use.

Effect of perfluorobutyric acid

Tests were conducted to determine the effect of perfluorobutyric acid on the colorimetric determination of magnesium. Aliquots of the stock solution of magnesium were diluted with perfluorobutyric acid ranging from 1 to 10 mmoles of the acid. This represents the greatest concentration of perfluorobutyric acid to be encountered in the analysis. From these test solutions aliquots were taken for the magnesium determination by the colorimetric Magon method.

As shown in Table I, perfluorobutyric acid does not affect the absorbance of the magnesium-Magon complex over the range of acid concentration tested.

TABLE I.—EFFECT OF PERFLUOROBUTYRIC ACID ON THE COLORIMETRIC DETERMINATION OF MAGNESIUM

Magnesium, 10 μg	
Perfluorobutyric acid, *mmole*	Absorbance
—	0·512
2·5	·498
5·0	·508
7·5	·528
10·0	·520

The spectrum of the solution of the magnesium complex containing perfluorobutyric acid is identical with the standard magnesium complex. There are two absorption peaks, the maximum occurring at 510 mμ. At this wavelength an absorbance index of 26,500 was reported by Mann and Yoe. The value found in this laboratory, 26,000 is in quite good agreement. This relationship is shown in Fig. 2.

Application to magnesium solutions which contain large amounts of beryllium

Tests were conducted to determine whether, by observing the aforementioned conditions, beryllium could be separated from magnesium in sufficient quantities to permit an accurate measurement of the magnesium. Beryllium was added to dilutions of the stock solution of magnesium. Following a separation of the beryllium by extracting the perfluorobutyrate into ether, the magnesium in the aqueous layer was measured colorimetrically. When the absorbance at 510 mμ is corrected for unused Magon reagent, the adherence to Beer's law is excellent; absorbance is a linear function of concentration. This relationship, which extends to solutions containing 0·4 μg of magnesium per ml (absorbance 0·5), is shown in Fig. 3.

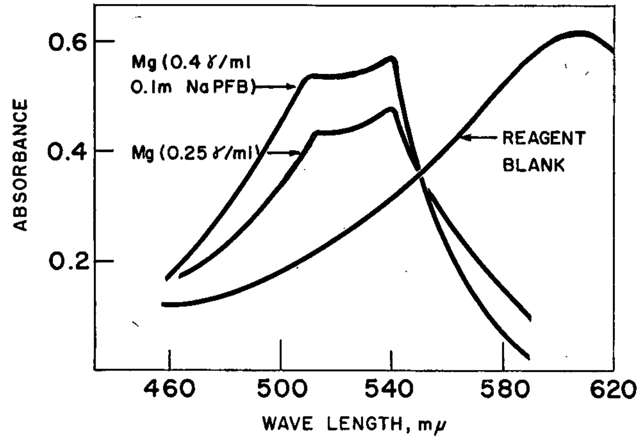

FIG. 2.—Effect of perfluorobutyric acid.
Cary recording spectrophotometer, Model 14M:
1-cm Corex cells.
Reference solution water.
Speed 10 Å/sec.

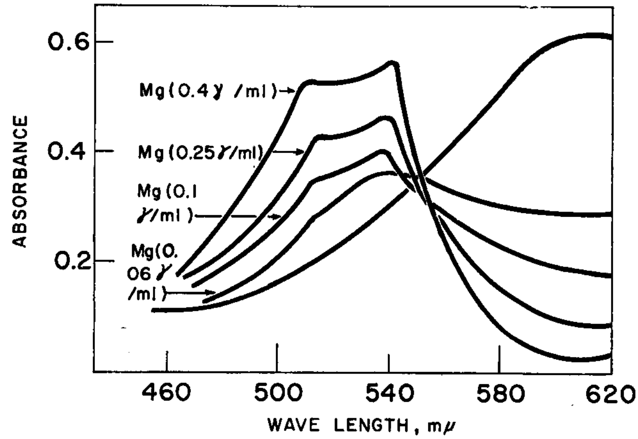

FIG. 3.—Effect of absorbance vs. concentration.
Cary recording spectrophotometer, Model 14M:
1-cm Corex cells.
Reference solution water.
Speed 10 Å/sec.

Precision of the method

The precision of the method was determined at three concentration levels of magnesium, approximately 10, 50, and 100 ppm of magnesium. In all tests the beryllium was removed by extracting it into perfluorobutyric acid in ether. The overall coefficient of variation is 2·5 %. There is no indication of a bias on the basis of these results.

Application of the method

Samples of beryllium metal and its oxide which contained determined amounts of magnesium were obtained, to assess the validity of the method. Typical results for

TABLE II.—PRECISION AND ACCURACY OF THE METHOD

Magnesium, *ppm*	10	50	100
Number of determinations, N	4	4	4
Average magnesium found, $\bar{x}$	12	49	104
Coefficient of variation, %	3·6	2·1	1·9

magnesium, as analysed by the spectrophotometric method, are illustrated in Table III. The results are in excellent agreement over a wide range of magnesium concentrations. The average difference is about 2%

TABLE III.—TYPICAL RESULTS FOR THE SPECTROPHOTOMETRIC DETERMINATION OF MAGNESIUM IN BERYLLIUM METAL AND ITS OXIDE

Magnesium, *ppm*		
Average value A	Found B	Difference A − B
15	17	−2
35	33	+2
40	45	−5
53	56	−3
185*	170	+15
450*	445	+5
700*	680	+20
1140	1100	+40
1500	1550	−50
4700	4730	−30

* Beryllium metal

Average	17
Coefficient of variation, %	4·5
Overall agreement, %	2

Recommended procedure

Weigh a 1- to 2-g sample of beryllium oxide to the nearest 10 mg and transfer to a platinum dish. Add 15 ml of concentrated hydrofluoric acid and 15 ml of concentrated perchloric acid. Heat to strong fumes of perchloric acid, and dilute to 200 ml with water.

Transfer an aliquot which contains 10 to 200 μg of magnesium to a 100-ml beaker, and add 1 ml of 1*M* NaPFB for each 2 mg of beryllium present. Adjust the pH of the test solution to 3–4 by the dropwise addition of a 20% sodium hydroxide solution. Transfer the solution to a 60-ml separatory funnel which contains 25 ml of ether, and equilibrate for 2 min. Drain the aqueous layer into a 50-ml beaker and place on a steam bath to drive off the soluble ether. Cool, and transfer the solution to a 25-ml volumetric flask which contains 4 ml of the polyvinyl alcohol. Add 1:4 ammonium hydroxide dropwise until the solution is just basic to phenolphthalein, and dilute to volume with water. To a 25-ml volumetric flask which contains exactly 5 ml of the Magon reagent, add an aliquot, less than 5 ml and containing 0·5 to 10 μg of magnesium. Add 0·5 ml of the buffer solution, mix and dilute to volume with ethyl alcohol. After 30 min, measure the absorbance of the samples and a blank versus water at 510 and 615 mμ. Since the absorbance at 510 mμ is the sum of the absorbances of the complex and the unreacted reagent, and since a proportional relationship exists between the absorbances at 510 and 615 mμ, the absorbance due to the magnesium is found by calculating and deducting the absorbance of the unreacted reagent.[4]

Zusammenfassung—Eine kolorimetrische Methode zur Bestimmung von Magnesium in Beryllium und dessen Oxyd wird beschrieben. Beryllium, welches bekannterweise in der photometrischen Bestimmung des Magnesiums mit üblichen Farbreagenzien stört, wird selektiv vom Magnesium abgetrennt. Dies geschieht durch Überführen des Berylliums in das Perfluorobutyratsalz bei pH 3–4 und Extraktion desselben durch wiederholtes Ausschütteln mit Äther. Durch Anwenden einer genügenden Anzahl von Extraktionsoperationen ist es möglich bis zu einem Gramm Beryllium von nur 10 μg Magnesium zu trennen. Das Magnesium wird anschliessend spectrophotometrisch bestimmt. Farbreagens ist das Natrium 1-azo-2-oxy-3-(2,4-dimethylcarboxanilido) naphthalin-1-(2-oxybenzol-5-sulphonat). Der Magnesium komplex hat ein Absortpionsmaximum bei 510 mμ. Über einen Bereich 0.04–040 μg Mg/ml wird Beer's Gesetz erfüllt. Die Methode wurde erfolgreich auf die Bestimmung von nur 10 μg Magnesium angewendet. Der Variationskoeffizient für Proben mit 200 μg Magnesium ist 2%.

Résumé—Les auteurs décrivent une méthode colorimétrique de dosage de traces de magnésium dans le béryllium et son oxyde. Le béryllium est connu pour gêner le dosage colorimétrique par les réactifs chromogènes convenables; il est séparé sélectivement du magnésium par formation du perfluorobutyrate de béryllium à pH 3–4, puis par extraction de ce dernier par différentes portions d'éther. En augmentant le nombre d'équilibrages avec l'éther, on peut séparer 1 g de béryllium de 10 μg de magnésium. Le magnésium est ensuite dosé par spectrophotométrie sous forme d'un complexe fortement coloré avec le "magon", 1-azo-2-hydroxy-3-(2,4-diméthylcarboxanilide) naphtalène-1-(2-hydroxybenzène-5-sulfonate) de sodium; ce complexe présente un pic d'absorption maximum à 510 mμ. Dans le domaine 0,04–0,40 μg de magnésium par ml., l'absorption obéit à la loi de Beer. La méthode a été appliquée avec succès au dosage de quantités de magnésium aussi faibles que 10 μg. Le coefficient de variation pour des échantillons de 200 μg de magnésium est de 2%.

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TITRIMETRIC DETERMINATION OF VANADIUM^{III} WITH SODIUM METAVANADATE USING REDOX INDICATORS

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Summary—Conditions have been developed for the accurate titrimetric determination of vanadium^{III} with sodium metavanadate, using diphenylbenzidine, barium diphenylamine sulphonate or *N*-phenylanthranilic acid as an internal indicator. A study of the indicator-oxidant and the oxidised indicator-reductant reactions shows that a satisfactory titration of vanadium^{III} is possible at 45°–50°, in 1–3*N* hydrochloric acid containing phosphoric acid. The indicator reactions are rapid under the conditions described. The titrations are carried out in an inert atmosphere.

