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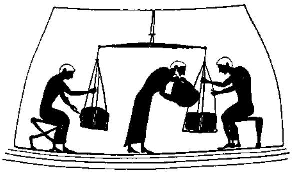

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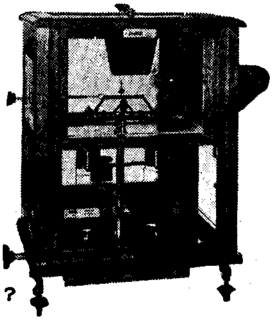

Incidental information

No.13

Items of interest from our laboratory notebooks

▶ Most analysts know about 1:10-phenanthroline and many use it for iron determinations. Not so many people seem to know that **4:7-diphenyl-1:10-phenanthroline** is twice as sensitive as 1:10-phenanthroline in the colorimetric determination of iron. There are several papers on the subject but the latest is *Analyst*, 1958, **83**, 80. The reagent is also called **Bathophenanthroline**, and we make it.

▶ Then, again the substitution of methyl groups in the 2:9 positions has the interesting effect of making the reagent insensitive to iron and we then have a selective and sensitive reagent for copper (see *Anal. Chem.*, 1956, **28**, 1158). Hopkin & Williams make **2:9-dimethyl-1:10-phenanthroline** (sometimes called **Neocuproin**).

▶ One does not think of sulphate as a radical one can determine absorptiometrically, but this is now possible for low concentrations. **Barium chloranilate** is the reagent and there are two papers on the subject—*Anal. Chem.*, 1957, **29**, 281 and *Anal. Chem.*, 1958, **30**, 202. Hopkin & Williams make it.

▶ Hopkin & Williams Ltd. were also early off the mark with supplies of the remarkable new colour-producing reagent for fluoride ions, **3-aminomethylalizarin-NN-diacetic acid**, described by Belcher, Leonard and West (*Talanta*, 1959, **2**, 92.) This important reagent is already available from stock.

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TITRIMETRIC DETERMINATION OF SOLUBLE SILICA AS MOLYBDOSILICIC ACID

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Institute of Industrial Science, University of Tokyo, Japan

(*Received* 28 *September* 1959)

Summary—A new method of direct reduction-titration of molybdosilicic acid with stannous ion in sulphuric acid solution has been developed for the determination of soluble silica in water. The amount of reducing agent required is measured spectrophotometrically. In reduction with either ferrous ion in oxalic acid solution or with stannous ion in sulphuric acid solution, the amount of reducing agent required is proportional to the amount of silica from which the molybdosilicic acid was formed. A direct reduction-titration has also been carried out, the end-point being determined potentiometrically. The results show that one molecule of molybdosilicic acid is reduced by four electrons, and that 1 ml of 0·01*N* solution of a reducing agent is equivalent to 0·152 mg of silica, SiO_2

INTRODUCTION

RECENTLY, the determination of soluble silica has tended to become important in the analysis of water. In general, soluble silica has been determined colorimetrically through the yellow coloration of molybdosilicic acid or the blue coloration of its reduced product. There has been, however, little interest in its determination by reduction of molybdosilicic acid. In the last few years, only some polarographic studies by Boltz *et al.*,[1] Strickland,[2] DeSesa *et al.*[3] and Pecsok *et al.*[4] have been reported. Veitsman[5] proposed a method for the determination, in which iodine liberated from potassium iodide by the oxidation of molybdosilicic acid, and extracted from the mother liquid by *iso*butyl alcohol, was determined colorimetrically or titrimetrically. There has been no attempt to determine soluble silica by direct reduction-titration of molybdosilicic acid. The present authors have confirmed that the amount of reducing agent required for the reduction of molybdosilicic acid is proportional to the amount of silica, and that molybdosilicic acid can be titrated potentiometrically by a suitable reducing agent under controlled conditions.

REAGENTS AND APPARATUS

Reagents

All the reagents were prepared from commercial chemicals of special grade (G.R.) or first grade

Standard silica solution: Dry about 1 g of "silica for chromatographic use" to constant weight at about 105° in an electric oven. Fuse 0·0915 g (weighed accurately) with about 5 g of sodium bicarbonate (G.R.) in a platinum crucible. After cooling, dissolve the fused mass in water, make up to 250 ml with water, and store in a polyethylene bottle as a stock solution. 1 ml of this solution contains 0·366 mg of SiO_2. In each experiment, the standard solution, containing 0·1 mg of SiO_2 per ml, was prepared from 27·3 ml of the stock solution by diluting to 100 ml with water.

2·5% *ammonium molybdate solution:* Dissolve about 2·5 g of ammonium molybdate ($[NH_4]_6Mo_7O_{24}\cdot4H_2O$, G.R.) in 100 ml of water.

0·04*N ferrous solution:* Dissolve 4 g of ferrous ammonium sulphate ($Fe[NH_4]_2[SO_4]_2\cdot6H_2O$, G.R.) in water, add 5 ml of 6*N* sulphuric acid, make up to 250 ml, and standardise with 0·04*N* potassium permanganate.

0·01*N ferrous solution:* Dissolve 1 g of ferrous ammonium sulphate in water, add 1 ml of 6*N* sulphuric acid, make up to 250 ml, and standardise with 0·01*N* potassium permanganate.

5% *oxalic acid solution:* Dissolve 5 g of oxalic acid (first grade) in 100 ml of water.

0·01*N stannous solution:* Dissolve about 1 g of stannous chloride ($SnCl_2 \cdot 2H_2O$, G.R.) in 5 ml of 6*N* hydrochloric acid, and store in a closely stoppered brown bottle under CO_2. The effective life of this solution is only a few days. In each experiment, 1 ml of this solution was diluted with 100 ml of 1*M* potassium chloride. The resulting solution was then successively diluted with the KCl to about 0·01*N* and the product was standardised with 0·01*N* iodine solution. This solution could be used with a negligible error in the factor for several hours.

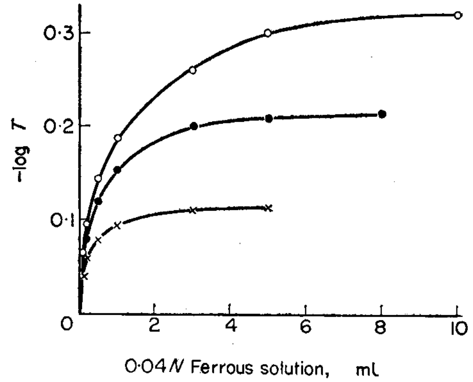

FIG. 1.—Reduction by ferrous ion in sulphuric acid solution.
Factor of ferrous solution: 0·964
SiO_2: ○ 0·126 mg
● 0·084 mg
× 0·042 mg

Water used in this experiment was obtained by distilling water previously purified by ion exchange.

Apparatus

A Hitachi EPU-2A type photo-electric spectrophotometer was used for the measurement of absorbancy (in a 10-mm cell). For the potentiometric titration, a Toa Denpa HM-3 type pH meter was used with a platinum electrode (ϕ1 mm × 5 mm) as indicator-electrode and with a saturated calomel electrode as reference-electrode.

EXPERIMENTAL RESULTS

I *Colorimetric method*

(*a*) *Reduction by ferrous ion in sulphuric acid solution:* An aliquot (1 ∼ 3 ml) of a sample solution (containing 42 μg of SiO_2 per ml) was mixed with 5 ml of 1*N* sulphuric acid and 1 ml of 2·5% ammonium molybdate solution and allowed to stand for several minutes in a 25-ml measuring flask. Varying volumes (0 ∼ 10 ml) of 0·04*N* ferrous solution were added and made up to 25 ml with water. After 10 minutes, the absorbancy was measured against water at 680 mμ. The results are given in Fig. 1, showing that the reduction of molybdosilicic acid by ferrous ion in sulphuric acid solution does not proceed quantitatively. It is believed that the reaction is reversible, since when excess ferrous ion was added to molybdosilicic acid and the resulting solution titrated with 0·04*N* potassium permanganate, the total amount of ferrous ion added initially was found.

(*b*) *Reduction by ferrous ion in oxalic acid solution:* An aliquot (0·25 ∼ 1 ml) of standard silica solution (containing 0·1 mg of SiO_2 per ml) was mixed with 3 drops of 6*N* sulphuric acid and 1 ml of 2·5% ammonium molybdate solution and allowed to stand for several minutes. After addition of 5 ml of 5% oxalic acid and varying volumes (0 ∼ 1·5 ml) of 0·01*N* ferrous solution, in this order, the solution was made up to 25 ml with water. After a short time the absorbancy was measured against water at 680 mμ. As shown in Fig. 2(*a*), the absorbancy, for a constant amount of silica, increases linearly with the amount of ferrous ion, finally reaching a constant value. In Fig. 2(*a*) the abscissa at the intersection of the two straight lines shows the minimum amount of ferrous ion

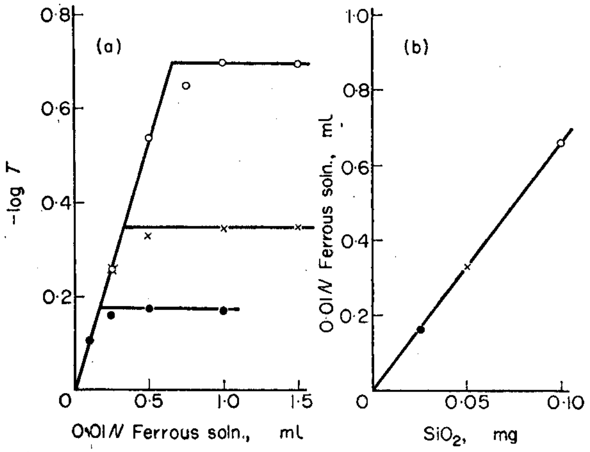

Fig. 2.—Reduction by ferrous ion in oxalic acid solution.
Factor of ferrous solution: 1·008
SiO_2: ○ 0·1 mg
× 0·05 mg
● 0·025 mg

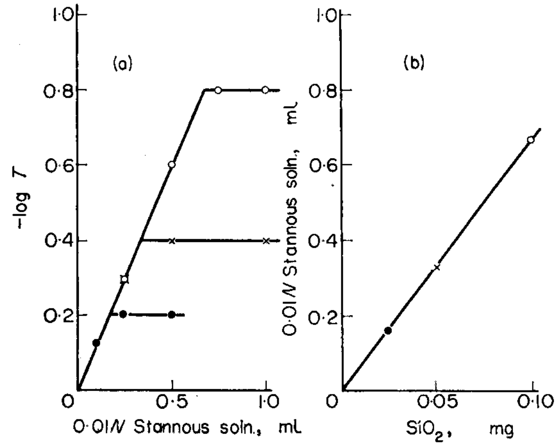

Fig. 3.—Reduction by stannous ion in sulphuric acid solution.
Factor of stannous solution: 1·024
SiO_2: ○ 0·1 mg
× 0·05 mg
● 0·025 mg

required to reduce the molybdosilicic acid. This corresponds to the equivalence point between molybdosilicic acid and ferrous ion. The relationship between amount of silica and of ferrous ion in Fig. 2(*b*) shows that 0·1 mg of silica is equivalent to 0·66 ml of 0·01*N* ferrous solution.

(*c*) *Reduction by stannous ion in sulphuric acid solution:* An aliquot (0·25 ~ 1 ml) of standard silica solution was mixed with 3 drops of 6*N* sulphuric acid and 1 ml of 2·5% ammonium molybdate solution and allowed to stand for several minutes. After addition of 5 ml of 6*N* sulphuric acid, about 10 ml of water and varying volumes (0 ~ 1 ml) of 0·01*N* stannous solution, the solution was made up to 25 ml with water. After a short time the absorbancy was measured against water at 680 mμ. The results are shown in Fig. 3(*a*) and 3(*b*). Here also the required amount of stannous ion is proportional to the amount of silica, and 0·1 mg of silica is equivalent to 0·56 ml of 0·01*N* stannous solution. This agrees with the value found for 0·01*N* ferrous solution. These results suggest that soluble silica may be determined by measuring the amount of reducing agent consumed in the reduction of molybdosilicic acid.