THE titrimetric determination of vanadium^{III} using redox indicators does not seem to have received much attention. Ramsay, Sugimoto and Vorkin[1] determined vanadium^{III} by treating a vanadium^{III} solution with an excess of standard potassium iodate solution and determining the unreacted iodate through reaction with potassium iodide. Furman and Garner[2] employed a similiar procedure. Syrokomskii and Zhukov[3] employed vanadium^{III} as a reducing titrant for the determination of potassium permanganate, potassium dichromate and vanadium^{V} using *N*-phenylanthranilic acid as indicator.

Murai[4] reported that vanadium^{III} can be determined in a mixture with vanadium^{IV} by titration with potassium permanganate, using diphenylamine as indicator. With the details available,* the present authors were unable to obtain satisfactory titrations because of the persistence of the colour of the oxidation product of diphenylamine, even after the addition of the first few drops of 0·05*N* potassium permanganate to a vanadium^{III} solution containing diphenylamine. This difficulty is doubtless due to the sluggishness of the reaction between the oxidised indicator and vanadium^{III}. This paper describes investigations on the titration of vanadium^{III} with sodium metavanadate using diphenylbenzidine, barium diphenylamine sulphonate or *N*-phenylanthranilic acid as internal indicators. Potentiometric results which will be presented elsewhere show that the reaction between vanadium^{III} and vanadium^{V} is very rapid at room temperature. Scherbina[5] gave the potential of the vanadium^{III}/vanadium^{IV} couple as +0·4 V at 18° in 1*N* solutions. Jones and Colvin[6] made measurements on cells of the type

$$Pt/VOSO_4.H_2SO_4.V_2(SO_4)_3.H_2SO_4/Hg_2SO_4.Hg$$

and calculated the standard potential of the couple to be +0·33 V at 25°. Syrokomskii and Avilov[7] gave the potential in dilute sulphuric acid as +0·359 V. The vanadium^{V}–vanadium^{IV} couple has a formal potential of 1·002 V in 0·5*M* sulphuric acid at 28°, according to our measurements. Hence it should be possible to titrate a vanadium^{III} solution with a vanadium^{V} solution using diphenylbenzidine or barium diphenylamine sulphonate as internal indicator, because they have transition potentials lying between

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* *Chemical Abstracts*

those of the two systems concerned. If these expectations are to be realised in practice, it is necessary that the reaction between the indicator and vanadium^{V} and the reaction between vanadium^{III} and the oxidised indicator must both be very rapid. The observations reported in Table I show that the speed of the reaction between the indicator and sodium vanadate is slow and slightly accelerated by phosphoric acid, but not sufficiently so to make it useful in a titration. It is also not induced by the vanadium^{III}–vanadium^{V} reaction. The oxidation of diphenylbenzidine or diphenylamine sulphonic acid by vanadium^{V} in the presence of phosphoric acid becomes very rapid only at 45–50°. The results in Table II show that the reaction between the oxidised indicator and vanadium^{III} in hydrochloric acid medium is slow at room temperature, but that the addition of phosphoric acid accelerates the reaction. Even with the addition of phosphoric acid, the oxidised indicator is not reduced quickly enough by vanadium^{III} at room temperature, but is sufficiently rapid at 45–50°. Hence both reactions, the oxidation of the indicator by a trace of vanadium^{V}, and the reduction of the oxidised indicator by a trace of vanadium^{III}, require a temperature of 45–50° and acceleration by phosphoric acid to become rapid enough for a successful titration.

EXPERIMENTAL

Reagents

Vanadium^{III} solution: An approximately 0·05*M* solution of vanadium^{III} was prepared according to the procedure recommended by Lingane and Meites Jr.[9] by reduction of vanadium^{V} in an HCl—H_2SO_4 mixture in a silver reductor. The reduction was carried out in an atmosphere of nitrogen because vanadium^{III} solutions are readily oxidised by atmospheric oxygen. The concentration of vanadium^{V} was kept about 0·1*M*, that of sulphuric acid 4·5*M* and that of hydrochloric acid 7·5*M*. The solution was passed through the reductor at the rate of 30 ml per min. The reduced solution was collected in a flask containing air-free water in an atmosphere of nitrogen. The reductor was washed with air-free water and the washings were collected in the same flask. The solution was then diluted with air-free water to give nearly 0·05*M* vanadium^{III} solution and this was stored in an atmosphere of nitrogen. The solution was standardised from time to time with a standard solution of potassium iodate, according to the method of Ramsay, Sugimoto and Vorkin.[1]

Sodium metavanadate solution: A 0·05*N* sodium metavanadate solution was prepared by dissolving 5·35 g of a sample of ammonium metavanadate (Analytical Reagent grade) in water and boiling with a slight excess of sodium carbonate until free from ammonia. After cooling, the solution was made up to 1 litre. It was standardised against a standard solution of ferrous ammonium sulphate which was previously standardised against a standard solution of potassium dichromate.

Indicator solutions: A 0·1% solution of diphenylbenzidine in concentrated sulphuric acid or a 0·1% solution of barium diphenylamine sulphonate in water or a 0·1% solution of *N*-phenylanthranilic acid in a 5% sodium carbonate solution were used. Other chemicals employed in this study were of Reagent grade.

Reaction between indicator and vanadium^{V}

To 50 ml of 1·0*N* hydrochloric acid solution in a beaker, 0·05 ml of diphenylbenzidine or barium diphenylamine sulphonate was added. To this mixture was then added 0·02 ml of 0·05*M* vanadium^{V} solution. The time taken for the appearance of the colour of oxidised indicator in the absence and presence of phosphoric acid and at different temperatures was noted. The results are presented in Table I.

From Table I it is evident (1) that the oxidation of the indicator by a trace of vanadium^{V} is very slow in 1*N* hydrochloric acid at room temperature, (2) that it is accelerated by phosphoric acid, (3) that it is accelerated by a rise in temperature, and (4) that a temperature of 45–50° and the presence of phosphoric acid are necessary to make the reaction speedy enough for a successful titration.

TABLE I.—INFLUENCE OF PHOSPHORIC ACID AND TEMPERATURE ON THE SPEED OF REACTION BETWEEN THE INDICATOR AND SODIUM METAVANADATE IN 1*N* HYDROCHLORIC ACID MEDIUM

Volume of phosphoric acid, *ml*	Temperature, °*C*	Diphenylbenzidine	Barium diphenylamine sulphonate
nil	25	Blue-violet colour after 120 sec	Pale purple colour after 120 sec
nil	45	Pale blue-violet colour after 30 sec	Pale purple colour after 60 sec
5	25	Blue-violet colour in 15 sec	Pale purple colour in 25 sec
5	45	Blue-violet colour in 2 to 3 sec	Pale purple colour in 3 to 4 sec

Reaction between the oxidised indicator and vanadium^{III}

To 50 ml of 1*N* hydrochloric acid solution, 0·05 ml of 0·1 % diphenylbenzidine or of 0·1 % barium diphenylamine sulphonate was added. The indicator was oxidised by the addition of 0·02 ml of 0·05*M* sodium vanadate solution. To this mixture, kept in an inert atmosphere, was added 0·02 ml of 0·05*M* vanadium^{III} solution, and the time taken for the discharge of the colour of the oxidised indicator was noted. The results are presented in Table II.

TABLE II.—INFLUENCE OF PHOSPHORIC ACID AND TEMPERATURE ON THE SPEED OF THE REACTION BETWEEN THE OXIDISED INDICATOR AND VANADIUM^{III}

Volume of syrupy phosphoric acid, *ml*	Temperature, °*C*	Diphenylbenzidine	Barium diphenylamine sulphonate
nil	25	Colour does not disappear even in 120 sec	Colour does not disappear even in 120 sec
nil	45	Colour disappears in 40 sec	Colour disappears in 60 sec
5	25	Colour disappears in 15 sec	Colour disappears in 10 sec
5	45	Colour disappears in 1 to 2 sec	Colour disappears in 2 to 3 sec

Observations similiar to those in Table II were made in experiments conducted in 2*N* and 3*N* hydrochloric acid. These show that while phosphoric acid accelerates the reaction between the oxidised indicator and vanadium^{III}, the acceleration is not sufficient for a rapid discharge of the colour of the oxidised indicator, which is a necessary condition for a satisfactory titration. The observations in Table II also show that a rapid discharge of the colour of the oxidised indicator is produced in the presence of phosphoric acid when the temperature is raised to 45–50°. Consequently, it should be possible to carry out a visual titration of vanadium^{III} at 45–50° in 1*N* to 3*N* hydrochloric acid in an inert atmosphere (CO_2 or N_2) using diphenylbenzidine or barium diphenylamine sulphonate as internal indicator, in the presence of 5 ml of syrupy phosphoric acid per 50 ml of the titration mixture.

Recommended procedure

The titrations of vanadium^{III} with sodium metavanadate are carried out in a 200-ml tall (titration) flask fitted with a rubber stopper having 5 holes, to accommodate the inlet and outlet tubes for nitrogen, a thermometer, and two burettes, (one burette containing sodium metavanadate solution of known strength and another burette connected to the vanadium^{III} reservoir). Simultaneous stirring and heating of the titration mixture are carried out using a B.T.L. magnetic stirrer and hot plate.

About 30 ml of 1*N* hydrochloric acid are taken in the titration flask, 2 drops of the indicator solution are added and the beaker is stoppered with all the connections duly made. Nitrogen is passed through the mixture, heated to 45–50° and stirred, for about 10 min, About 5 to 15 ml of vanadium^{III} solution are now run into the titration flask, and the mixture is titrated with the standard sodium vanadate solution at the usual speed, until the colour of the oxidised indicator persists. Typical results are presented in Table III.

TABLE III

Indicator	Vanadium^{III} taken, *m moles*	Vanadium^{III} found, *m moles*
Diphenylbenzidine	0·3026	0·3031
	0·3249	0·3254
	0·4586	0·4582
	0·6538	0·6539
	0·7368	0·7371
	0·8643	0·8641
Barium diphenylamine sulphonate	0·3265	0·3268
	0·4532	0·4536
	0·7262	0·7265
	0·8642	0·8639
	0·9486	0·9481

The use of *N*-phenylanthranilic acid has also been investigated in this titration. Even with this indicator, the addition of syrupy phosphoric acid and the use of an elevated temperature have been found necessary to accelerate the reaction between the oxidised indicator and vanadium^{III}. The acidity of the titration mixture should be kept at 4*N* with respect to hydrochloric acid. Although good results have been obtained in these titrations, it has been observed that the colour of the oxidised indicator fades away slowly after the end-point is reached, in contrast to the titration of iron^{II} with sodium vanadate at room temperature. Titrations at room temperature are possible, if carried out dropwise towards the end, and waiting for 30 sec after the addition of each drop.

Zusammenfassung—Bedingungen wurden gefunden zur genauen Bestimmung von Vanadin(III) durch Titration mit Natriumvanadat und Diphenylbenzidin, Bariumdiphenylaminsulfonat oder N-Phenylanthranilsäure als Indicator. Eine Studie der Indicatorreaktionen führte zum Schluss, dass die Titration am besten bei 45–50°C in 1–3 n Salzsäure und 5 ml sirupöser Phosphorsäure per 50 ml Titrationslösung erfolgt. Der Indicatorumschlag unter diesen Bedingungen ist rasch. Die Titration muss in inerter Atmosphäre durchgeführt werden.

Résumé—Les auteurs ont mis au point les conditions du dosage titrimétrique précis du vanadium (III) par le métavanadate de sodium, utilisant comme indicateur interne la diphénylbenzidine, le diphénylamine sulfonate de baryum ou l'acide N-phénylanthranilique. D'après une étude des réactions de l'indicateur, c'est-à-dire des réactions indicateur-oxydant et indicateur oxydé-réducteur, les auteurs ont conclu qu'un titrage satisfaisant du vanadium (III) est possible à 45–50° dans l'acide chlorhydrique 1–3 N, en utilisant 5 ml d'acide phosphorique sirupeux pour chaque portion de 50 ml du mélange à titrer. Les réactions de l'indicateur ne sont rapides que dans ces conditions. Les titrages sont effectués sous atmosphère inerte.

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SALTING-OUT CHROMATOGRAPHY—VII

ANALYSIS OF MIXTURES OF DIALKYLPHOSPHORIC ACIDS, ALKANEPHOSPHONIC ACIDS, AND ORTHOPHOSPHORIC ACID

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Summary—Attempted separations of several phosphorus acids by gas-partition and anion-exchange chromatography were unsuccessful. This paper describes a quantitative method of separation by salting-out chromatography on special Dowex 50-X4 resins of low capacity.

ONE of the research problems of this laboratory is the development of a method of analysis of mixtures of the phosphorus-containing decomposition products of the various insecticides and similar substances. These include the alkanephosphonic acids, their monoalkyl esters, orthophosphoric acid and its dialkyl esters. The alkyl groups found in these compounds include methyl, ethyl, isopropyl and n-butyl. The symbols Pr and Bu are hereinafter used to designate the last two. This paper is concerned with a part of the whole problem, *viz.*, the separation of a mixture composed of the alkanephosphonic acids, the dialkyl esters of phosphoric acid, and orthophosphoric acid.

The phosphorus acids studied in this investigation are not sufficiently volatile to be separated by gas chromatography. A mixture consisting of the ethyl ester of methanephosphonic acid and the methyl ester of ethanephosphonic acid dissolved in ether was subjected to gas-partition chromatography at 270° and 350°. At the lower temperature, the elution graph indicated complete non-volatility. At the higher temperature, decomposition of the acids was observed. Attempted separations of the phosphorus acids by anion-exchange chromatography were unsuccessful because of the small differences in the exchange constants of their conjugate bases and in the ionisation constants of the acids themselves.[1-3]

Results obtained during the investigation of anion-exchange chromatography indicated that van der Waals forces leading to sorption of the phosphorus acids by the anion-exchange resin were of greater importance in determining the distribution coefficient than simple exchange processes. This led to the belief that a cation-exchange resin would be more suitable than an anion-exchanger for the separation of the phosphorus compounds. In the first place, the theoretical treatment with the cation-exchangers is simpler because only van der Waals forces are operating, whereas both van der Waals sorption and ion-exchange occur with the anion-exchangers. In the second place, a change in the hydrogen-ion concentration of the eluent should be more effective in changing the distribution coefficients with a cation-exchanger than with an anion-exchanger because, with the latter, an increase in the acidity of the

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eluent increases the van der Waals sorption but decreases the ion-exchange sorption. Thus, better separations may be expected with a cation-exchanger.

SALTING-OUT CHROMATOGRAPHY

The theory and applications of salting-out chromatography have been discussed in recent publications.[4–9] In this paper the basic equation of the plate theory[10]

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

is used to calculate C values. The symbol U^* represents the volume of eluate collected from the addition of the sample to the peak of the elution graph; V is the interstitial volume of the column; and C is the distribution ratio, defined as the quantity of sample constituent in the resin of any plate divided by the quantity of the same constituent in the interstitial solution of the same plate at equilibrium. Sargent and Rieman[4] have shown that the relationship

$$\log C = \log C_0 + kM \tag{2}$$

is applicable to salting-out chromatography. Here C_0 is the distribution ratio with water as eluent; C is the distribution ratio with an aqueous salt solution of molarity M; and k is the salting-out constant. Investigation of low-capacity Dowex resins has revealed their superiority in achieving separations by salting-out chromatography.[8] Therefore, Dowex resins of low capacity were used throughout this study.

CHOICE OF ELUENT

The following compounds were investigated as possible salting-out agents: NH_4NO_3, $(NH_4)_2SO_4$, $NaNO_3$, $MgCl_2$, NaCl and LiCl. Ammonium nitrate and ammonium sulphate were rejected because of their comparatively small salting-out power. Sodium nitrate was not used because it crystallised from concentrated solutions at the tip of the stopcock attached to the ion-exchange column. Lithium chloride was chosen in preference to magnesium chloride and sodium chloride because its solutions gave a greater number of theoretical plates for the same length of column. Investigation of the effect of the hydrogen-ion concentration on the ratio of the C values for EtPO(OH)OEt and MePO(OH)OPr indicated that this ratio did not increase greatly with an increase in hydrogen-ion concentration above $1M$.[1] In view of these considerations, a solution $4{\cdot}0M$ in LiCl and $1{\cdot}0M$ in HCl was chosen as the best possible eluent for the separation of the acids of lower molecular weight.

EXPERIMENTAL WORK

Materials

Most of the phosphorus compounds were supplied by the Army Chemical Center. The phosphonic acids $EtPO(OH)_2$ and $PrPO(OH)_2$ were prepared by hydrolysing the respective esters EtPO(OH)OPr and PrPO(OH)OEt in boiling $6M$ hydrochloric acid.[11] The orthophosphoric acid used was of assayed reagent-grade.

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

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

Determination of the interstitial volume

The interstitial volumes of the resin columns were determined under the conditions used in this investigation, *viz.*, with eluents of 0, 2, 4, 6 and $8M$ LiCl, each also $1M$ with HCl. These values are necessary in order to calculate C, the distribution ratios of the several phosphonate esters with the various eluents. These, in turn, are needed to plan the separation intelligently.

Methods

Five methods were used:

(1) *Centrifuge.* Short columns were prepared in centrifuge tubes. The eluent was drained to the upper level of the resin; the tube was weighed, centrifuged, and reweighed. The loss in weight represents the interstitial solution. Corrections were applied (*a*) for the liquid removed from the filter disc during centrifugation and (*b*) for the interstitial solution (3 % of the bed volume) that clings to the resin even after centrifugation.

(2) *Break-through experiment with polystyrene sulphonic acid.* A column was equilibrated with the eluent to be studied containing $0{\cdot}001N$ linear polystyrene sulphonic acid. Then the same eluent, free of the polystyrene sulphonic acid, was passed through the column. Fractions of the effluent were analysed to locate the break-through of the polymer-free eluent. This break-through was sharp. The volume of effluent collected when the concentration of the polystyrene sulphonic acid was $0{\cdot}0005N$ was taken as the interstitial volume. A correction was applied for the volume of liquid in the pores of the filter disc and clinging to the inside walls of the tube below the filter. Polystyrene sulphonic acid was used for this purpose because its large molecular size prevents it from penetrating into the resin beads.[12]

(3) *Determination of interstitial polystyrene sulphonic acid.* A column was equilibrated with the eluent in question containing $0{\cdot}001N$ polystyrene sulphonic acid. After draining the eluent to the upper level of the resin, the same eluent without the polyelectrolyte was passed through the column until all the polyelectrolyte was removed. The polyelectrolyte in the effluent was determined. This quantity, in milliequivalents, divided by the normality of the polyelectrolyte, gives the interstitial volume. A correction was applied as in the foregoing method.

(4) and (5) *Analogous methods with sodium polyphosphate.* Methods (4) and (5) are analogous to methods (2) and (3), respectively, except that sodium polyphosphate was employed as the polyelectrolyte. Also, in order to avoid degradation of the polyphosphate, the hydrochloric acid was omitted from the eluents.

Elution

The preparation of columns for ion-exchange separation has been described.[13] The resin, having a capacity of 3·82 meq per g, was equilibrated with the eluent, $4{\cdot}0M$ in LiCl and $1{\cdot}0M$ in HCl, by passing 1 litre of this solution through the column. The eluent was then drained to the top of the resin bed. The height of the resin column at this point was 61·8 cm. A sample of 1·00 ml was pipetted on to the top of the resin bed and was allowed to drain into the resin. At this point, collection of the effluent was initiated. The sample was then completely washed into the resin with the aid of three small portions of the first eluent (3–4 ml). After each addition the solution was permitted to drain into the resin. All eluent changes were made after draining the previous eluent completely into the resin bed. The column was maintained at a temperature of 50 ± 2°. The hydrostatic head of the eluent was adjusted (1·5 metres) so as to give an initial flow rate of 0·11 cm per min. Small fractions (2·76 or 3·10 ml) were collected with the aid of a siphon pipette[14] and a Misco fraction collector.

Analysis of eluate fractions

The procedure used involved the conversion of the organophosphorus acids to orthophosphate, and the determination of the resulting orthophosphate by the molybdovanadate method. [15–17]

The investigation of Kolmerten and Epstein[18] indicated the vital role played by the ratio of the chloride ion to sodium hydroxide concentrations in the persulphate oxidation of organophosphorus compounds. They used sodium sulphite to destroy the excess persulphate that remained after 1 hour of heating. This step was eliminated in this work by extending the period of heating to 2 hours. The phosphovanadomolybdate method, originally proposed by Misson,[17] was used to determine the concentration of the orthophosphate.