II *Titration method*

(*a*) *Titration with ferrous ion in oxalic acid:* 1 ml of the standard silica solution was mixed with 3 drops of 6*N* sulphuric acid and 1 ml of 2·5% ammonium molybdate solution and allowed to stand for several minutes. After adding 5 ml of 5% oxalic acid and dilution with water to about 25 ml, the solution was titrated with 0·01*N* ferrous solution using a 2-ml microburette. An example of the potentiometric titration curve is shown in Fig. 4, indicating that the potential change in the neighbourhood of the equivalent point is sufficiently marked to permit detection of the point from the curve.

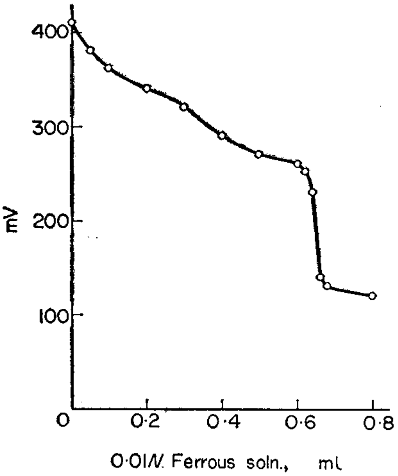

FIG. 4.—Potentiometric titration curve of silicomolybdic acid with 0·01*N* Fe^{II} solution (f = 1·008) in oxalic acid.

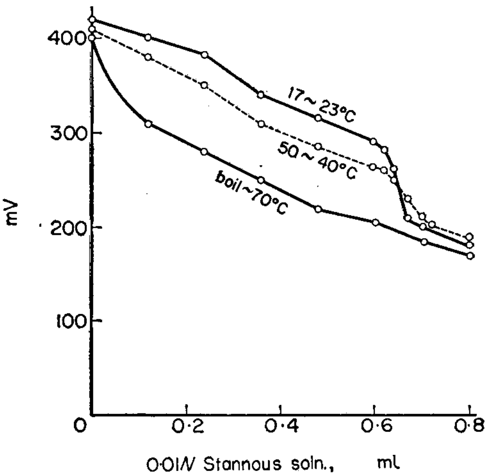

FIG. 5.—Potentiometric titration curves of silicomolybdic acid with 0·01*N* Sn^{II} solution (f = 1·010) in sulphuric acid.

From the curve, 0·1 mg of silica is equivalent to 0·65 ml of 0·01*N* ferrous solution. This coincides with the results from the colorimetric methods described above. However, the response becomes slow in the neighbourhood of the equivalence point. For example, in the titration of Fig. 4, it took more that ten minutes to decrease the potential from 275 mV (at 0·64 ml of ferrous solution) to 150 mV (at 0·66 ml of ferrous solution). It would appear that the titration method with ferrous ion is unsuitable for practical use.

(*b*) *Titration with stannous ion in sulphuric acid*: 1 ml of the standard silica solution was mixed with 3 drops of 6*N* sulphuric acid and 1 ml of 2·5% ammonium molybdate solution and allowed to stand for several minutes. After adding 5 ml of 6*N* sulphuric acid and dilution with water to about 25 ml, the solution was titrated with 0·01*N* stannous solution. Potentiometric titration curves at different temperatures are shown in Fig. 5, in which the temperatures of the solution at the initial and the final points of the titration are noted. The potential change in the neighbourhood of the equivalence point increases with decrease in the temperature of the solution. On the other hand, the response rate of the potential change decreases with decreasing temperature. The optimum range of the titration temperature seems to be at 25 ~ 30°, but even in this range a few minutes is necessary for the potential change to occur on the addition of 0·02 ml of titrant in the neighbourhood of the equivalence point. The titration with stannous ion appears to be preferable to that with ferrous ion, and can be applied to the determination of soluble silica in aqueous solution. Fig. 6 shows the calibration curve for silica by this method, and it is found that 0·1 mg of silica is just reduced by 0·66 ml of 0·01*N* stannous solution.

In the above experiments, the composition of the solution for colorimetric determination was that indicated by Snell and Snell,[6] and it had previously been confirmed that this composition is optimum for the potentiometric titration. In the titration with stannous ion, no significant error was observed either in air or in a CO_2 atmosphere. All experiments were carried out at a room temperature of 28 ~ 30°.

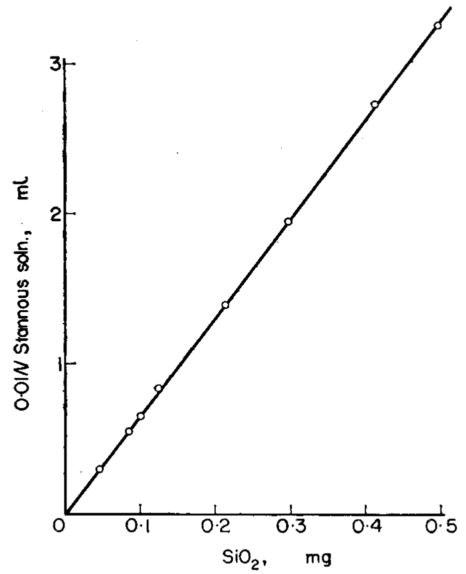

FIG. 6.—Calibration curve for silica in the potentiometry.

III *Application of the titration method to soluble silica in water*

The potentiometric titration method with stannous ion was applied to the determination of soluble silica in water. The results are compared in Table I with those obtained by the colorimetric method. In this work 2 ml were taken for the colorimetric method and 5 ml for the titration method.

TABLE I.—DETERMINATION OF SOLUBLE SILICA IN WATER BY POTENTIOMETRIC TITRATION METHOD

Colorimetry, *mg/ml*	Titrimetry			
	No. of analyses	*mg/ml*		
		max.	min.	average
0·0415	10	0·043	0·041	0·042

DISCUSSION

From the literature on the reduction reaction of molybdosilicic acid, it seemed probable that the amount of reducing agent required for the reduction of molybdosilicic acid would be proportional to the amount of silica from which the molybdosilicic acid was derived. However, the literature was mainly concerned with the colorimetric method, paying little attention to the reduction method for molybdosilicic acid.

If the amount of reducing agent in this reaction were proportional to the amount of silica, soluble silica could be determined by measuring the amount of the reducing agent consumed in the reduction. The present study shows that this is possible.

According to the experiments, the molybdosilicic acid formed from 0·1 mg of silica is reduced by 0·65 $\sim$ 0·67 ml of 0·01*N* solution of a reducing agent. The reduction is, therefore, a reaction involving the transference of four electrons per molecule of molybdosilicic acid. According to Strickland,[2] the molecular structure of molybdosilicic acid is $H_4[Si(Mo_3O_{10})_4]$, in which one mole of silica is combined with twelve moles of molybdenum trioxide. The reduction of molybdosilicic acid corresponds to the transformation of Mo^{VI} to Mo^{V} involving four atoms out of the twelve atoms of molybdenum combined to one molecule of silica. The calculated volume of 0·01*N* solution of a reducing agent required to reduce molybdosilicic acid formed from 0·1 mg of soluble silica is on this basis 0·657 ml, and 1 ml of 0·01*N* solution of a reducing agent corresponds to 0·152 mg of silica. Strickland has also reported that molybdosilicic acid exists in two forms, α and β; the α-form of molybdosilicic acid develops a green colour for four-electron reduction and a blue colour for five-electron reduction, when it is reduced by stannous chloride. In the present experiments, a difference such as that pointed out by Strickland was not found.

As described in the colorimetric experiments, when the quantity of either silica or reducing agent is constant, the absorbancy of the reduced product of molybdosilicic acid is proportional to the amount of either reducing agent or silica. Therefore photometric titration can be used for detection of the end-point in the reduction, but this has no particular advantage over the colorimetric method.

On the other hand, it is significant that soluble silica can be determined by the potentiometric method, because it can therefore be applied to coloured, turbid or somewhat concentrated samples that are sometimes found in natural or industrial water, which are difficult to determine by the colorimetric method. It has, furthermore, a great advantage that it can be applied to conventional coulometry. On the other hand, the disadvantage of this method is the instability of stannous solution and the interference of oxidising and reducing agents. The former may be suppressed by using coulometry, but there is no cure for the latter other than removal of the interfering substance.

The accuracy of this method for the determination of about 0·2 mg of silica is given in Table I. It seems to be quite satisfactory for practical analysis.

Note—The present study was carried out as a part of the work commissioned by the Taga works, Hitachi Ltd.

Zusammenfassung—Eine neue Methode zur reduktometrischen Bestimmung von Silicomolybdensäure mit Zinn(II)ion in schwefelsaurer Lösung wirde ausgearbeitet und auf die Bestimmung von gelöster Kieselsäure in Wasser angewendet. Die benötigte Menge an reduzierendem Reagens wurde spectrophotometrisch gemessen. Bei Verwednung von Eisen(II)ion in oxalsaurem Medium und Zinn(II)ion in schwefelsaurer Lösung ist die Menge an reduzierendem Agens proportional der Menge an Kieselsäure, die in Silicomolybdänsaure übergeführt wurde. Auch eine direkte reduktometrische Titration mit potentiometrischer Anzeige wurde durchgeführt. Die Ergebnisse zeigen, dass eine Molekel Silicomolybdänsäyre zur Reduktion vier Elektronen benötigt. 1·00 ml Reduktionslösung zeig 0.152 mg SiO_2 an.

Résumé—Les auteurs ont élaboré une nouvelle méthode de titrage direct de l'acide silico-molybdique par réduction avec l'ion stanneux en solution dans l'acide sulphurique pour le dosage de la silice soluble dans l'eau. La quantité d'agent réducteur nécessaire a été déterminée par spectrophotométrie. Par réduction soit avec l'ion ferreux en solution dans l'acide oxalique, soit avec l'ion stanneux en solution dans l'acide sulfurique, la quantité d'agent réducteur nécessaire est proportionnelle à la quantité de silice à partir de laquelle on forme l'acide silico-molybdique. Un titrage direct par réduction a été aussi effectué, le point équivalent étant déterminé par potentiométrie. Les résultats ont montré qu'une molécule d'acide silico-molybdique est réduite en faisant intervenir 4 électrons, et que 1 ml d'une solution 0,01 N d'un agent réducteur est équivalente à 0,152 mg de silice SiO_2

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EINE NEUE SCHNELLMETHODE ZUR BESTIMMUNG VON THORIUM

IN GEGENWART VON ZIRKONIUM, EISEN, LANTHAN, URAN UND SONSTIGEN SCHWERMETALLEN

R. Přibil und K. Burger
Analytisches Laboratorium, Chemisches Institut der Tschechoslowakischen
Akademie der Wissenschaften, Prag, Tschechoslowakei

(*Received* 3 *October* 1959)

Zusammenfassung—Es wurde ein neues komplexometrisches Verfahren zur Bestimmung von Thorium ausgearbeitet. Prinzip der Methode ist, dass das Thoriumkomplexonat unter pH = 1 mit Natriumsulfat zersetzt und das freiwerdende Komplexon(III) in Gegenwart von Xylenolorange als Indikator mit Wismutnitrat Messlösung titriert werden kann.

Das Verfahren ist bei Gegenwart grösserer Mengen Zirkonium, Eisen, Lanthan, Uran, Mangan und Magnesium, sowie geringerer Mengen Kobalt und Nickel anwendbar.

Bei der Analyse von Thoriumerzen muss das Thorium in der Regel in Gegenwart grösserer Mengen von Zirkonium, Eisen(III), Lanthan, Uran, Mangan, Magnesium und sonstiger Metalle bestimmt werden. Die zu diesem Zwecke verwendeten früheren analytischen Verfahren[1] sind meist umständlich und langwierig. Milner und Edwards[2] arbeiteten zwar ein komplexonmetrisches Verfahren zur Bestimmung von Zirkonium und Thorium nebeneinander aus, berücksichtigten jedoch die gleichfalls störenden begleitenden Elemente nicht. Die früher ausgearbeiteten komplexometrischen Verfahren[3–8] sind in Gegenwart von Zirkonium und Eisen(III) überhaupt nicht anwendbar.

Kürzlich arbeiteten wir nun ein neues Schnellverfahren zur Bestimmung von Thorium aus.[9]

Die Methode basiert auf jener Beobachtung, wonach bei Zugabe von viel Sulfat (1 g Na_2SO_4) zu Thorium-Lösungen, die bei pH = 2–3,5 in Gegenwart von Xylenolorange mit Komplexon(III) titriert wurden und Einstellen des pH-Wertes der Lösung auf weniger als pH = 1, die dem vorhandenen Thorium äquivalente Menge Komplexon(III) in Freiheit gesetzt wird. Letzteres kann dann mit Wismutnitratlösung in Gegenwart von Xylenolorange als Indikator titriert werden. Auf Grund zahlreicher Untersuchungsergebnisse überzeugten wir uns davon, dass das Thorium mit dieser Methode sowohl in 0,05 n-, als auch in 0,01 n-Konzentrationen mit einer Genauigkeit von $\pm 1\,\%$ bestimmt werden kann.

Im Laufe weiterer Versuche untersuchten wir nun, ob das erwähnte Verfahren auch in Gegenwart der fast immer vorhandenen Begleitelemente des Thoriums ebenfalls anwendbar ist. Besonderes Gewicht wurde bei den Untersuchungen auf die Klärung des Verhaltens des Eisens und Zirkoniums gelegt, mit Rücksicht darauf, dass diese Elemente die komplexometrischen Bestimmungsverfahren des Thoriums schon in geringen Mengen stören.

Wir versetzten Zirkonium oder Eisen(III) enthaltende Thoriumlösungen mit überschüssigen Mengen von Komplexon(III)-Messlösung und stellten die Lösung mit

Hilfe eines kleinen Streifens Universalindikatorpapier auf pH = 2–3,5 ein. Der Komplexon(III)-Überschuss wurde dann in Gegenwart von Xylenolorange als Indikator mit Wismutnitraglösung zurücktitriert. Diese Messung ergab den Zirkonium-bzw. Eisengehalt der Lösung. Mit Rücksicht darauf, dass in den Wismut-Lösungen zur Verhinderung der Hydrolyse immer eine starke Säure vorhanden sein muss, wurde der pH-Wert der titrierten Lösung einige Male während der Titration und ebenso auch beim Endpunkt mit 2 n-Ammoniaklösung auf pH = 2–3,5 eingestellt. Der Farbumschlag des Indikators erfolgte von gelb auf rötlichviolett, in Gegenwart von Eisen(III) von gelb auf orangegelb. Nach sorgfältiger Einstellung des Endpunktes wurde 1 g Natriumsulfat in das Reaktionsgemisch eingetragen und mit 1–2 ccm 2 n-Salpetersäure angesäuert. Die mit dem Thorium äquivalente Menge Komplexon(III) konnte nun mit Wismutnitratlösung titriert werden. Der Farbumschlag des Indikators im Endpunkt ist der gleiche, wie bereits oben beschrieben wurde. Sollte die Farbe des Reaktionsgemisches während der Titration von zitronengelb auf schwach orangegelb wechseln, muss mit einigen Tropfen 2 n-Salpetersäure nochmals angesäuert werden.

In Gegenwart grösserer Mengen Zirkonium oder Eisen(III) verwendeten wir zur Bindung dieser Elemente 0,05 m-oder 0,1 m-Komplexon(III)-Lösung und bestimmten dann das Thorium nach Rücktitration des Komplexon-Überschusses in 0,01 molarer Konzentration. In diesem Falle musste der Endpunkt der ersten Titration natürlich in der auf den entsprechenden pH-Wert (2–3,5) sorgfältig eingestellten Lösung mit 0,01 m-Komplexon-bzw. Wismutnitratlösung eingestellt werden. Nach Zugabe von Natriumsulfat und entsprechendem Ansäuern wurde die mit dem Thorium äquivalente Menge Komplexon in 0,01 molarer Konzentration zurücktitriert. Auf diese Weise konnten 5–30 mg Thorium selbst in Gegenwart grösserer Mengen Zirkonium und Eisen erfolgreich bestimmt werden. Der Fehler der Methode lag auch in diesem Falle nicht höher als ±1 %.

Im Laufe der weiteren Arbeiten untersuchten wir den Einfluss jener Begleitmetalle auf die Messergebnisse bei denen die scheinbare Komplex-Stabilitätskonstante ihrer Komplexonate bei pH $\simeq$ 3 unter dem Wert pK′ = 5 liegt. In Betracht kamen unter diesen in erster Linie das Eisen(II), Lanthan, Uran, Magnesium und Mangan.

In Gegenwart von Eisen(II)-Ionen ist der Endpunkt der Titration ungenau. Falls ungefähr die gleichen Mengen Eisen(II)-Ionen vorhanden waren wie Thorium, erhielten wir niedrigere Werte. Diese Erscheinung kann damit erklärt werden, dass Eisen(II) in saurem Medium mit Komplexon keine stabilen Komplexe bildet, im Laufe der Titration jedoch in Gegenwart von überschüssigem Komplexon teilweise zu Eisen(III) oxydiert wird, das dann bedeutende Mengen des mit dem Thorium äquivalenten Komplexons zu binden imstande ist. Dieser Fehler kann selbst in askorbinsäure-haltigen-reduzierenden-Medien nicht vollkommen ausgemerzt werden. Um seine störende Wirkung auszuschalten, muss das Eisen noch vor der Bestimmung zu Fe(III) oxydiert werden. Am besten gelingt die Oxydation mit Kaliumpermanganat, die gebildeten Mangano-Ionen stören die Bestimmung nicht. Der Überschuss des Kaliumpermanganats kann mit einigen Tropfen Wasserstoffperoxyd zersetzt werden.

Nach unseren Untersuchungen stört die Gegenwart von Lanthan-, Uranyl- und Magnesiumionen nicht.

In Gegenwart von Kobalt und Nickel gelingt die Bestimmung nur dann, wenn die Menge dieser Metalle 10–20 % des Thoriumgehalts nicht übersteigt. Aber auch in diesem Falle muss bei der Einstellung des pH-Wertes der Lösung während der Titration und beim Endpunkt besonders sorgfältig verfahren werden. Die scheinbaren Stabilitätskonstanten des Kobalt- und Nickelkomplexonats bei pH = 3 sind: pK'_{CoY} 2- = 5,7, pK'_{NiY} 2- = 8,0. Bei der Zersetzung des Thoriumchelats mit Sulfat und Säure wird ausser dem durch das Thorium gebundenen Komplexon auch das durch Nickel oder Kobalt gebundene Komplexon frei. Die ermittelten Werte liegen in diesem Falle also höher als die berechneten. Bei niedrigeren pH-Werten muss mit der Bildung von Kobalt- und Nickelkomplexonaten jedoch nicht mehr gerechnet werden.

Auf Grund zahlreicher Versuche schlagen wir zur Bestimmung von 5–30 mg Thorium in Gegenwart von Eisen, Lanthan, Uran, Magnesium und Mangan folgendes Verfahren vor:

Reagenzien

Komplexon(III)-Lösung, 0,05 m bzw. 0,1 m.
Wismutnitratlösung, 0,05 m bzw. 0,1 m.
Komplexon(III)-Messlösung, 0,01 m.
1 %ige wässrige Xylenolorange-Lösung.
Ammoniaklösung, 2 n.
Salpetersäure 2 n.
Natriumsulfat, wasserfrei.
Universalindikatorpapier.

Die 5–30 mg Thorium enthaltende Lösung wird analytisch genau in einen 100 ccm-Titrationskolben eingemessen und je nach dem Zirkonium-bzw. Eisen(III)-Gehalt werden 10–20 ccm 0,05 m bzw. 0,1 m-Komplexon(III)-Lösung zugegeben. Der pH-Wert der Reaktionsmischung wird mit einem kleinen Streifen Universalindikatorpapier mit 2 n–Ammoniaklösung auf pH = 2–3,5 eingestellt. Nach Zugabe von 3–4 Tropfen Xylenolorange-Lösung als Indikator wird der Überschuss von Komplexon mit 0,05 m bzw. 0,1 m-Wismutnitratlösung zurücktitriert. Mit Rücksicht auf den Säuregehalt der Wismutnitratlösung muss der pH-Wert der titrierten Flüssigkeit mit 2 n-Ammoniaklösung einige Male während der Titration und beim Endpunkte derselben auf pH = 2–3,5 eingestellt werden. Der Farbumschlag des Indikators erfolgt von zitronengelb auf rötlichviolett (in Gegenwart von Eisen(III) von gelb auf orangegelb). Nach Einstellung des pH-Wertes wird der Endpunkt mit 0,01 m-Komplexon(III)-bzw. Wismutnitratlösung erneut sorgfältig eingestellt. Man fügt nun 1 g Natriumsulfat zur Lösung, säuert mit 1–1,5 ccm 2 n-Salpetersäure an und titriert die mit dem Thorium äquivalente Menge Komplexon mit 0,01 m-Wismutnitratlösung. Sollte die zitronengelbe Farbe der Lösung während der Titration eine schwach orangegelbe Tönung annehmen, wird mit einigen Tropfen 2 n-Salpetersäure erneut angesäuert. Der Farbumschlag von gelb auf rötlichviolett ist besonders scharf.

1 ccm 0,01 m-Wismutnitratlösung entspricht 2,321 mg Thorium (log 36571).

Die Genauigkeit der Methode beträgt ±1 % (siehe Tabelle 1).

Summary—A new procedure for the complexometric determination of thorium has been worked out; thorium-complexone is decomposed below pH 1 by sodium sulphate, and the liberated complexone-III can then be titrated with bismuth nitrate solution using Xylenol Orange as indicator.

The procedure may be used in the presence of large amounts of zirconium, iron, lanthanum, uranium, manganese and magnesium, as well as smaller amounts of cobalt and nickel.

Résumé—Les auteurs ont mis au point un nouveau procédé de dosage complexométrique du thorium; le complexe thorium-complexon est décomposé à pH 1 par le sulfate de sodium, et l'on peut doser le complexon III libéré par une solution de nitrate de bismuth avec l'orange de xylénol comme indicateur.

Ce procédé peut être utilisé en présence de grandes quantités de zirconium, fer, lanthane, uranium, manganèse et magnésium, ainsi que de faibles quantités de cobalt et de nickel.

TABELLE I.

Einwaage Thorium *mg*	Begleitionen		Verbrauch 0,01 m Komplexon, *cc*		Gefunden Thorium *mg*	Genauigkeit	
	Ionenart	Menge	einzeln	Durchschnitt		*mg*	%
10,20	—	—	4,39 4,41 4,40	4,40	10,21	+0,01	+0,1
20,52	—	—	8,93 8,93 8,93	8,93	20,73	+0,21	+1,0
6,44	Zr^{3+}	20	2,75 2,76 2,75	2,75	6,38	−0,06	−1,0
13,00	Zr^{3+}	20	5,60 5,62	5,61	13,02	+0,02	+0,2
25,50	Zr^{3+}	50	11,05 11,05 11,04	11,05	25,65	+0,15	+0,6
11,83	Fe^{3+}	50 33	5,10 5,08	5,09	11,81	−0,02	−0,2
22,31	Fe^{3+}	50 33	9,71 9,70	9,70	22,51	+0,20	+0,9
11,83	UO_2^{2+}	30	5,08 5,09	5,09	11,81	−0,02	−0,2
11,83	UO_2^{2+}	70	5,09 5,08	5,09	11,81	−0,02	−0,2
11,05	La^{3+}	75	4,75 4,72	4,74	11,00	−0,05	−0,5
22,31	La^{3+}	75	9,71 9,75	9,73	22,59	+0,28	+1,2
11,05	Mn^{2+}	25	4,72 4,74	4,73	10,98	−0,07	−0,7
11,83	Mg^{2+}	20	5,06 5,06	5,06	11,75	−0,08	−0,7

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SEPARATION AND DETERMINATION OF URANIUM AND THORIUM WITH 3-ACETYL-4-HYDROXY-COUMARIN

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Summary—The separation of uranium from thorium, and the determination of these elements, even in the presence of more than ten times the amount of cerium^{III} and lanthanum, can be readily accomplished by using 3-acetyl-4-hydroxycoumarin as complexing agent, because of the marked differences in the solubilities in ethanol of the complexes.