Each fraction, containing 2·76 or 3·10 ml of a solution $4{\cdot}0M$ in LiCl and $1{\cdot}0M$ in HCl plus no more than 0·03 mmols of phosphorus, was treated with 1·0 ml of $18M$ sodium hydroxide and 2·0 ml of $1{\cdot}0M$ ammonium persulphate. Distilled water was added to bring the final volume to approximately 20 ml. The contents of each test-tube were thoroughly mixed, and the test-tubes were placed in a beaker of boiling water. The samples were digested for a period of 2 hr. Fractions that contained 1·0*M* HCl or water, plus no more than 0·03 m mols of phosphorus, were treated in the same way except that only 0·5 ml of 18*M* sodium hydroxide was used. The contents of each test-tube were then quantitatively transferred to a 100-ml volumetric flask with the aid of 50 ml of 0·3*M* nitric acid. Exactly 25 ml of vanadomolybdate reagent, prepared according to the method of Barton,[15] were pipetted into each flask. The solutions were then diluted to the mark with distilled water, and the contents of each flask were thoroughly mixed. The absorbance at 400 $m\mu$,[15,16] versus a blank prepared in the same manner, was determined after a 2-hr development period. All absorbance measurements were made with a Beckman DU spectrophotometer with 1-cm Corex cells. Calibration curves were prepared according to the method proposed by Goudie and Rieman.[19]

RESULTS AND DISCUSSION

The interstitial volumes

Table I gives a summary of the determinations of the relative interstitial volumes, *i.e.*, the ratio of the interstitial volume to the bed volume.

TABLE I.—RELATIVE INTERSTITIAL VOLUME OF DOWEX 50-X4 (325 mesh, 4·03 meq per g)

Eluent	0·0*M* LiCl 1·0*M* HCl	2·0*M* LiCl 1·0*M* HCl	4·0*M* LiCl 1·0*M* HCl	6·0*M* LiCl 1·0*M* HCl	8·0*M* LiCl 1·0*M* HCl
Mean relative interstitial vol.	0·325	0·335	0·346	0·355	0·380

The standard deviation never exceeded 0·20. Thus, these results have about the same precisions as those reported elsewhere.[12] As is to be expected from the fact that the resin shrinks and becomes less deformable in concentrated LiCl, the interstitial volume increases with increasing concentration of eluent.

Changes in column height

The volume of a bead of ion-exchange resin increases with decreasing concentration of electrolytes in the eluent. When the eluent was changed from a solution 4·0*M* in LiCl and 1·0*M* in HCl to 1·0*M* HCl, the first effect of this swelling was a decrease in the interstitial volume and hence in the flow rate; the rate diminished to about one-half of its original value. Later, the resin bed expanded and the column height rose to a steady value of 77·0 cm. During this expansion, the flow rate gradually increased to about its original value. The second change of eluent from 1·0*M* HCl to pure water caused another gradual increase in column height to 99·5 cm without great changes in the flow rate.

Temperature effect

Resins of lower capacities do not swell as much as resins of normal capacities.[8] Since the former have less internal water, diffusion within these resins is restricted. Thus slow flow-rates would be necessary to ensure the attainment of equilibrium conditions and symmetrical elution graphs. Higher temperatures increase the diffusion rates within the resins, thereby permitting higher flow-rates. Temperatures above 50° are not desirable because of the formation of air bubbles in the ion-exchange columns.

Flow-rates between 0·03 and 0·20 cm per min resulted in symmetrical elution curves. Flow-rates greater than 0·20 cm per min were not used because some of the elution graphs began to exhibit tailing. Flow-rates below 0·03 cm per min are not convenient.

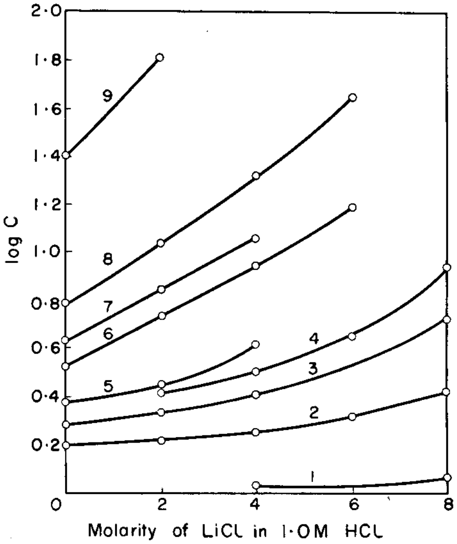

FIG. 1.—Plots of log C *vs.* molarity of LiCl in 1·0M HCl with Dowex 50-X4, 4·03 meq per g. 1. H_3PO_4; 2. $CH_3PO(OH)_2$; 3. $EtPO(OH)_2$; 4. $HOPO(OMe)_2$; 5. $PrPO(OH)_2$; 6. $HOPO(OEt)_2$; 7. $BuPO(OH)_2$; 8. $HOPO(OPr)_2$; 9. $HOPO(OBu)_2$.

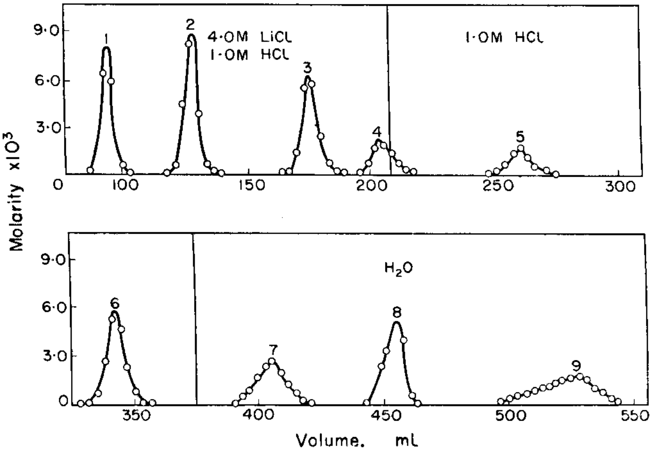

FIG. 2.—Separation of a nine-component mixture. 61·8 cm × 2·76 cm^2 Dowex 50W-X4, 325 mesh, 3·82 meq per g. The numbers correspond to the compounds listed in Fig. 1.

Results of analysis of known mixtures

Fig. 1 demonstrates that the plots of log C versus concentration of the lithium chloride are not linear. This is to be expected since equation (2) is applicable only if the resin remains in the same ionic form.[9] This is not the case with the results of Fig. 1; the mole fraction of lithium resin decreases with decreasing LiCl in the eluent.

Fig. 2 reveals the quantitative separation of the nine compounds under investigation. No theoretical explanation can be given by the authors for the heading exhibited by $(BuO)_2PO(OH)$. Table II lists the recoveries obtained from three separate analyses. The recoveries are within the experimental limits observed in the determination of known concentrations of organophosphorus compounds under the same condition.

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Zusammenfassung—Versuche einige Phosphorsäure durch Gaschromatographie und Anionenaustauschchromatographie zu trennen waren erfolglos. Die vorliegende Arbeit beschreibt eine quantitative Trennungsmethode durch Aussalzchromatographie an einem speziellen Harz Dowex 50-X4 mit niederer Kapazität.

Résumé—Une tentative de séparation de différents acides phosphoreux par chromatographie de gaz et d'échanges anioniques n'a pas réussi. Cet article décrit une méthode quantitative de séparation par chromatographie d'exclusion d'ions sur des résines spéciales Dowex 50-X4 de faible capacité.

TABLE II.—ANALYSIS OF KNOWN MIXTURES

Mixture no.	1			2			3		
Compound	Taken, mmoles.	Found, mmoles.	% recovery	Taken, mmoles.	Found, mmoles.	% recovery	Taken, mmoles.	Found, mmoles.	% recovery
H_3PO_4	0·0362	0·0378	104	0·0362	0·0375	103	0·0422	0·0401	95
$MePO(OH)_2$	0·0481	0·0481	100	0·0481	0·0505	105	0·0561	0·0556	99
$EtPO(OH)_2$	0·0444	0·0415	94	0·0444	0·0446	100	0·0513	0·0495	97
$HOPO(OMe)_2$	0·0177	0·0168	95	0·0177	0·0174	98	0·0206	0·0220	107
$PrPO(OH)_2$	0·0140	0·0139	99	0·0140	0·0145	103	0·0163	0·0165	101
$HOPO(OEt)_2$	0·0484	0·0454	94	0·0484	0·0520	108	0·0564	0·0532	94
$BuPO(OH)_2$	0·0331	0·0286	86*	0·0331	0·0347	105	0·0386	0·0379	98
$HOPO(OPr)_2$	0·0379	0·0383	100	0·0379	0·0395	104	0·0442	0·0452	102
$HOPO(OBu)_2$	0·0379	0·0367	97	0·0379	0·0398	105	0·0442	0·0453	102
Mean			98			103			99
Standard deviation			4			3			4

* A failure of the automatic fraction collector caused the loss of eluate from $U = 398$ to $U = 428$. Since this portion contained some $BuPO(OH)_2$, the recovery of this compound is low. This value has been excluded from the mean and standard deviation.

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TITRIMETRIC DETERMINATION OF TITANIUM^{III} WITH SODIUM METAVANADATE—I

USE OF NEUTRAL RED, PHENOSAFRANINE OR SAFRANINE-T AS REDOX INDICATORS

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Summary—Conditions have been developed for the titrimetric determination of titanium^{III} with sodium metavanadate in a hydrochloric acid medium at room temperature, using neutral red, or phenosafranine, or safranine-T as redox indicators. A study of the indicator reactions has shown that while the reduced dye is rapidly oxidised by a trace of sodium metavanadate, the oxidised dye is only very slowly reduced by titanium^{III} in a hydrochloric acid medium. The reaction is, however, markedly accelerated by oxalic acid even at room temperature. This catalysis enables the satisfactory functioning of any of these dyes as internal indicators for the titration of titanium^{III} with vanadium^{V}. The colour of the dye which is discharged by titanium^{III} in a hydrochloric acid + oxalic acid medium is sharply restored when all of the titanium^{III} is oxidised to titanium^{IV}. In this titration the vanadium^{V} is reduced to vanadium^{III}. Iron^{II} and low concentrations of vanadium^{III} do not interfere in the titration. Methylene blue cannot be used as a redox indicator in this titration.