URANYL ion is generally determined as oxide after the precipitation of ammonium diuranate. This method is accurate when other metals precipitated by ammonia are absent, but carbon dioxide must be absent, particularly when small quantities of uranium are involved. Oxine is a sensitive reagent, but is not specific.[1] Some of the reagents suggested for the gravimetric determination of uranium are ethylene diamine,[2] oxalic acid,[3–5] quinaldinic acid,[6] salicylic acid,[3] tannin,[7–10] cupferron,[11–13] hexamethylenetetramine,[14] isatin β-oxime[15–16] and pyridine.[17] None of these reagents is suitable when thorium and other rare earths are also present. Saxena and Seshadri[18] used 1-hydroxy-3-methoxyxanthone for the separation of uranium from thorium in the presence of cerite earths.

No reagent has been recommended for the separation of uranium from thorium in the presence of rare earths and for the determination of these two metals. The present authors have found that 3-acetyl-4-hydroxycoumarin (also known as 3-acetyl benzotetronic acid) can be used to separate uranium and thorium from each other in presence of large amounts of cerium^{III} and lanthanum, and can also be employed for the gravimetric determination of both elements after separation. The presence of cerium^{IV} ions, even in minute amounts, interferes with the determinations.

Anschütz *et al.*[19] reported the formation of the ammonium, sodium and silver salts of this compound, and after analysis gave their composition as $NH_4C_{11}H_7O_4$, $NaC_{11}H_7O_4$ and $AgC_{11}H_7O_4$ respectively.

When an alcoholic solution of 3-acetyl-4-hydroxycoumarin is added to uranium^{VI} salt solution, a pale yellow precipitate insoluble in ethyl alcohol is formed. This precipitate on ignition yields U_3O_8. In this way uranium can conveniently be determined between pH 1·5 and 7. Under these conditions, as little as 5·5 mg of uranium can be determined. The determination is not practicable below pH 1·5 as the reagent itself is then completely precipitated.

The thorium complex of this reagent is very soluble in ethyl alcohol and is completely precipitated between pH 2 and 4. By taking advantage of the marked difference in the solubilities in alcohol of their complexes it has been possible to separate uranium from thorium. As the reagent does not form a complex with cerium^{III} or lanthanum, the separation of uranium from thorium can be accomplished in the presence of these elements even when they are present in amounts more than ten times those of the uranium and thorium.

EXPERIMENTAL

Preparation of 3-*acetyl*-4-*hydroxycoumarin*

4-Hydroxycoumarin is acetylated with acetyl chloride in dry pyridine containing a few drops of piperidine. Of the various methods,[20–23] that have been employed for the synthesis of 4-hydroxycoumarin, that recommended by Stahman *et al.*[23] has been used during the present investigation. The acetylation of 4-hydroxycoumarin was carried out by the method of Link *et al.*[24]

All metallic salts used were of A. R. quality.

The pH measurements were made with a Beckmann pH Meter Model H2 and a glass electrode.

Determination of uranium with 3-*acetyl*-4-*hydroxycoumarin*

To about 150 ml of an aqueous solution of uranyl nitrate (containing about 50 mg of U_3O_8) 10 ml of a 1% ethanolic solution of 3-acetyl-4-hydroxycoumarin were added slowly with constant stirring. A pale yellow precipitate of the uranyl complex was produced. The precipitate was allowed to settle for about 10 minutes in the cold, and after filtration through Whatman Filter paper No. 40 was washed with water, dried and ignited to U_3O_8. The results obtained are given in Table I.

TABLE I.

Wt. of U_3O_8 by oxine method, *mg*	Wt. of U_3O_8 by coumarin method, *mg*
5·50	5·50
10·98	11·00
21·80	21·80
28·50	28·50
54·60	54·60

Effect of pH on the formation of the uranyl complex

The effect of pH on the formation of the complex was studied by buffering the uranyl salt with ammonium acetate-acetic acid for higher pH values (above pH 3·5) and by adding 0·1*N* HCl for lower pH values (below pH 3·5). The determination can conveniently be carried out within quite a broad pH range (1·5 to 7). At pH values above 4·5, however, the separation of uranium from thorium, cerium^{III} and lanthanum cannot be achieved because of the hydrolysis of Th^{IV}, Ce^{III} and La^{III} salts at these pH values.

Determination of uranium in presence of cerium^{III} *and lanthanum*

Since the reagent does not form a complex with cerium^{III} or lanthanum, the procedure for the determination of uranium in their presence is the same as for the determination of uranium alone. The precipitate of the uranyl complex was washed thoroughly with water to remove completely any adsorbed ions of cerium^{III} and lanthanum from it. The results obtained are illustrated in Table II.

TABLE II.

Wt. of U_3O_8 taken, *mg*	Wt. of CeO_2 added, *mg*	Wt. of La_2O_3 added, *mg*	Wt. of U_3O_8 found, *mg*
22·6	20·0	20·0	22·6
22·6	40·0	40·0	22·6
22·6	100·0	100·0	22·7
22·6	200·0	—	22·7
22·6	—	269·2	22·6
22·6	250·0	—	22·7
22·6	250·0	269·2	22·6

Determination of thorium

To about 150 ml of an aqueous solution of thorium nitrate (containing about 0·1 g of thorium dioxide and adjusted to pH 3–3·5) 2% ethanolic solution of the reagent was added with constant stirring till precipitation started. On warming the solution to remove ethanol and subsequent cooling, a yellowish-red precipitate was obtained which after filtration was washed with water, dried and ignited to thorium dioxide. Table III illustrates the results obtained.

TABLE III.

Wt. of ThO_2 by oxine method, *mg*	Wt. of ThO_2 by coumarin method, *mg*
14·7	14·7
22·4	22·4
48·6	48·6
72·8	72·6
113·0	113·2
29·4	29·4

Determination of thorium in the presence of cerium^{III} and lanthanum

The determination of thorium was carried out in the presence of varying amounts of cerium^{III} and lanthanum ions. On the removal of ethanol from the solution by warming, and subsequent cooling, the precipitate, consisting of thorium complex and excess reagent, was filtered, and thoroughly washed with water to remove any adsorbed ions of La^{3+} and Ce^{3+}. The results obtained are illustrated in Table IV.

TABLE IV.

Wt. of ThO_2 taken, *mg*	Wt. of CeO_2 added, *mg*	Wt. of La_2O_3 added, *mg*	Wt. of ThO_2 found, *mg*
48·6	50·0	—	48·6
48·6	—	50·0	48·6
48·6	50·0	50·0	48·6
29·4	50·0	50·0	29·4
29·4	147·0	—	29·5
29·4	—	147·0	29·4
14·7	110·0	110·0	14·7
48·6	500·0	—	48·8
48·6	—	500·0	48·7
48·6	250·0	250·0	48·6

Separation of uranium and thorium from each other and their gravimetric determination

Solutions of uranium^{VI} and thorium nitrate (containing 1 : 1 to 1 : 2 of uranium and thorium oxides) were used. Ethanol was added until the ethanol : water ratio in the solution was 1 : 1 by volume. Where the ratio $U_3O_8 : ThO_2$ was more than 1 : 2 (by weight) the ethanol-water ratio in the solution was raised to 3 : 1 by volume. To the warm solution, 2% ethanolic solution of the reagent was added with constant stirring. On cooling, the uranyl complex was precipitated. The precipitate, after filtration, was washed with about 200 ml of hot aqueous 1 : 1 ethanol, dried, and ignited to U_3O_8.

After separation of the uranium the filtrate was warmed to remove the ethanol, and on cooling a yellowish-red precipitate separated. After filtration, this was washed with water, dried and ignited to thorium dioxide. The results obtained are illustrated in Table V.

If more than five times as much thorium as uranium is present, the determination is not accurate.

Studies of the dissociation constant of the reagent and the stability constants of its metal-complexes are in progress and the results will be communicated in due course.

TABLE V.

Wt. of U_3O_8 taken, *mg*	Wt. of ThO_2 added, *mg*	Wt. of U_3O_8 found, *mg*	Wt. of ThO_2 found, *mg*
15·6	20·0	15·6	20·0
28·6	48·6	28·6	48·6
22·6	72·8	22·6	72·6
22·6	113·0	22·6	113·2
54·6	54·0	54·6	54·0

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Zusammenfassung—Die Trennung von Uran von Thorium sowie die Bestimmung beider Elemente selbst in Gegenwart von mehr als der zehnfachen Menge Cer(III)- und Lanthanion kann leicht durchgeführt werden, wenn 3-Acetyl-4-Oxycumarin als komplexierendes Mittel verwendet wird. Die Methode beruht auf dem ausgeprägten Unterschied in der Alkohollöslichkeit der betreffenden Metallkomplexe.

Résumé—On peut réaliser facilement la séparation de l'uranium et du thorium, et le dosage de ces éléments, même en présence de quantités de cérium (III) et de lanthane plus de dix fois plus importantes, en utilisant la 3-acétyl-4-hydroxycoumarine comme agent complexant, grâce à la différence marquée de solubilité des complexes dans l'éthanol.

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THE SEPARATION AND IDENTIFICATION OF MANGANESE, TECHNETIUM, RHENIUM, RUTHENIUM AND MOLYBDENUM ON THE ULTRAMICROSCALE

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Summary—A scheme is presented for the separation and detection of manganese, technetium, rhenium, ruthenium and molybdenum on the ultramicroscale. A number of comfirmatory tests for these elements on this scale have been investigated and the results are reported.

A survey of reagents suitable for the approximate estimation of technetium, rhenium and molybdenum has been carried out and these are combined in a separation scheme for these elements.

THE elements manganese, technetium and rhenium constitute group VII of the periodic classification. Of these three elements, technetium is by far the least common and, even today, quantities available are very small.[1] Attention has been drawn to the lack of information on the analytical chemistry of this element[2] and the need for the development of reliable non-radiochemical procedures for the detection of small amounts.[3]

In its known behaviour technetium is very similar to rhenium and is likely also to show some similarity to manganese. One of the main attempts to obtain workable amounts of technetium has been by neutron bombardment of a molybdenum target. In this process the principal task is the separation of small amounts of the element from the target material molybdenum. This was recently achieved by means of anion exchange.[4]

Attempts have also been made to extract workable amounts of technetium from the fission products of ^{235}U.[5] In this process the major difficulty is to remove ruthenium from technetium.

In an earlier publication[6] we have reported new reagents for the detection of the element technetium. It was felt, however, that a comprehensive separation scheme, covering not only technetium and rhenium, but also manganese, ruthenium and molybdenum, would provide a very valuable advance in the analytical chemistry of technetium and its associated elements, and was indeed a necessity.

In this laboratory, at the time of this work, the amount of technetium originally available was 30 μg, and later approximately 1 mg. To carry out the proposed separations, therefore, it was necessary to use ultramicro techniques.

As far as the authors are aware no separation schemes involving technetium and its associated elements have up to the present appeared in the literature. The present paper reports the results of investigations arising from these considerations.