Smith and Kurtz[1] employed cerium^{IV} sulphate for the differential visual titration of titanium^{III} and iron^{II} in a carbon dioxide atmosphere using methylene blue and ferroïn as indicators for the first and second parts of the titrations. Shippy[2] carried out the same determination with potassium permanganate. The mixture was first titrated at 60° in a carbon dioxide atmosphere with potassium permanganate using methylene blue as indicator, then titrated at room temperature using ferroïn as indicator. The first titre gives a measure of titanium^{III} and the second titre gives a measure of iron^{II}. Syrokomskii and Silaeva[3] titrated titanium^{III} with cerium^{IV} sulphate solution, using cacotheline as indicator. They stated that the titration could be carried out even in the presence of air, if the mixture is treated with 15 ml of saturated ammonium sulphate solution or 10 ml of acetic acid. They believe that the complexes formed by titanium^{III} with ammonium sulphate or acetic acid are suffiently stable to resist oxidation by atmospheric oxygen during the titration. Wehber, Johannsen and Heydecke[4] carried out the determination of titanium^{III} and iron^{II} in a mixture, employing potassium dichromate as an oxidimetric titrant and cacotheline and the sodium salt of *N*-methyldiphenylamine sulphonic acid as redox indicators. From a survey of the literature, it appears that the titrimetric determination of titanium^{III} has not so far been made with sodium metavanadate using redox indicators. When vanadium^{V} solution is added slowly to a titanium^{III} solution, the vanadium^{V} is reduced to vanadium^{III}:

$$VO_2^+ + 2Ti^{3+} \rightarrow V^{3+} + 2TiO^{2+} \qquad (1)$$

Although vanadium^{IV} may appear as an intermediate, it will be reduced further to vanadium^{III}. The vanadium^{III} is capable of reacting further with vanadium^{V}:

$$V^{3+} + VO_2^+ \rightarrow 2VO^{2+} \qquad (2)$$

The end of (1) can be detected by indicators having such low redox potentials that their reduced forms are easily oxidised by vanadium^{IV}. We have carried out the titration of titanium^{III} using neutral red, phenosafranine and safranine-T as redox indicators. According to Tomiček,[5] these indicators have normal potentials of 0·34 V, 0·25 V and 0·289 V, respectively, at pH 7 and a temperature of 30°. From the results presented in Table I, it will be evident that the speed of reduction of any one of these dyes by titanium^{III} in a 1·0*N* hydrochloric acid medium is very slow at room temperature. The reduction of the dye by titanium^{III} is, however, much accelerated by a small concentration of oxalic acid. It has therefore been found possible to carry out titrations of titanium^{III} with sodium metavanadate in a hydrochloric acid medium at room temperature, using any one of these dyes as an internal indicator in an inert gas atmosphere.

EXPERIMENTAL

Reagents

Titanium^{III} solution: The sample of titanium^{III} chloride employed in this investigation was of Analytical Reagent quality supplied by May and Baker, London. It was tested and found to be free from iron^{II}. A 0·05*N* solution of titanium^{III} in 2*N* hydrochloric acid solution was prepared from this sample and stored in the customary manner in an atmosphere of nitrogen. It was standardised by adding an aliquot to an excess of iron^{III} alum solution and titrating the iron^{II} formed against standard potassium dichromate solution, using diphenylbenzidine as internal indicator.

Sodium metavanadate solution: A 0·05*N* solution was prepared from B.D.H. AnalaR-grade ammonium metavanadate, by dissolving the requisite quantity of the sample in 300 ml of water and heating with a slight excess of sodium carbonate until all the ammonia was driven off. The solution was cooled and made up to 1 litre, and was standardised against a solution of Mohr's salt, which in turn had been standardised against a standard solution of potassium dichromate.

Indicator solutions: A 0·1% aqueous solution of each indicator was prepared from a sample supplied for use as a biological stain. A 0·1-ml portion of this solution was added to 50 ml of the titration mixture. In 1·0*N* hydrochloric acid the colours of the three indicators (neutral red, phenosafranine and safranine-T) are found to be purple, reddish-purple and red, respectively. These change to colourless when reduced to the leuco state. Fresh solutions of the indicators should be used. An aged sample of phenosafranine gives considerable trouble in the detection of the true end-point.

RESULTS AND DISCUSSION

Influence of oxalic acid on the speed of reduction of neutral red, phenosafranine, and safranine-T by titanium^{III}

Fifty ml of 1*N* hydrochloric acid containing 0·1 ml of the indicator solution were transferred to a vessel fitted with a three-holed stopper. Through the central hole passed a microburette connected to the storage bottle containing titanium^{III}, and the two other holes carried the inlet and outlet tubes for passing carbon dioxide. Carbon dioxide was passed through the vessel for about 10 min, and 0·05 ml of about 0·05*N* titanium^{III} chloride solution was then added from the microburette. The time taken for the discharge of the indicator colour was noted. The observations are recorded in Table I.

It is evident from Table I, that the speed of reduction of the indicator by titanium^{III} is very slow and that it is markedly accelerated by oxalic acid. The formal potential of the Ti^{IV}/Ti^{III} couple in 1*N* hydrochloric acid at 28° was found to be 0·027 V against the normal hydrogen electrode. The formal potential was not altered by the addition of oxalic acid at concentrations lying between 0·005 to 0·100 moles per litre to a solution containing titanium^{III} and titanium^{IV} each at 0·005*M* concentration. Although no change in potential was observed on the addition of oxalic acid to the titanium^{III}–titanium^{IV} mixture, the mixture developed a yellow-brown colour even in 1·0 *N* hydrochloric acid. This indicates the formation of a complex which is quite

TABLE I. INFLUENCE OF OXALIC ACID ON THE SPEED OF REDUCTION OF NEUTRAL RED, PHENOSAFRANINE AND SAFRANINE-T BY TITANIUM^{III} IN 1·0N HYDROCHLORIC ACID

Concentration of oxalic acid, *moles per litre*	Time taken for the discharge of the colour of the dye, *sec*		
	Neutral red	Phenosafranine	Safranine-T
Nil	840	840	840
0·005	160	100	120
0·005	60	40	50
0·010	15	8	10
0·020	5	2	5
0·050	immediate	immediate	immediate
0·100	immediate	immediate	immediate

stable to hydrochloric acid. Pecsock[6] has already reported that the titanium^{III}–oxalate complex is yellow and has the composition titanium^{III}:oxalate = 1:2, and that the titanium^{IV}–oxalate complex is colourless. Our observation that there is no change of potential on adding oxalic acid to the titanium^{III}-titanium^{IV} mixture leads to the conclusion that both the oxalate complexes of titanium^{III} and titanium^{IV} have nearly the same stability constants. A similar conclusion appears to have been arrived at by Pecsock[6] from his polarographic studies. It is very significant that oxalic acid exerts a marked accelerating action on the reduction of the dye by titanium^{III}, although it does not change the redox potential of titanium^{III}. The transition potentials of the three indicators were found to be +0·1 V, +0·16 V and +0·17 V for neutral red, phenosafranine and safranine-T, respectively. These are the potentials at which the indicator colour is discharged in 1·0N hydrochloric acid in the presence of oxalic acid and in an atmosphere of carbon dioxide at 28°. Under the conditions of titration recommended below, the indicator correction has been found to be negligible.

Recommended procedure

Twenty-five ml of 2N hydrochloric acid, 10–15 ml of 0·5M oxalic acid and 0·1 ml of 0·1% indicator solution are transferred to a titration flask fitted with a four-holed stopper. Through two holes pass the inlet and outlet tubes for passing carbon dioxide and through the other two holes pass the microburette containing sodium metavanadate solution and the microburette attached to the titanium^{III} reservoir. A stream of carbon dioxide is passed through the mixture for 10 min to free it from air. An aliquot of the titanium^{III} solution (about 3–5 ml of about 0·05N solution) is then added to the mixture. The mixture is titrated with sodium metavanadate solution while carbon dioxide continues to pass rapidly. The end-point of the titration is sharply indicated by the appearance of the original colour of the dye. The progress of the titration is also indicated by the gradual disappearance of the yellow-brown colour of the titanium^{III}–oxalate complex, the titanium^{IV}–oxalate complex being colourless. In dealing with dilute solutions, the blue-green colour of vanadium^{III} does not mask the strong purple colour of neutral red, the reddish-purple colour of phenosafranine or the red colour of safranine-T. In titrations of titanium^{III} solutions of higher concentration than that indicated above, this difficulty arises.

A large number of titrations have been made under the conditions recommended and some typical results are presented in Table II. In this titration the vanadium^{V} is reduced to vanadium^{III}. Hence the equivalent weight of sodium metavanadate is equal to half the formula weight.

TABLE II. VANADAMETRIC DETERMINATION OF TITANIUM^{III}

Indicator	Amount of titanium^{III} taken, *millimoles*	Amount of titanium^{III} found, *millimoles*
Neutral red	0·8463	0·8458
	0·6356	0·6361
	0·5328	0·5324
	0·2664	0·2659
	0·2234	0·2232
Phenosafranine	0·9486	0·9482
	0·7434	0·7430
	0·4743	0·4748
	0·3665	0·3656
Safranine-T	0·8764	0·8766
	0·6822	0·6824
	0·4368	0·4362
	0·2436	0·2440

Variation of hydrochloric acid concentration

The acid concentration of the titration mixture can be varied from $1N$ to $3N$ hydrochloric acid without affecting the accuracy of the titration. All three indicators have a purple colour in $3{\cdot}0N$ hydrochloric acid which is slightly different from the colours in $1{\cdot}0N$ hydrochloric acid.

Advantages of the vanadametric procedure

As the transition potentials of neutral red, phenosafranine and safranine-T are lower than the redox potentials of vanadium^{III} and iron^{II}, it is obvious that titanium^{III} can be titrated with sodium metavanadate in the presence of vanadium^{III} and iron^{II} using these indicators. Vanadium^{III} and iron^{II} interfere in the titration of titanium^{III} with sodium metavanadate if indicators like diphenylbenzidine, *N*-phenylanthranilic acid and ferroïn are employed. A large number of titrations of titanium^{III} have been made with sodium metavanadate, using neutral red, phenosafranine or safranine-T in the presence of iron^{II} or vanadium^{III} under the recommended conditions, and these have shown that iron^{II} and vanadium^{III} do not interfere. The vanadium^{III} should not be present in such a concentration as to mask the colour of the indicator.

Potassium dichromate has been tried as the oxidimetric titrant in place of sodium metavanadate but the results were found to be high and erroneous, presumably because of the reaction between titanium^{III} and chromium^{VI} inducing a reaction between oxalic acid and chromium^{VI}.