A wide range of reactions of the elements was investigated. The most important and those upon which the separation scheme is based were as follows:

1. Manganese and ruthenium in the lower valency states precipitate readily as the hydrous oxides on treatment with a strong base. Under the same conditions,

however, molybdate, pertechnetate or perrhenate remain unchanged. The hydrous oxides of manganese and ruthenium are precipitated from permanganate and the higher valency states of ruthenium by boiling with 95% ethanol in the presence of sodium hydroxide. As before, perrhenate, pertechnetate and molybdate are unaffected and remain in solution.

2. Ruthenium can be separated from manganese by precipitating the former as sulphide from a hydrochloric acid medium.

3. Attempts to precipitate Tc^{IV} as hydroxide from moderately concentrated solutions produced a dark brown precipitate which was insoluble in excess of precipitant, in dilute hydrochloric acid, and in glacial acetic acid, but readily soluble in concentrated hydrochloric and nitric acids. The precipitate is thought to be the hydrous oxide.

4. The lower valency states of rhenium, technetium or molybdenum are readily raised to their highest states by oxidising with hydrogen peroxide in an alkaline medium.

5. The purple-red compound obtained when a technetium solution is treated with an aqueous solution of potassium xanthate is readily extractable into carbon tetrachloride[6] or chloroform and permits separation of the element from rhenium.

6. Unlike molybdenum, $technetium^{VII}$ does not precipitate as the insoluble oxinate from an acetate-buffered solution and thus provides a means of separation of the two elements.

EXPERIMENTAL

The apparatus and manipulative technique employed in these investigations has been described elsewhere.[7,8]

Stock solutions of the elements containing 0·2 μg/50 mμl of solution were prepared.

SEPARATION OF THE ELEMENTS

The scheme for the separation of the elements, based on the reactions described above is outlined in Table I.

CONFIRMATORY TESTS

Almost all the confirmatory tests recommended for the detection of manganese, rhenium, ruthenium and molybdenum on the milligram scale were found to be suitable. The majority of these tests were investigated and the best selected.

For technetium new confirmatory tests were developed. These have already been reported.[6]

Manganese

(*a*) *Potassium persulphate-silver nitrate*[9]: Deliver 50 mμl of solution by a micropipette to a cone. Add an equal volume of concentrated H_2SO_4 or 2*N* HNO_3 followed by about 20 mμl of silver nitrate. Now add about 50 mμl of potassium persulphate. Seal the cone in a heating capillary and heat for 2 minutes at 60°. A pink colour confirms the presence of manganese.

Reagents: 1% silver nitrate solution; a saturated solution of potassium persulphate

(*b*) *Benzidine*:[10] Place 50 mμl of test solution on filter paper. Add twice the volume of sodium hydroxide to the spot followed by excess of benzidine reagent. A blue stain confirms the presence of manganese.

Reagents: 10% sodium hydroxide solution; benzidine, 0·05 g in 100 ml of 10% acetic acid.

Notes

1. The elements technetium, rhenium and molybdenum should be present in the form TcO_4^-, ReO_4^-, and MoO_4^- respectively before starting the analysis. This may be ensured by oxidising lower valency states with alkaline hydrogen peroxide and boiling to expel excess peroxide.

TABLE I

Treat 50–100 mμl of the test solution with about half its volume of 10% NaOH, Agitate and seal in a heating capillary. Heat to boiling for 5 minutes. Centrifuge.

- **S 1**
  May contain molybdate, perrhenate and pertechnetate. Make slightly acid with 2*N* HCl. Reduce to small bulk, add about 70 mμl of 8-hydroxyquinoline reagent (2% in 4*N* acetic acid), heat for 5 minutes and centrifuge.
  - **S 3**
    Add an equal volume of potassium xanthate reagent (sat. aqueous soln.). Mix well and add about 80 mμl of either CCl_4 or $CHCl_3$. Centrifuge.
    - *Upper Layer*
      Test for **Re** (see confirmatory tests).
    - *Lower Layer*
      Purple-red. Tc is present
  - **R 3**
    An orange-yellow precipitate indicates **Mo**. Dissolve in HCl and test for **Mo** (see confirmatory tests).
- **R 1**
  Wash with about 50 mμl of distilled water. Combine the washings with **S 1**. Dissolve in the minimum volume of 4*N* HCl. Heat and add an equal volume of ammonium sulphide. The solution should now react acidic. Heat to boiling for 3 minutes; cool and centrifuge
  - **S 2**
    Test for **Mn** (see confirmatory tests).
  - **R 2**
    Wash once with water and add the washings to **S 2**. Dissolve in the minimum volume of hot 2*N* HNO_3. Centrifuge.
    - **S 4**
      Test for **Ru** (see confirmatory tests).
    - **R 4**
      Discard.

2. Solutions containing permanganate or perruthenate must be reduced before starting the analysis. This may be carried out in the following way: Add half the volume of 95% ethanol to the solution under examination which should be already 4–6*N* in sodium hydroxide. Boil for 2–3 minutes. The heating removes excess ethanol and any by-products formed. After centrifuging proceed as under **R 1** and **S 1**.

3. By heating the solutions to boiling after adding 10% NaOH the formation of colloidal hydrous oxides of manganese and ruthenium is prevented.

4. After dissolving **R 1** in 4*N* HCl and adding ammonium sulphide, the solution must be distinctly acid, otherwise manganese sulphide may co-precipitate with the ruthenium sulphide. Boiling for 3 minutes at this stage prevents the formation of colloidal ruthenium sulphide.

5. Complete precipitation of molybdenum as oxinate occurs in the range pH 3–7·3.

6. Before adding potassium xanthate reagent under **S 3**, ensure that the solution is acid so that xanthic acid, which reacts with technetium, is liberated.

7. Potassium xanthate gives a similar reaction with molybdenum.[6] Care must be taken, therefore, that molybdenum is completely removed before applying the test for technetium.

Rhenium

(*a*) *Dimethylglyoxime-stannous chloride*:[9] To the test solution in a capillary cone, add an equal volume of dimethylglyoxime followed by an excess of stannous chloride solution. In the presence of rhenium a red-orange coloration is obtained.

Reagents: A saturated solution of dimethylglyoxime in ethanol; 25% stannous chloride in 10*N* HCl.

(*b*) *Potassium thiocyanate-stannous chloride*:[11] Measure out a volume of potassium thiocyanate equal to that of the test solution in the cone. Mix well and add a small excess of stannous chloride solution. In the presence of rhenium an orange to pale yellow coloration is produced.

Reagents: 20% potassium thiocyanate; 10–15% stannous chloride in 1 : 1 HCl.

Technetium

The reagents used in the detection of this element have already been reported.[6]

Ruthenium

(*a*) *Potassium thiocyanate*:[12] This is a new, very sensitive test for ruthenium in which the thiocyanate undoubtedly reduces the element to a lower valency state. In the presence of 4–5*N* HCl, a blue-violet colour is obtained which is completely extractable by methyl *iso*butyl ketone (hexone).

For testing the following procedure is used:

Add an equal volume of 20% potassium thiocyanate to the test solution. Heat the solution for 5 minutes at 95°. Add sufficient concentrated HCl to make the solution about 3*N* in the acid. In the presence of ruthenium a blue-violet colour appears which is readily extracted with hexone.

(*b*) *Thiocarbamide*:[9] Mix equal volumes of the test solution and concentrated hydrochloric acid in a capillary cone. Add half the total volume of 10% thiourea solution and heat in a capillary cone for 2 minutes at 80°. In the presence of ruthenium a blue coloration is produced.

Molybdenum

(*a*) *Potassium xanthate*:[10] To the acidic test solution in a cone add an equal volume of potassium xanthate reagent. Stir, and add about 50 mμl of carbon tetrachloride. Centrifuge. If the organic solvent layer is coloured purple-red, molybdenum is present.

(*b*) *Potassium thiocyanate-stannous chloride*:[11] Treat the solution to be investigated with 60 mμl of potassium thiocyanate reagent and add about half the total volume of stannous chloride. A violet or purple colour indicates the presence of molybdenum.

REDUCTIONS WITH THIOCYANATE

In the present work and in other investigations carried out in these laboratories,[12] the influence of thiocyanate on some metals has proved to be extremely interesting and valuable.

Some of the results obtained in this work are tabulated below:

Metal	Colour obtained		Extraction with hexone from		
	Room temp.	Boiling temp.	Nitric acid	Sulphuric acid	Hydrochloric acid
Rhenium	—	blood-red colour	incomplete	incomplete	complete
Technetium	purple	purple	incomplete	incomplete	complete
Manganese	—	green-yellow	incomplete	incomplete	complete
Ruthenium	—	bluish-violet	incomplete	incomplete	complete
Molybdenum	blood-red colour	blood-red colour	incomplete	incomplete	complete

Reagents: 20–30% Potassium thiocyanate; 3*N* Nitric acid; 3*N* Sulphuric acid; 4–6*N* Hydrochloric acid; Hexone.

A more comprehensive investigation of these reactions may provide valuable results.

THE APPROXIMATE ESTIMATION OF TECHNETIUM, RHENIUM AND MOLYBDENUM

In this type of estimation on the ultramicroscale the volume of precipitate formed by a particular ion is assumed to be directly proportional to the amount of ion present. Comparisons, however, must be made under strictly identical conditions of temperature, time and rate of centrifuging, etc. Precipitants were, therefore, selected in such a way that (1) complete precipitation of a particular ion occurred in the presence of other ions, (2) excess of precipitant did not interfere with subsequent precipitations, (3) precipitates were easily collected at the apex of the cone with the minimum-time and rate of centrifuging, (4) precipitates were stable and not easily decomposed by acids, bases or dilution, (5) the colours of the precipitates were intense, since transparent or faintly coloured precipitates were found difficult to measure under the microscope.

A series of volumes of precipitates was prepared for each metal, ranging from 0·5–0·06 μg per 50 mμl, and these were measured and used as standards.

A wide range of reagents were investigated to find the ideal precipitant for each metal, applying the conditions already described above.

Molybdenum

Preliminary investigations showed that the following reagents were most suitable and these were subjected to a more detailed study. (*a*) α-benzoin oxime, (*b*) sodium thiosulphate and hydrochloric acid, (*c*) 8-hydroxyquinoline. Of these reagents 8-hydroxyquinoline was found to be most suitable for the ultramicroscale, the yellowish-orange precipitate of molybdenum oxinate having the properties which made for successful estimation of the element.

Procedure: Add about 70 mμl of oxime reagent to 50 mμl of the test solution at pH 3·3–7·5. Collect the precipitate formed in the taper of the cone by centrifuging for 5 minutes. Estimate the volume of precipitate.

Note: If particles of the precipitate cling to the walls of the cone, place about 10 mμl of ethanol on the opposite sides of the mouth of the cone and centrifuge rapidly for a minute.

The following figures, arranged in order of ascending magnitude, were obtained for the volume of the molybdenum oxinate precipitate in 10 separate experiments. The volumes are expressed in mμl per μg of molybdenum.

58·0; 58·5; 59·8; 62·3; 66·2
71·0; 71·0; 71·0; 74·9; 77·0.

Average value = 67 mμl/μg Mo

Standard deviation for a single estimation = ±6·9 mμl/μg Mo
Coefficient of variation = ±10·3%,

Rhenium

The reagents investigated were (*a*) tetraphenylarsonium chloride, (*b*) sodium thiosulphate and hydrochloric acid, (*c*) nitron. Of these reagents (*a*) and (*b*) were found to be quite satisfactory.

(*a*) *Tetraphenylarsonium chloride*:[13] Although this reagent forms a white crystalline precipitate of tetraphenylarsonium perrhenate it is suitable for the estimation of rhenium in solutions containing more than 0·1 μg.

Procedure: Treat 50 mμl of test solution with sufficient sodium chloride to make the final solution 0·25*M* in sodium chloride. To this add an equal volume of a 1% aqueous solution of tetraphenylarsonium chloride. Centrifuge and estimate the volume of precipitate.

The following figures, arranged in order of ascending magnitude, were obtained for the volume of tetraphenylarsonium perrhenate in 10 separate estimations. The volumes are expressed in mμl per μg microgram of rhenium.

189·8; 203·1; 205·0; 209·0; 221·7
227·0; 237·8; 241·0; 250·0; 252·4

Average value = 223·7 mμl/μg Re.

Standard deviation for a single estimation = ±21·4 mμl/μg Re.
Coefficient of variation = ±9·52%.

(*b*) *Sodium thiosulphate and hydrochloric acid*: By the interaction of the perrhenate ion with sodium thiosulphate solution in the presence of concentrated hydrochloric acid, rhenium sulphide Re_2S_7 is precipitated. Complete precipitation occurs if the acid strength is at least 6*N*. Above 8*N*, however, the form of the precipitate was found unsuitable for estimation on this scale.

Procedure: Treat 50 mμl of the test solution with about the same volume of 10% sodium thiosulphate and stir well. Add to this a sufficient volume of hydrochloric acid to make the final concentration 6*N*–8*N* in the acid. Seal the cone in a heating capillary and heat to boiling for 5 minutes. Centrifuge for 5 minutes. Measure the volume of the precipitate.

The following figures, arranged in order of ascending magnitude, were obtained for the volume of rhenium sulphide in 10 separate experiments. The volumes are expressed in mμl per μg of Re.

173·4;	173·4;	173·4;	191·4;	193·4
193·4;	193·4;	193·4;	212·9;	212·9

Average value = 191·1 mμl/μg Re.

Standard deviation for a single estimation = ±14·6 mμl/μg Re.
Coefficient of variation = ±7·6%.

It will be seen from the coefficient of variation that rhenium sulphide is very suitable for the estimation of the element.

Technetium

Some new reagents for the detection of technetium have already been reported.[6] For the approximate estimation of the element, however, investigations were carried out with three reagents. (*a*) ammonium sulphide in alkaline medium, (*b*) nitron acetate, and (*c*) tetraphenylarsonium chloride. Of these reagents the last proved to be the most successful on the ultramicroscale. A 1% aqueous solution of tetraphenylarsonium chloride was used.

Procedure: To the test solution containing approximately 0·2 μg Tc add, with continuous stirring, 20% sodium carbonate solution until the mixture becomes just alkaline. Centrifuge for a short time and reduce the solution to a small bulk by evaporation. Add an equal volume of reagent. Centrifuge, collect and measure the precipitate.

The following data, expressed in mμl/μg Tc, were obtained in six different determinations.

189·0;	197·3;	204·0;	219·0;	239·0;	249·0.

Average value = 214·2 mμl/μg Tc.

Standard deviation for a single estimation = ±24·2 mμl/μg Tc.
Coefficient of variation = ±11·3%.

THE SEPARATION OF RHENIUM, TECHNETIUM AND MOLYBDENUM

The separation of these elements for the purpose of their approximate estimation was considered. Based on the following observations, a separate scheme was drawn up.

(1) Molybdenum is readily precipitated as the oxinate by 8-hydroxyquinoline reagent. Under the same conditions of precipitation, however, rhenium as perrhenate and technetium as pertechnetate are unaffected.

(2) A complete separation of technetium and rhenium is achieved by precipitating the former, in the presence of ferric or manganous salts as carriers, with ammonium hydroxide. In no case was rhenium found to be occluded by the hydroxide precipitate of techentium. The technetium precipitate, which contains Tc^{IV}, is easily oxidised to Tc^{VII} preparatory to precipitation of the element as tetraphenylarsonium pertechnetate, by dissolving in dilute sulphuric acid and treating with hydrogen peroxide.

The detailed separation scheme is outlined in Table II.

TABLE II

Treat 100 mμl of the neutral or slightly acid test solution with about 70 mμl of 8-hydroxyquinoline reagent. Mix well and centrifuge for five minutes.

- **S 1**
  Reduce to small volume. Add sufficient concentrated HCl to bring the final concentration of acid to 9*N*. Heat at 80° for about 40 mins. Add about 40 mμl of 1 % $FeCl_3$ solution. Agitate and add sufficient concentrated ammonia to precipitate the iron present. Centrifuge.
  - **S 2**
    Add 50 mμl of 10% $Na_2S_2O_3$ solution, followed by sufficient concentrated HCl to make the final concentration of the solution about 6*N* in acid. Mix well and heat at 100° for 5 mins. Centrifuge for 5 mins.
    - **S 3**
      Discard.
    - **R 3**
      Black precipitate.
      Estimate as rhenium sulphide. (p. 22)
  - **R 2**
    Wash once with water and combine the washings with **S 2**. Dissolve in the minimum of dil. H_2SO_4. Add 30 mμl of 6% H_2O_2. Re-precipitate the ferric hydroxide with concentrated ammonia added in small amounts at a time with stirring. Centrifuge.
    - **S 4**
      Reduce in bulk. Make just alkaline. Add 70 mμl of tetraphenylarsonium chloride reagent (1%). Centrifuge for 7 mins.
      - **S 5**
        Discard.
      - **R 5**
        White precipitate
        Estimate as tetraphenylarsonium pertechnetate. (p. 22).
    - **R 4**
      Discard.
- **R 1**
  Yellow precipitate
  Estimate as under Molybdenum (oxinate, p. 21). Wash once with boiling water and combine the washings with **S 1**.

Notes

(1) To avoid precipitation of the ferric ion carrier as ferric oxinate with the excess oxine reagent remaining after precipitation of the molybdenum, the pH of the solution should be less than 2.[14]

(2) Under **R 2** a few mμl of concentrated HNO_3 will serve the dual purpose of dissolving the hydroxide and oxidation of Tc^{IV} to Tc^{VII}. The excess of nitric acid is removed by evaporation with concentrated HCl. Experience has shown, however, that the process of decomposition of the nitric acid is laborious and time-consuming. Low results are also obtained, probably due to loss of technetium as a volatile oxide.

(3) Hydrogen peroxide stronger than 6% reacts violently with ammonia, with the evolution of a large volume of oxygen which tends to eject the contents of the cone.

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Zusammenfassung—Ein Analysengang zur Trennung und Bestimmung von Mangan, Technetium, Rhenium, Ruthenium and Molybdän im Ultramikrosmaßstab wird mitgeteilt. Eine Anzahl von Identifizierungsreaktionen für die genannten Elemente wurde nachgeprüft und die Ergebnisse werden dargelegt. Untersuchungen zur Auffindung von Reagenzien zur halbquantitativen Bestimmung von Technetium, Rhenium und Molybdän wurden angestellt und die Ergebnisse dieser Forschungen zur Ausarbeitung des Trennungsschemas verwendet.

Résumé—Les auteurs présentent un plan pour séparer et déceler le manganèse, le technétium, le rhénium, le ruthénium et le molybdène à l'échelle ultramicro. Ils ont étudié un certain nombre de tests confirmatoires pour ces éléments à cette échelle, et ils mentionnent les résultats. Ils ont effectué une étude des réactifs pour le dosage semi-quantitatif du technétium, du rhénium et du molybdène et ils ont appliqué cette étude à l'établissement d'un schéma de séparation de ces éléments.

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OXIDATION-REDUCTION REACTIONS ON ION-EXCHANGE COLUMNS

REDUCTION OF IRON^{III} IONS ON ION-EXCHANGE-STANNOUS COLUMNS.

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Summary—The authors have examined the behaviour of redox systems adsorbed on ion-exchange resins and the possibilities of their analytical application. A method has been developed for the reduction of iron^{III} ions on cation-exchange resins. The reduction can be carried out with ascorbic acid. Iron^{II} ions, after elution with 4*N* sulphuric acid, can be titrated with potassium permanganate. A cation-exchange resin saturated with iron^{II} ions can act either as a reductor, or as a catalyst of redox reactions in solution. A tin^{II} chloride-complex, bound on an anion-exchange resin is suitable for the reduction of some dissolved metallic ions. A method has been developed for the reduction of iron^{III} ions in a solution containing hydrochloric acid. The method is also useful for analytical purposes.

Resins suitable for oxidation or reduction instead of for ion-exchange were first developed by Cassidy and his co-workers.[1] On these so-called "redoxite" resins the active radical is not an acidic or alkaline group but one which is able to oxidise or reduce. To prepare a good oxidation-reduction resin is not an easy task. There is a series of requirements which must be fulfilled by a solid redox system suitable for analytical purposes. First of all redox resins must have analogous advantages to ion-exchange resins; they must be practically insoluble and must have a great redox capacity. It is very important too, that the resin should be unaffected by warm, dilute acids and alkalis. In addition, the composition of the redox group and the technical data of the resin are also important factors. The redox system must be reversible. When the oxidising or reducing agent is present the reaction must be rapid and complete. It is very important also that the system should have a suitable redox potential. Among the organic redox systems there are few which seem to satisfy the requirements mentioned above. An obvious alternative is to use inorganic redox systems as active groups, where the oxidation or reduction takes place by simple electron exchange. Using multivalent metal ions it is possible to develop reversible redox potentials. Since it is not easy to build an inorganic redox system into a large organic molecule we have tried to bind to simple ion-exchange resins such cations or anions as are able to oxidise or to reduce, and with these ion-exchange resins transformed into an oxidised or reduced state, we have examined oxidation-reduction reactions.

By this method ion-exchange resins can be transformed into oxidising or reducing agents. The ions to be oxidised or reduced, as well as the pH of the solution, must be selected so that the sorption of the oxidising or reducing ions bound on the resin should not be affected during the reaction.

B. Sansoni[2] adsorbed iron^{II} ions, leuco methylene blue etc. on cation-exchange resins. These reducing resins could be regenerated with sodium hydrogen sulphite. In the same way he could bind hydroquinone, anthraquinone and indigo sulphonic acid on anion-exchange resins.

As the result of our investigations we have developed two different methods for the reduction of iron^{III} ions on ion-exchange resin columns. These show the possibility of using either cation- or anion-exchange resins for oxidation-reduction reactions and of applying them for analytical purposes.

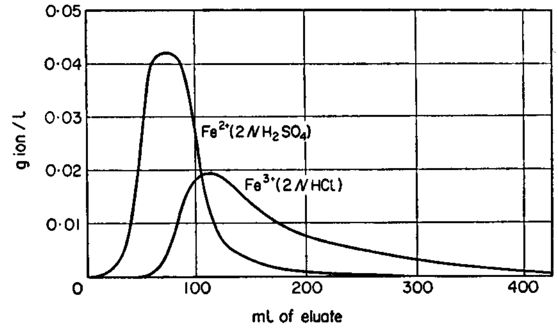

Fig .1.

REDUCTION OF IRON^{III} IONS ON CATION-EXCHANGE RESIN COLUMNS

The principle of this method is to reduce by means of ascorbic acid iron^{III} ions bound on a cation-exchange resin and after elution with dilute sulphuric acid to titrate the iron^{II} ions with potassium permanganate. According to Erdey and Bodor[3] reduction of iron^{III} by means of ascorbic acid is stoichiometric. The reaction takes place instantaneously without formation of any unpleasant gaseous products, in contrast to the use of sodium hydrosulphite or hydroxylamine. The excess of ascorbic acid, as well as the dehydroascorbic acid formed, can be washed out easily from the ion-exchange column.

A minor advantage is that iron^{III} can be separated from a solution which contains hydrochloric acid, and, after reduction and elution with sulphuric acid, iron^{II} ions can be titrated directly with standard potassium permanganate. It is advantageous also to use this method when iron^{III} and phosphate ions are to be separated quantitatively, especially when iron^{III} ions are present in a great excess. Ordinary ion-exchange columns do not give satisfactory results.[4] After prior reduction of iron^{III} ions to iron^{II}, however, separation of phosphate ions can be carried out quantitatively.[5] A further advantage of the method occurs when iron^{III} must be determined in the presence of organic materials (for example, organic acids) which are easily oxidised. In this case complete separation can be achieved. Finally there is an advantage due to the fact that elution of iron^{II} ions can be carried out more easily, using less solution than for iron^{III} ions. This is shown in Fig. 1, where the concentrations of iron^{III} and iron^{II} ions are plotted against the volume of the eluting solution. Aliquots of $0{\cdot}1M$ $FeCl_3$ solution adsorbed on a column filled with the H-form of Wofatite KPS-200 resin and (*a*) reduced with ascorbic acid and eluted with $2N$ sulphuric acid, (*b*) eluted with $2N$ hydrochloric acid. Under comparable conditions complete recovery (as Fe^{II}) was obtained in (*a*) but only 92·5 % recovery in (*b*) . Smaller amounts of $4N$ H_2SO_4 are more efficient. On the basis of these results the following procedure has been devised.