Zusammenfassung—Bedingungen zur titrimetrischen Bestimmung von Titan(III) mit Natriummetavanadate in salzsaurer Lösung, bei Zimmertemperatur und unter Verwendung von Neutralrot, Phenosafranin oder Safranin T als Redoxindicator wurden entwickelt. Es wurde gefunden, dass der reduzierte Indicator sehr rasch durch Metavanadat oxydiert wird, während die oxydierte Form nur sehr langsam durch Titan(III) reduziert wird. Die letztere Reaktion wird jedoch durch Zusatz von Oxalsäure wesentlich beschleunigt und das selbst bei Raumtemperatur, sodass jeder der erwähnten Farbstoffe als Indicator verwendet werden kann. Die Farbe der Indicatoren verschwindet in Salz-Oxalsäuremedium auf Zugabe von Titan(III), wird jedoch rasch wiederhergestellt, wenn alles Titan zur vierwertigen Stufe oxydiert ist. In dieser Titration wird Vanadin(V) zu Vanadin(III) reduziert. Eisen(II) und kleine Mengen von Vanadin(III) stören die Bestimmung. Methylenblau kann als Indicator nicht verwendet werden.

Résumé—Les auteurs ont mis au point les conditions du dosage titrimétrique du titane(III) par le métavanadate de sodium en milieu acide chlorhydrique à la température ambiante, en utilisant le rouge neutre, la phénosafranine ou la safranine T comme indicateurs d'oxydo-réduction. Une étude des réactions de l'indicateur a montré que, tandis que le colorant réduit est oxydé rapidement par une trace de métavanadate de sodium, le colorant oxydé est réduit seulement très lentement par le titane(III) en milieu acide chlorhydrique. Cependant, la réaction est notablement accélérée par l'acide oxalique, même à la température ambiante. Cette catalyse permet à n'importe lequel de ces colorants de fonctionner comme indicateur interne pour le dosage du titane(III) par le vanadium(V). La couleur du colorant, qui est masquée par le titane(III) en milieu acide chlorhydrique-acide oxalique, réapparaît nettement quand tout le titane(III) est oxydé en titane(IV). Dans le titrage le vanadium(V) est réduit en vanadium(III). Le fer(II) et de faibles concentrations de vanadium(III) ne gênent pas. Le bleu de méthylène ne fonctionne pas comme indicateur interne.

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PRELIMINARY COMMUNICATION

Die Bestimmung von Fluor in Mineralwässern mittels Zr-Xylenolorange

(*Received* 28 *December* 1960; *revised paper received* 9 *March* 1961)

ZUR Bestimmung kleiner Mengen von Fluor nützt man meistens ihre Fähigkeit aus, färbige Chelate oder Komplexe einiger Metalle zu zersetzen. Aus der Tabelle ist ersichtlich, dass der Einfluss der Komponenten, welche bei dieser Bestimmung stören, klein ist, wenn man zu diesem Zweck Zr-Xylenolorange benützt. Im Vergleich mit der das erstemal von Megregian[1] veröffenslichten Zr-Eriochromcyanin-Methode, welche für eine der besten gegenwärtigen Fluorbestimmungen gehalten wird,[2] ist in der neu vorgeschlagenen Methode z.B. der Einfluss von Phosphaten um zwei und der Einfluss der Sulphate um mehr als eine Grössenordnung kleiner. Ausserdem ist die Zr-Xylenolorange-Methode um eine halbe Grössenordnung empfindlicher. Ausführlichere Angaben werden später veröffentlicht.

TABELLE I.—DER EINFLUSS DER HAUPTSÄCHLICH STÖRENDEN KOMPONENTEN IN 1,2 n HCl

μg/50 ml	Einfluss %
10 F^- + 5000 PO_4^{3-}	0
10 F^- + 50 Al^{3+}	0
10 F^- + 2000 Fe^{3+}	0
6 F^- + 6000 SO_4^{2-}	+15
10 F^- + 10000 SO_4^{2-}	+12*
16 F^- + 16000 SO_4^{2-}	+8

* Bei dem Gebrauch verschiedener Präparate von Xylenolorange (der Fma. Chemapol) wurde der Einfluss von 6–24% festgestellt. Grössere Fehler entstehen wahrscheinlich infolge der Zersetzung von Xylenolorange. Wenn man nämlich die Lösung des Präparates mit kleinstem Sulphateinfluss mit ultraviolettem Licht beleuchtete, verminderte sich das Absorptionsmaximum (440 mμ) der Lösung und der Einfluss der Sulphate erhöhte sich.

Der Hauptgrund des kleineren störenden Einflusses fremder Ione in der neu vorgeschlagenen Methode ist die grössere Stabilität des Chelates von Zirkon mit einem Farbstoff, welches zwei N,N-di(carboxymethyl)-aminomethyl Gruppen hat. Diese Stabilität ermöglicht die Bestimmung von Fluor in einem relativ stark sauren Milieu, welches z.B. den Ion AlF^{2+} zersetzt, welcher bei der Fluorbestimmung schon bei gleicher Menge von Aluminium und Fluor oft beträchtliche negative Fehler verursacht.[3] Beim Gebrauch stabiler Chelate äussert sich auch am besten der Unterschied in der Festigkeit der Bindung von Zirkon mit z.B. Fluorid und Sulphat. Wenn im Gegenteil die Bindung von Zirkon mit dem Farbstoff schwächer ist als die zwischen Zirkon und Sulphat, ist die Destruktionswirkung der Sulphate und Fluoride gegenüber einem solchem Chelat praktisch dieselbe.

ARBEITSVORSCHRIFT

Wenn das analysierte Naturwasser ungefähr 1 mg F/l enthält, werden 10 ml der Probe in einen 50 ml Messkolben mit 10 ml Zirkon-Lösung* pipettiert. Nach einer 20 Min. dauernden Erwärmung

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* Bei der Herstellung der Zirkon-Lösung wurden 30,0 mg $ZrOCl_2.8\ H_2O$ in etwa 40 ml dest. Wasser aufgelöst und einer ausgekühlten verdünnten Salzsäure (500 ml konc. HCl + ca 400 ml H_2O) beigemischt und auf 1000 ml aufgefüllt. Damit die Polymerisation der Zirkonionen ausgeschlossen wird, ist es nicht ratsam, die Temperatur der Lösung unter 20° sinken zu lassen.

bei etwa 60° und einer 40 Min. dauernden Abkühlung der Lösung werden 2,00 ml einer 0,20% wässerigen Lösung von Natrium-Xylenolorange beigegeben und das Volumen der Lösung auf 50 ml aufgefüllt. Nach ungefähr 1 St. werden die Lösungen in Küvetten von 4 cm Messlänge bei 540 mμ gegenüber einer gleich zubereiteten Bezugslösung mit 20 μg F/50 ml photometriert.

Der summare Fluorgehalt der Proben wird mittels einer Eichkurve ausgewertet, deren Verlauf man inmitten jeder Bestimmungsserie mit Hilfe einiger Eichlösungen und mittels eines Korrektionsnomogrammes für den Sulphatgehalt bestimmt.

Die Messungen wurden mit Hilfe des Spektrophotometers Uvispek der Fma Hilger durchgeführt.

Ebenfalls wird die Ausnützung weiterer der Xylenolorange ähnlicher Farbstoffe wie z.B. Sarkosinkresol-Rot, Methyl-, Butylthymol-Blau usw. und auch Arsenazo III verfolgt.

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Zusammenfassung—Die neue vorgeschlagene Methode, welche die Entfärbung des Chelates von Zirkon mit Xylenolorange im Milieu einer beiläufig 1,2*N* Salzsäure ausnützt, ermöglicht eine schnelle Bestimmung von Fluor in Mineralwässern und anderen Materialen mit hohem Gehalt an Phosphaten, Sulfaten, Eisen (III) und Aluminium und anderen Ionen.

Summary—The method proposed, based on the decolorisation of the zirconium–Xylenol Orange chelate in a 1·2*N* hydrochloric acid medium, permits rapid determination of fluorine in mineral waters and other materials containing relatively large amounts of phosphate, sulphate, aluminium, iron^{III} and other ions.

Résumé—Le dosage du fluorure est basé sur la décoloration du chélate zirconium-xylénolorange en milieu acide chlorhydrique environ 1,2*N*. Cela permet de doser rapidement le fluor dans les eaux minérales et dans d'autres produits contenant de plus grandes quantités de phosphate, sulfate, aluminium, fer ferrique et autres ions.

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SHORT COMMUNICATIONS

Precipitation from homogeneous solutions of mixed solvents

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The literature pertaining to methods of achieving precipitation from homogeneous solution has been carefully reviewed by Gordon, Salutsky and Willard.[1] A study of this compilation reveals that past procedures may be broadly classified into one of two groups. One of these involves the direct *in situ* generation of the precipitating ion by a controlled reaction, usually hydrolysis; and the other is an indirect method which utilises a gradual change of pH to decrease the solubility of the desired compound slowly. Although the precipitant may be a general reagent capable of the precipitation of several ions, serious limitations exist in the application of either of these methods. In the first case the generation reaction usually has a high pH dependence and thus the acidity of the solution must be within a specific range in order to achieve the required rate of precipitation. In the second case the use of a pH change to effect the precipitation results in the precipitation of all salts insoluble over the pH range employed. In neither case is one permitted a free choice of the pH required for selective precipitation.

This project represents an attempt to arrive at a method whereby a general precipitating agent may be used to effect precipitation from an initially homogeneous solution of any desired pH. The general principle of the procedure involves the use of an organic precipitant which is added to a mixture of the solution containing the ion to be precipitated and a water-miscible organic solvent. Then, after the addition of the buffer, the organic solvent is removed by a slow volatilisation and precipitation of the desired compound at a pre-selected pH is permitted. That such a process should yield the desired increase in crystallinity, with its associated increase in ability to separate similiar species, is borne out by recently reported work of Firsching[2] and by an earlier paper by Wilson and Wilson.[3]

The present authors have shown that this method may be successfully employed for precipitating aluminium^{III} 8-quinolinate from a homogeneous acetone-water mixture to which all the requisite components, including buffering reagents, have been added. The procedure employed was to mix in a 250-ml beaker exactly 10 ml of an aluminium^{III} solution and 50 ml of distilled water. To this mixture were then added 60 ml of acetone, 4 ml of 5% 8-hydroxyquinoline in $2N$ acetic acid, and 40 ml of $2N$ ammonium acetate. The reaction mixture was placed on a water bath at 70°–75° and left uncovered for 3 hr. Visible precipitation began after about 15 min. At the end of the evaporation period the beakers were removed from the bath, allowed to cool, and filtered through medium-porosity sintered-glass crucibles. The precipitates were washed three times with distilled water and dried for 3 hr at 135°–140°. The product was weighed as anhydrous $Al(C_9H_6ON)_3$.