Determination of iron^{III} ions on a cation-exchange column

Reagents: (1) 0·01N and 4N sulphuric acid. The solutions must be boiled out and cooled before use. (2) 2% ascorbic acid solution. This must be prepared freshly with distilled water which was boiled out and cooled. (3) 0·1N potassium permanganate standard solution.

Preparation of ion-exchange column: A strongly acidic ion-exchange resin (Wofatite KPS 200 or Lewatit S-100) with a grain size of 0·2–0·5 mm is used. The resin must be kept under distilled water for 24 hours, and then it must be washed through with 4N hydrochloric acid and N sodium hydroxide solutions alternately. After this treatment it must be washed once more with a greater amount of water. Finally the grains of the resin are to be filled into the tube shown in Fig. 2 through a thick funnel. The tube must be filled with water before introducing of the resin and precautions taken to prevent the inclusion of air bubbles. There must always be a water-layer over the top of the resin. After filling the tube, the funnel is replaced by another which has a stop-cock. The resin is converted to the H-form with 100 ml of 4N sulphuric acid and excess acid is washed out with 100 ml of 0·01N sulphuric acid.

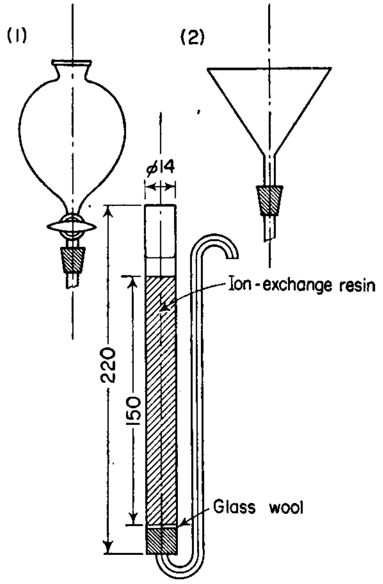

FIG. 2.

Procedure: 50 ml of the solution to be examined, which contains 5–100 mg of Fe and has a free acid content of at most 0·2N, is introduced through the funnel to the column. (If the solution contains greater amounts of free acid it must be neutralised with ammonium hydroxide). A flow rate of 5 ml/min is used. After adding the solution, the column is washed out with 50–100 ml of 0·1N hydrochloric acid to separate interfering elements, and 50 ml of 2% ascorbic acid are introduced. Excess ascorbic acid is washed out with 150–200 ml of 0·01N sulphuric acid until a small amount of the effluent solution does not bleach 1 ml of 0·01N potassium permanganate solution. Iron^{II} ions are then eluted with 200 ml of 4N sulphuric acid, and the solution is titrated with a standard solution of potassium permanganate.

Remarks: If the solution contains other ions in addition to iron^{III} ions, these will also be on the ion-exchange column. In this case the capacity of the column must be taken into consideration. Since the sorption ability of iron^{III} ions is greater than that of bivalent alkaline earth and monovalent alkali metals, the latter do not disturb the sorption of iron^{III} even if they are present in a high concentration. Among metallic ions which are reduceable by ascorbic acid, those which are reduced to metal (silver, gold, mercury) do not interfere, but can however, spoil the resin. Other reduceable ions (such as vanadate) interfere.[6]

The results of experiments carried out with iron^{III} chloride are shown in Table I. Both Wofatite KPS-200, and Lewatit S-100 resins were used. The results indicate that the determination can be carried out satisfactorily in the presence of other ions.

The capacity of a column filled with Wofatite KPS-200 resin in a $0{\cdot}1N$ sulphuric acid medium was found to be almost the same for iron^{III} and iron^{II} ions. Although theoretically the capacity for iron^{II} ions should be 1·5 times that for iron^{III} ions, in fact they are almost the same because the sorption ability of iron^{II} is lowered in the $0{\cdot}1N$ sulphuric acid medium. A column saturated with iron^{II} ions in a $0{\cdot}1N$ sulphuric acid medium can also be used as a reductor without dissolution of iron^{III} ions. The reductor column can of course only be used where cations which have a high sorption ability are absent. The reductor can be easily regenerated by washing through with ascorbic acid.

TABLE I. REDUCTION OF IRON^{III} CHLORIDE.

Composition of solution to be examined	$0{\cdot}1N$ $KMnO_4$, *ml consumed*	mean	Difference from true value %	Deviation %
25·20 ml $0{\cdot}1N$ $FeCl_3$ (free acid: $0{\cdot}1N$ HCl)	25·16 25·20 25·18	25·18	−0·08	0·04
21·30 ml $0{\cdot}1N$ $FeCl_3$ + 20·0 ml $0{\cdot}1M$ KH_2PO_4 (free acid: $0{\cdot}1N$ HCl)	21·20 21·28 21·28	21·25	−0·23	0·12
10·10 ml $0{\cdot}1N$ $FeCl_3$ + 20·0 ml $0{\cdot}5M$ $CaCl_2$ (free acid: $0{\cdot}1N$ HCl)	10·05 10·12 10·10	10·09	−0·10	0·13

An inorganic redox system adsorbed on a cation-exchange resin can be also used as a catalyst. On pouring 30% hydrogen peroxide into a solution of methyl orange in a $0{\cdot}1N$ sulphuric acid medium, if free of metallic ions the colour does not change even after a week. On adding to the solution some grains of a resin saturated with iron^{II} ions and washed with $0{\cdot}1N$ sulphuric acid, the colour of methyl orange disappears in a few hours. It is known[7,8] that hydrogen peroxide decomposes in an acidic media, under the action of Fe^{II} ions, yielding free radicals which destroy azo dyes.

REDUCTION OF IRON^{III} IONS WITH AN ANION-EXCHANGE-STANNOUS COLUMN

It is known from the work of Kraus and Nelson[9] and of Jentzsch[10] that tin^{II} ions can be held on an anion-exchange resin in hydrochloric acid medium. We have found that an anion-exchange resin containing tin^{II} ion can be used as a reductor in a $3N$ hydrochloric acid medium. With the aid of the column iron^{III} ions can be reduced quantitatively to iron^{II}. In Table II are compiled, according to data of Jentzsch and co-workers[11,12], the elution constants of tin^{II}, tin^{IV} and iron^{II} ions corresponding to various hydrochloric acid concentrations. Elution constants are defined by the following equation:

$$E = -d\frac{A}{V}.$$

Where A represents the cross-section of the column (cm^2), V the volume in ml of eluting solution (in this case hydrochloric acid) and d the moving of the sorption boundary in cm. The figures in the case of tin^{II} and tin^{IV} ions correspond to the appearance of the first traces of ions, while in the case of iron^{II} they correspond to the disappearance of the so called "last traces". These data are only a guide since experimental conditions (size, type of the resin) were not the same in our investigation.

TABLE II.—ELUTION CONSTANTS

Concentration of hydrochloric acid $M/1$	1	2	3	4
E^{II}_{tin} (first traces)	0·10	0·06	0·05	0·06
E^{IV}_{tin} (first traces)	0·61	0·27	0·11	0·06
E^{II}_{iron} (last traces)	0·21	0·21	0·20	0·19

According to the figures tin^{II} ions can be bound even in a $2N$ hydrochloric acid medium. On the other hand a higher acid concentration ($>3N$) is needed when tin^{IV} ions are to be bound. The negligible sorption of iron^{II} is not altered in this range of acid concentration. On the basis of these facts we used a $3N$ hydrochloric acid medium for our investigations because the sorption of tin^{IV} ions is also significant at this concentration. It is not advisable, however, to choose a higher acid concentration, because a greater amount of solution for washing through the iron^{II} ions is then required, and the oxidimetric determination of iron^{II} ions at such a high acid concentration cannot be carried out easily.

Calculating from elution constants of Jentzsch, preliminary experiments were devised which showed that on basic Lewatit MN three portions of $0{\cdot}1N$ iron^{III} chloride can be reduced and eluted in the $3N$ hydrochloric acid without elution of tin^{II} ions. At the third reduction, however, tin^{IV} ions appear in the effluent solution together with iron^{II} ions. Complete removal of tin^{II} and tin^{IV} ions, *i.e.* complete regeneration of the column is a very lengthy process when $0{\cdot}005N$ hydrochloric acid is used. Using an alkaline solution of sodium chloride regeneration can be carried out quickly.

When $1N$ HCl is used for the elution of iron^{II} ions, titration of the latter can again be carried out with $0{\cdot}1N$ potassium permanganate, after addition of Zimmermann–Reinhardt solution. In this case however it is advisable to regenerate the column after every determination. On the basis of these experiments a procedure has been devised.

Reduction and determination of iron^{III} ions on an anion-exchange-stannous column

Reagents: (1) $3N$ hydrochloric acid. (2) Tin^{II} chloride solution: Dissolve 10 g of crystallised tin^{II} chloride in 75 ml of 2 + 1 HCl with heating, and make it up to 100 ml. (3) $0{\cdot}1N$ cerium^{IV} sulphate standard solution. (4) Ferroïn indicator solution: Dissolve 1·624 g of *o*-phenanthroline hydrochloride and 0·695 g of iron^{II} sulphate in 100 ml of water. (5) Regenerating solution (for the elution of tin ions): dissolve 100 g of sodium chloride and 10 g of sodium hydroxide in 1 litre of water. (6) H_2O_2 reagent. (7) KSCN-solution. (8) $0{\cdot}1N$ potassium permanganate standard solution. (9) Zimmermann–Reinhardt solution.

Preparation of ion-exchange column: The strongly basic resin, (Lewatit MN, average grain diameter 0·2–0·5 mm.) is kept under cold water, and, before use, is treated with $4N$ HCl and then with $0{\cdot}5N$ sodium hydroxide. After thorough washing, the resin is filled into the tube shown in Fig. 2. The column is placed in a water bath at 40–50°. After adding a funnel with a stop-cock, the resin is washed through with 100 ml of $3N$ hydrochloric acid.

Procedure: From 1–2 ml of tin^{II} chloride solution according to the amount of iron^{III} ions to be reduced, are poured on the resin and 2–10 ml of the solution to be examined are introduced, containing, apart from hydrochloric acid, 10–60 mg of iron^{III} ions. The flow rate is adjusted to 0·6 ml/min, and iron^{II} ions are eluted with 3*N* hydrochloric acid. After 50 ml of the latter is added, the flow rate can be increased to 2–3 ml/min. Elution is carried out until 1 drop of the solution gives no red colour with 1 ml of 3% hydrogen peroxide and 1 drop of 1*N* potassium thiocyanate. About 100 ml of 3*N* hydrochloric acid are sufficient. The solution is titrated, after cooling, with 0·1*N* cerium^{IV} sulphate in the presence of 1 drop of ferroïn indicator. A second reduction can be carried out without the regeneration of the resin, after pouring a new portion of tin^{II} chloride solution on the resin. Complete regeneration must be carried out in the following manner: excess of hydrochloric acid is washed out with 100 ml of water, and tin ions are eluted with 50–100 ml of alkaline sodium chloride solution. A further wash with 50 ml of water and finally with 100 ml of 3*N* hydrochloric acid is given, and the column is ready for a new determination. The flow rate during regeneration can be 2–3 ml/min.