The aluminium^{III} solution was prepared from $KAlSO_4 \cdot 12H_2O$ so that 10 ml contained $10{\cdot}06 \pm 0{\cdot}03$ mg of Al^{III} as shown by the analysis of ten samples by the method of Olson, Koch and Pimentel.[4] When the above procedure was followed, the Al^{III} recovered from ten samples of 10 ml each was $10{\cdot}04 \pm 0{\cdot}04$ mg. The precipitates obtained were highly crystalline and were very easily filtered and washed.

Using a similar procedure, samples containing 10 mg of Mg^{II} have been analysed with good precision and accuracy, but with little improvement over conventional methods in the crystallinity of the precipitates formed or in the ease of filtering and washing. Precipitates obtained by both the evaporation method and the usual method of direct addition are grainy and easily handled.

In the case of zinc^{II} even large amounts of acetone fail to retard precipitation longer than about 1 min after the addition of the buffer solution. A co-precipitation study of magnesium^{II} 8-quinolinate on zinc^{II} 8-quinolinate was made, and the results obtained were essentially identical to those of Moyer and Remington.[5]

In addition to these studies, research on other solvent systems, cations, interfering ions and organic precipitating agents is in progress. Qualitative precipitations of aluminium^{III} 8-quinolinate from ethanol-water mixtures have been accomplished although the use of such mixtures entails evaporation times longer than those required when acetone is the organic component.

Acknowledgement—The authors gratefully acknowledge the financial support provided by the Research Corporation.

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Summary—It has been shown that precipitation from homogeneous solutions of mixed solvents may be effected by the preferential volatilisation of one of the solvent components. The precipitation of aluminium^{III} 8-quinolinate from an acetone-water system yields quantitative results and a highly crystalline precipitate.

Zusammenfassung—Es wird gezeigt, dass Fällung aus homogener Lösung erzielt werden kann, indem man eine der Lösungsmittelkomponenten binärer Solventien bevorzugt verdampfen lässt. Die Fällung von Aluminiumoxinat ergibt quantitative Fällung aus Azeton-Wassermischung und ein schön kristalliner Niederschlag wird erzielt.

Résumé—Les auteurs montrent que la précipitation homogène à partir de solvants mixtes peut être effectuée par la volatilisation préférentielle de l'un des constituants du solvant. La précipitation du 8-quinolate d'aluminium dans le système eau-acétone donne des résultats quantitatifs et un précipité fortement cristallin.

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XXIX. Mitteilung über quantitative organische Analyse[1]

Eine automatische Methode zur Mikrobestimmung von Kohlenstoff, Wasserstoff und Stickstoff in organischen Substanzen

(*Received* 21 *December* 1960. *Accepted* 19 *January* 1961)

Wir haben gefunden, dass sich Mikroeinwaagen organischer Substanzen blitzartig verbrennen lassen, wenn man sie auf dem Schiffchen mit aktiven, durch thermischen Zerfall von Kobaltoxalat erhaltenem Co_3O_4 mischt. Die Verbrennung kann man in einigen Sekunden ohne Explosionsgefahr durchführen, wobei die Oxydation quantitativ verläuft, falls man die Produkte über eine Schichte von Co_3O_4 auf einem geeigneten Katalysatorträger[2] sowohl in Sauerstoff- als in Stickstoff- wie auch in Kohlendioxyd-Atmosphäre führt.

Damit wurden einerseits die Methoden zur gravimetrischen Bestimmung von Kohlenstoff und Wasserstoff sowie zur gasvolumetrischen Bestimmung von Stickstoff extrem vereinfacht und wesentlich beschleunigt,[3] anderseits konnten wir zur direkten Bestimmung der Verbrennungsprodukte mittels Wärmeleitfähigkeit schreiten und damit den Weg zur Ausarbeitung von einfachen, volautomatischen Methoden der Elementeranalyse eröffnen.

Bei der blitzartigen Verbrennung verlassen die Verbrennungsprodukte das Verbrennungsrohr in einer Konzentrationswelle (siehe z.B. Abb. 1); zu Druckveränderungen kommt es im Messystem in kurzen Zeitintervellen und das noch früher, ehe die Front der Verbrennungsprodukte die Messzellen erreicht, sodass die Messung unbeeinflusst bleibt und die Bestimmung der Produkte ohne nötige Vorkondensation ermöglicht wird.

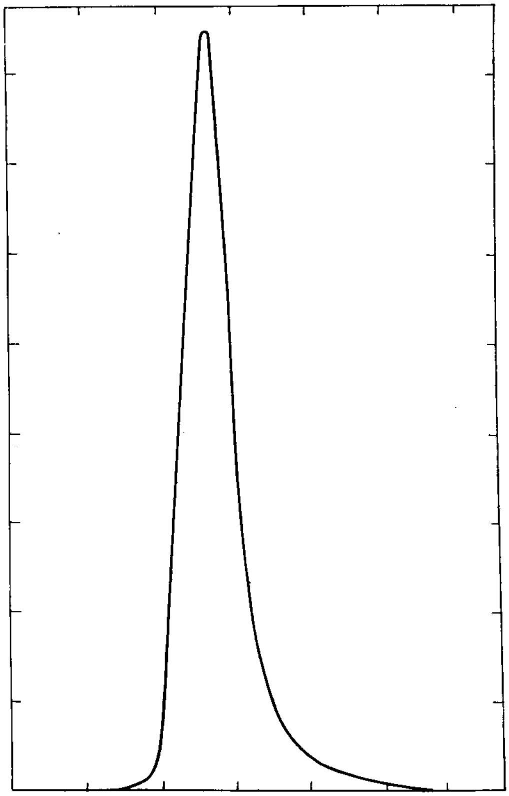

Abb. 1. Blitzartige Verbrennung von 1,203 mg des Acetanilids im Sauerstoffstrom. Die Konzentrationsaufnahme von CO_2.

Bei der Kohlenstoffbestimmung wird die eingewogene Substanz im Sauerstoffstrom verbrennt; nach Auffangen der Halogene, Schwefeloxyde, des Wassers und der Stickoxyde wird das Kohlendioxyd durch Messung der Änderung der Wärmeleitfähigkeit bestimmt, die mittels eines Schreibers registriert wird. Bei der Wasserstoffbestimmung wird die Substanz im Stickstoffstrom verbrannt, wobei die oxydierende Füllung des Verbrennungsrohres eine Schichte von CuO und Co_3O_4 auf Korund bildet in einer weiteren Schichte von Eisenfeilspänen kommt es zur Konversion von Wasser in Wasserstoff, der durch Änderung der Wärmeleitfähigkeit bestimmt wird. Die Bestimmung von Stickstoff wird im Kohlendioxydstrom in ähnlicher Weise ausgeführt, wie die Kohlenstoff und Wasserstoffbestimmung; als oxydierende Rohrfüllung dient Co_3O_4 und eine Schichte von CuO.

Die Auswertung und Berechnung erfolgte vorläufig durch Wägung der vom Schreiber aufgezeichneten ausgeschnittenen Flächen. In Zukunft soll ein Integrator verwendet werden. Die Eichungskurven wurden durch Analysen von Standardsubstanzen erhalten. Bisher wurden Resultate folgender Genauigkeit erreicht; Kohlenstoffbestimmung s = ±0,46%; Wasserstoffbestimmung s = ±0,16%; Stickstoffbestimmung s = ±0,27%. Einige Resultate befinden sich in Tabelle I.

TABELLE I.

Substanz	Formel (Mol. Gewicht)	Berechnet %	Gefunden %
		Wasserstoff	Wasserstoff
1-Chloranthrachinon	$C_{14}H_7O_2Cl$ (242,6)	2,91	2,89 2,93 2,98
Sacharose	$C_{12}H_{22}O_{11}$ (342,3)	6,48	6,26 6,62 6,66
Cholesterolazetat	$C_{29}H_{48}O_2$ (428,7)	11,29	11,44 11,33 11,10
		Kohlenstoff	Kohlenstoff
Sacharose	$C_{12}H_{22}O_{11}$ (342,3	42,11	42,32 42,60 41,82
Benzoesäure	$C_7H_6O_2$ (122,1)	68,84	68,03 68,06 69,64
Pikrinsäure	$C_6H_3O_7N_3$ (228,1)	31,45	31,14 31,18 32,06
		Stickstoff	Stickstoff
Antipyrin	$C_{11}H_{12}ON_2$ (188,2)	14,88	14,67 14,79 14,89
Acetanilid	C_8H_9ON (135,2)	10,36	10,55 10,15 10,61
Phenazetin	$C_{10}H_{13}O_2N$ (179,2)	7,82	7,60 8,03 7,69

Die Methoden sollen weiter durchgearbeitet werden, mit dem Ziel, ihre Genauigkeit zu steigern; es soll eine spezielle automatische Apparatur konstruiert werden und die Methode soll ebenfalls im Ultramikromassstab ausgeführt werden. Es wird auch die Überprüfung anderer Methoden der Endbestimmung geplant (z.B. mittels Ionisationsdetektoren), Ausarbeitung einer Methode zur gleichzeitigen Bestimmung von Kohlenstoff und Wasserstoff, möglicherweise die Verwendung anderer Trägergase.

Weitere Einzelheiten werden in der *Zeitschrift Collection Czechoslov. Chem. Commun.* angeführt werden.

EXPERIMENTELLER TEIL

Zur Bestimmung der Verbrennungsprodukte wurde ein semidiffuses Thermoelement verwendet, dessen Brücke mit 100–150 mA gespeist wurde (Bestimmung von Kohlenstoff und Wasserstoff) oder mit 200 mA (Bestimmung von Stickstoff), eingestellt mit einer Genauigkeit von $\pm 0,2\%$; die graphische Aufzeichnung erfolgte mit dem automatischen linearen Schreiber "Honeywell" mit einem Skalenumfang 10 mV.

Das pulverförmige Co_3O_4 wurde durch thermischen Zerfall von Kobaltoxalat bereitet,[4] weiter wurde dieser Katalysator auf Korund als Träger[4] verwendet. Die übrigen Reagentien waren die bei der Elementaranalyse üblichen (siehe z.B.[5]).

Zur Verbrennung und Erwärmung wurde die elektrische Universalapparatur verwendet, die schon früher beschrieben wurde.[6]

Kohlenstoffbestimmung

Das Verbrennungsrohr aus Quarz (Durchmesser 9 mm, Länge 320 mm) wird beginnend am Schnabel mit Silberwolle in einer Länge von 50 mm gefüllt; die Temperatur an dieser Stelle ist 600°.

Dann folgt eine 50 mm lange Schichte von Co_3O_4 auf Korund (Temperatur 700°). Die eingewogene Substanz (1–2 mg) wird mit 30–40 mg pulverförmigen Co_3O_4 bedeckt. Die Geschwindigkeit des Sauerstoffstromes ist 15 ml/min, die Zeitdauer der Bestimmung 5–7 Minuten.

Wasserstoffbestimmung

Im Quarzrohr (Durchmesser 9 mm, Länge 450 mm) befindet sich eine Schichte von Eisenspänen (120 mm), eine Schichte von CuO (30 mm) und Co_3O_4 auf Korund (50 mm) und wiederum eine Schichte von CuO (20 mm). Die ganze Füllung wird auf eine Temperatur von 650° erwärmt; die Geschwindigkeit des Stickstoffstromes ist 20 ml/Min., die Zeitdauer der Bestimmung 4–7 Minuten. Es wurde festgestellt,[7] dass es unter den gawählten Bedingungen zu einer 97–99% igen Konversion des Wassers zu Wasserstoff kommt.

Stickstoffbestimmung

Im Quarzrohr (Durchmesser 11 mm, Länge 600 mm) befindet sich eine Silberschicht (30 mm, Temperatur 550°), eine Schichte von Cu (40 mm, Temperatur 550°), eine Schichte von Co_3O_4 und CuO (50 resp. 200 mm, Temperatur 700°). Die eschwindigkeit des Kohledioxydstromes ist 10 ml/Min. Die Zeitdauer der Bestimmung 7–10 Minuten.

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Zusammenfassung—Eine Methode zur automatischen Bestimmung von C,H und N in organischen Verbindungen wird beschrieben. Die Methode arbeitet unter Ausnützung der Wärmeleitfähigkeit und verwendet Cobaltioxyd als Verbrennungskatalysator.

Summary—A method for the automatic determination of carbon, hydrogen and nitrogen in organic compounds is described. The method makes use of heat conductivity measurements, and Co_3O_4 is the combustion catalyst.

Résumé—L'auteur décrit une méthode automatique de microdosage du carbone, de l'hydrogène et de l'azote dans les composés organiques. La méthode dépend de la mesure de conductivité calorifique et utilise Co_3O_4 comme catalyseur de combustion.

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BOOK REVIEW

Proceedings of the Symposium on the Chemistry of Co-ordination Compounds. Agra, India, February 7th and 8th, 1959. In three volumes: Part One, **General Survey,** pp. 148 + iii, Rs. 15.00: Part Two, **Valence Bond Considerations, Stereochemistry and Structure, Techniques and Methods of Investigation,** pp. 203 + ii, Rs. 25.00: Part Three, **Reactions, Stability and Thermodynamic Considerations, Stabilisation of Valence States, Analytical Applications, Miscellaneous,** pp. 302 + x, Rs. 35.00. Published by National Academy of Sciences, India, Lajpatrai Road, Allahabad, 1960.

THERE are about ninety papers in these volumes, of which twenty-three come from laboratories outside India, and the rest from various Indian research establishments. Most of the papers describe rather humdrum investigations by conventional methods, which will interest the reader chiefly to the extent that they happen to impinge on his own field of work. In the reviewer's opinion the main value of symposium publications of this sort lies not in the research reports, which could be and should be published in the ordinary chemical journals, but in the sprinkling of general review papers by outstanding contributors. Unfortunately the papers of this type given at the Agra symposium are not all in Part One, as might have been expected from the title, but are also to be found in Part Two, with a couple in Part Three. Among these the following deserve special mention: a paper from J. Chatt's laboratory on Pt^{II} complexes with acetylenic substances; V. Gutmann on the properties of arsenic trichloride and phosphorus oxychloride as solvents; D. G. Bradley on metal alkoxides; H. L. Nigam on bonding in carbonyl complexes; F. J. C. and Hazel Rosetti on stability constants; G. Mitra's papers on fluoro and hydroxyfluoro complexes, especially of boron; and the Presidential Address by P. Ray reviewing concisely the whole field of co-ordination chemistry.

While many of the papers in this publication are excellent and interesting, the general impression it gives is of a vast mass of not very closely related material, collected from almost every branch of inorganic chemistry. Consequently anyone who buys it for his private bookshelf is likely to end up reproaching himself for extravagance and poor judgement. It does, however, deserve a place as a work of reference in chemical libraries.

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NOTICES

Tuesday-Thursday 10–12 *October* 1961: **Oak Ridge National Laboratory:** *Fifth Conference on Analytical Chemistry in Nuclear Reactor Technology* and *Second Conference on Nuclear Reactor Chemistry.* Gatlinburg, Tennessee, U.S.A.

The Conference on Analytical Chemistry in Nuclear Reactor Technology will be devoted to improved methods and instruments for the analysis of many nuclear reactor materials and products. Papers are especially solicited on the following or related subjects: measurement of burnup of uranium or plutonium fuels; isotopic analysis; determination of gases in reactor materials; methods and instruments for on-line analyses; remote analysis of radioactive materials; non-destructive testing of nuclear fuel elements and other reactor materials; analysis of (a) beryllium, beryllium oxide, cermets containing beryllium oxide, (b) zirconium and niobium alloys, (c) heavy water, and (d) plutonium and plutonium-base fuels.

In addition to papers setting forth specific achievements, review papers critically evaluating the "state of the art" with respect to any of the foregoing subjects are solicited.

Authors are requested to submit an abstract of 200–400 words of their paper not later than 15 July, 1961, and at the same time to indicate the time required for their presentation (not to exceed 20 min).

Proceedings of the conferences are to be published. Manuscripts of papers for publication should be submitted prior to or at the time of the conferences.

Abstracts of papers and enquiries regarding the analytical chemistry section should be addressed to: C. D. SUSANO, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee, U.S.A.

Enquiries concerning accommodation or requests for reservations should be addressed to: Reservation Services, Chamber of Commerce, Gatlinburg, Tennessee, U.S.A.

The seventeenth Annual General Meeting of the Microchemistry Group of the Society for Analytical Chemistry was held at Burlington House, London, W.1, on Friday, 24 February 1961. The Chairman of the Group, Mr. F. HOLMES, presided.

The following were elected Officers of the Group for the forthcoming year:

Chairman: Mr. C. WHALLEY
Vice-Chairman: Miss M. CORNER
Hon. Treasurer: Mr. G. INGRAM
Hon. Secretary: Mr. D. W. WILSON, Chemistry Department, Sir John Cass College, Jewry Street, Aldgate, London, E.C.3.

Talanta, 1961, Vol. 8, p. 452. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Continuous coulometric titration of micro quantities of iron in water. TAKEO TAKAHASHI and HIROSHI SAKURAI. (29 *March* 1961).

Titrimetric analysis with chloramine-T—IV: The chloramine-T-iodide reaction. E. BISHOP and V. J. JENNINGS. (6 *April* 1961).

The use of ruthenium as a catalyst in redox titrations. C. J. KEATTCH. (6 *April* 1961).

Determination of alkali sulphides by direct titration. SÁNDOR A. KISS. (14 *April* 1961).

Untersuchung der Kationensorption aus Komplexanmedium-I: Chromatograpische Trennung des Calciums und Strontiums. PAVEL POVONDRA, ZDENĚK ŠULCEK, RUDOLF PŘIBIL und RICHARD STANGL. (18 *April* 1961).

Precipitation of metal 8-hydroxyquinolates from homogeneous solution—IV: Uranium. JON BORDNER, E. D. SALESIN and LOUIS GORDON. (19 *April* 1961).

Use of nickel phthalocyanine sulphonic acid as a redox indicator in cerimetry—I. G. GOPALA RAO and N. VENKATESWARA RAO. (20 *April* 1961).

5-Amino-2-benzimidazolethiol as a new analytical reagent—II: Spectrophotometric determination of rhodium, and the simultaneous determination of rhodium and palladium. J. G. SEN GUPTA. (27 *April* 1961).

Cerimetric determination of nickel phthalocyanine. N. VENKATESWARA RAO and G. GOPALA RAO. (27 *April* 1961).

Cerimetric determination of triphenylmethane dyes—I: Determination of crystal violet. G. GOPALA RAO and N. VENKATESWARA RAO. (27 *April* 1961).

NOTES FOR CONTRIBUTORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable.

Original papers, short communications, preliminary communications and reviews will be published. Suitable books submitted to the Editor-in-Chief will be reviewed.

Since TALANTA is an international journal, contributions are expected to be of a very high standard. Research papers should make a definite contribution to the subject. 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, and should be critical. The Editor will welcome correspondence on matters of interest to analytical chemists.

All papers and short communications submitted for consideration will be refereed in the normal way. Referees will be encouraged to present critical and unbiassed reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor 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.

It is hoped that research and review papers will be published within approximately three to four months of acceptance, and short communications within two months.

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

2. Script Requirements

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

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

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

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

5. Illustrations should be separate from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require redrawing should include all relevant details and clear instructions for the draughtsman. If figures are already well drawn, it may be possible to reproduce them direct from the originals, or from good photoprints, if these can be provided; it is not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The following standard symbols should be used on line drawings, since they are easily available to the printers:

▲ △ ⊡ □ ● ○ ◬ ⊙ ⊕ ⊖ ⌽ ⊗

6. Tables should if possible be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarise results by an accepted method of expression, *e.g.*, standard deviation. The same information should not be reproduced in both tables and figures.

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

8. **References should be indicated in the text by consecutive superior numbers; and the full reference, including title of paper where desired, should be given in a list at the end of the paper in the following form:**

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

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

9. Except in the case of preliminary communications, proofs will be sent out to authors for correction. For papers these will be in page form. **It is emphasised that at this stage extensive alterations to the text or failure to return the corrected proofs promptly may result in serious delay in publication.**

10. Because of the international character of the Journal, no rigid rules concerning spelling, notation or abbreviation need be observed by authors, but each paper or series of papers should be self-consistent as to symbols and units. In editing papers for publication the conventions used, on the whole, will be English spelling for all matter in the English language, and the general usages described in *Handbook for Chemical Society Authors* (The Chemical Society, London, Special Publication No. 14, 1960). It would be helpful if authors would consult this for guidance in the preparation of their manuscripts. (Authors who wish to retain American spelling, or to adhere to other generally accepted usages, should indicate this clearly at the time of submission of the manuscript.)

11. Where several authors are involved in a paper, an indication of the author to whom requests for reprints should be addressed may be given by placing the symbol ® after the name of that author.

By following the Script Requirements carefully, authors will assist greatly in ensuring rapid publication.

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Preliminary communication

Short communications

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