TABLE III.—DETERMINATION WITH CERIC SULPHATE

0·1*N* $FeCl_3$ solution, *ml*	0·1*N* $Ce(SO_4)_2$, *ml* *consumed after reduction*	Mean	Diff. from true value %	Deviation %
12·20	12·17 12·23 12·22	12·21	+0·08	0·04
6·10	6·08 6·10 6·08 6·10 6·20 6·11	6·11	+0·16	0·1
2·44	2·45 2·44 2·46 2·50 2·41	2·45	+0·4	0·24

When a permanganometric determination of iron^{II} ions is used, the procedure is altered as follows: the column is washed with 100 ml of 4*N* hydrochloric acid, and after adding the tin^{II} chloride and the solution to be examined, elution is carried out with 1*N* hydrochloric acid. The process is carried out at 40–50°. The solution is diluted with freshly boiled and cooled water to double its original volume, and 25 ml of Zimmermann–Reinhardt solution are added. Finally the solution is titrated with 0·1*N* potassium permanganate standard solution.

Remarks: The free acid content of the solution to be examined should be between 0·1–5*N*. The temperature must be strictly maintained between 40–50°. When double amounts of the stoichiometric requirment of tin^{II} chloride are used, reduction seems to be fairly complete. When 2·5 ml of tin^{II} chloride solution was poured on the resin, reduction of 5 ml of 0·1*N* iron^{III} chloride can be carried out twice completely, without addition of a new portion of tin^{II} chloride. Those cations which are not bound to the resin or reduced by tin^{II} ions (alkaline and alkaline earth metals, aluminium) do not interfere.

Results obtained with a 0·1*N* iron^{III} chloride stock solution are shown in Tables III and IV. The results can be seen to be both accurate and precise.

Summarising, it has been established that an anion-exchange-tin^{II} reductor system is fairly useful for analytical purposes. Other substances can be reduced with this resin, and these will be discussed in a further communication.

TABLE IV.—DETERMINATION WITH POTASSIUM PERMANGANATE

0·1*N* $FeCl_3$ solution, *ml*	0·1*N* $KMnO_4$, *ml consumed after reduction*	Mean	Diff. from true value, %	Deviation, %
10·51	10·62 10·59 10·41 10·60 10·61 10·59 10·70 10·60	10·59	+0·76	0·08
5·28	5·25 5·32 5·30 5·30 5·30 5·40 5·32	5·31	+0·56	0·1
2·11	2·12 2·11 2·11 2·13	2·12	+0·5	0·1

Zusammenfassung—Die Autoren studierten die Eigenschaften von an Ionenaustauschern adsorbierten Redoxsystemen sowie deren analytische Anwendungsmöglichkeiten. Eine Methode zur Reduktion von Fe(III) an Kationenaustauschharzen wurde entwickelt. Die Reduktion kann mit Ascorbinsäure erfolgen. Das Eisen(II) kann nach Elution mit 4 n Schwefelsäure permanganometrisch titriert werden. Ein Kationenharz mit Eisen(II) gesättigt, kann entweder als Reduktor oder aber auch als Katalysator von Redoxreaktionen in Lösungen dienen. Experimente haben gezeigt, dass Zinn (II) chloridkomplex, an Anionenaustauschharz gebunden, als Reduktor für einige in Lösung befindliche Metallionen dienen kann. Eine Methode wurde entwickelt um Eisen (III) ionen in salzsäurer Lösung zu reduzieren, was für analytische Zwecke verwendet werden kann.

Résumé—Les auteurs ont étudié le comportement de systèmes oxydoréducteurs adsorbés sur des résines échangeurs d'ions et les possibilités de leurs applications analytiques. On propose une méthode pour la réduction des ions fer III sur résines échangeurs de cations. La réduction peut être obtenue par action de l'acide ascorbique. Les ions fer II, après élution par l'acide sulfurique 4N peuvent être titrés par le permanganate de potassium. Une résine échangeur de cations saturée d'ions fer II peut agir soit comme réducteur, soit comme catalyseur de réactions d'oxydo-réduction en solution. L'expérience a montré que le complexe chlorure de l'étain II lié à une résine échangeur d'anions est utilisable pour la réduction de certains ions métalliques en solution. On propose une méthode pour la réduction des ions fer III en solution d'acide chlorhydrique. Cette méthode peut être utilisée à des fins analytiques.

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ORGANIC ANALYSIS—XXIII*

DETERMINATION OF BLOOD SUGAR AND URINE SUGAR WITH 3:6-DINITROPHTHALIC ACID

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Summary—A new colorimetric method for determination of blood sugar and urine sugar has been established, using 3 : 6-dinitrophthalic acid as a colour-developing agent.

WHEN 3 : 6-dinitrophthalic acid is heated with a reducing sugar in aqueous sodium carbonate solution, in a few minutes an orange-red to wine-red colour appears according to the amount of the sugar. This first colour turns to orange to orange-red on prolonged heating. If the amount of reducing sugar is very small, the final colour changes rapidly to yellow, but it is very stable when the reaction is carried out in the presence of sodium thiosulphate. This colour reaction is much more sensitive than those given by the other nitro compounds which are used for the same purpose.[1] These include picric acid,[2] 3:5-dinitrosalicylic acid,[3] and 3:4-dinitrobenzoic acid.[4] This paper describes the determination of blood sugar and urine sugar with the reagent.

CONDITIONS FOR DETERMINATION OF GLUCOSE

A preliminary study was carried out to find colorimetric conditions for the determination with the reagent dissolved in a dilute solution of sodium carbonate. To a glucose solution, the reagent solution and a concentrated sodium carbonate solution were successively added, and the mixture was heated in a water bath. Sodium thiosulphate was previously dissolved in the sodium carbonate solution. The absorption curve of the final colour developed with glucose is shown in Fig. 1. The absorption maximum was at 450 mμ. Prolongation of the reaction time increased the absorption intensity without changing the shape of the curve, and 10 minutes heating should be suitable for routine estimations because of the economy in time. A blank test solution of the reagent had a faint yellow colour, and its absorption curve is also shown in Fig. 1.

The concentration of 3 : 6-dinitrophthalic acid affected the absorption intensity. A more concentrated solution of the reagent gave a stronger intensity, but a 0·2% solution of the reagent was useful for the determination because it gave the minimum absorption in the blank test. The concentration of sodium carbonate also affected the intensity. Experiments showed that a 20% solution of sodium carbonate was preferable, because a more dilute solution gave less intensity in the developed colour, and a more concentrated solution caused a deeper colour in the blank test. An increased concentration of sodium thiosulphate also gave a deeper colour in the blank test, and a 5% concentration of the reagent was enough to stabilise the developed colour.

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* Part XXII: Bunseki Kagaku in press.

DETERMINATION OF BLOOD SUGAR

Reagents and apparatus

3 : 6-*Dinitrophthalic acid solution*: 1·00 g of 3 : 6-dinitrophthalic acid[5]* and 0·50 g of anhydrous sodium carbonate (Japanese Industrial Standards 1st Grade) are successively dissolved in sufficient water to measure 500 ml. This almost colourless solution is stored in a light-resistant bottle, to which an automatic micro-burette, 10-ml, is attached.

Sodium carbonate solution: 100·0 g of anhydrous sodium carbonate (Japanese Industrial Standards 1st Grade) and 25·0 g of sodium thiosulphate pentahydrate (Pharmacopoeia Japonica VI) are successively dissolved in water and made up to 500 ml. The solution is filtered after three days with a washed filter paper, and stored in a light-resistant bottle, to which an automatic micro-burette, 10-ml, is attached. It is protected from carbon dioxide.†

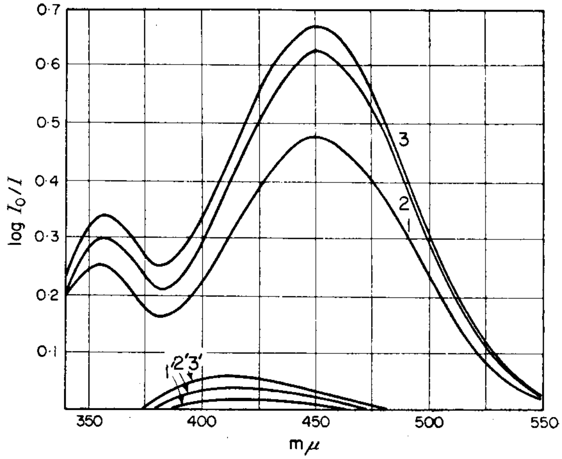

FIG. 1.—Absorption curves for developed and blank solutions.
2 ml of glucose solution, (80 μg/ml) heated with 1 ml of 3:6-dinitrophthalic acid solution and 1 ml of sodium carbonate solution for (1) 5, (2) 10, (3) 15 mins, and diluted to 20 ml. (1'), (2') and (3') are the corresponding blanks.

Deproteinising agents are prepared by Somogyi's method[6] as follows.

Zinc sulphate solution: 25·0 g of zinc sulphate heptahydrate is dissolved in water, made up to 500 ml, and stored in a bottle, to which an automatic micro-burette, 2-ml, is attached.

Barium hydroxide solution: 25 g of barium hydroxide octahydrate is dissolved in 500 ml of water in a bottle to which an automatic micro-burette, 2-ml, is attached, and protected from carbon dioxide. To adjust the concentration, 2·00 ml of zinc sulphate solution is diluted with 20 ml of water, and titrated, dropwise, with barium hydroxide solution using phenolphthalein as indicator. The more concentrated solution is diluted with water to match the other, volume by volume.

Absorption curves were measured by a Beckman DK-2 Ratio Recording Spectrophotometer. Absorption intensities were measured by a Hitachi EPU-2 Spectrophotometer with a glass cell of 10 mm optical length.

Procedure

0·100 ml of blood is haemolysed with 3·50 ml of water in a test-tube, and 0·20 ml of barium hydroxide solution is added. When the mixture turns brown, 0·20 ml of zinc sulphate solution is added, and the test-tube shaken vigorously. The mixture is then transferred to a centrifuge tube and centrifuged. 2·00 ml of the supernatant clear solution is pipetted into a test-tube, and 1·00 ml of

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* This reagent will be available in the near future from Chugai Seiyaku Kabushiki Kaisha, 3,3-chome, Nihonbashi Honcho, Chuo-ku, Tokyo, and Chugai S.A., Seebahnstrasse 85, Zurich.

† Crystalline sodium carbonate decahydrate may separate from this solution at a room temperature below 18°, and then it is preferable to use 125.0 g of potassium carbonate instead of sodium carbonate.

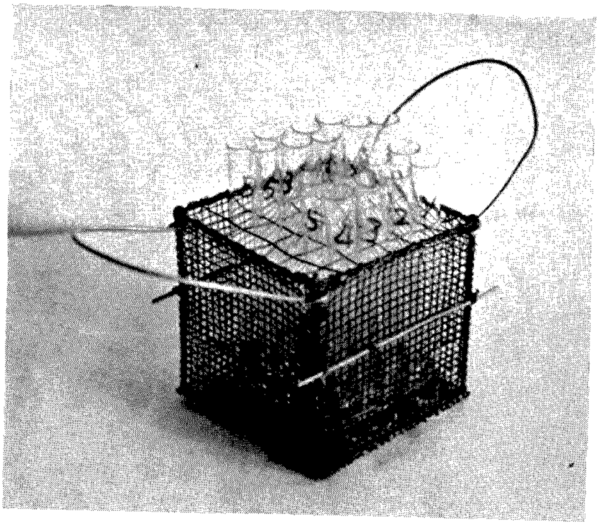

FIG. 2.—Heating basket.

3 : 6-dinitrophthalic acid solution and 1·00 ml of sodium carbonate solution are successively added. At the same time, 2·00 ml of water is mixed with the developing solutions in another test-tube as a blank. Both tubes are heated in a boiling water bath for exactly 10 minutes, cooled in running water for 3 minutes, and diluted with water to the 20·0-ml on the tubes. The absorption intensity of the sample is read at 450 mμ with the reagent blank, and the blood sugar value is obtained from the calibration curve which is drawn up below.

Careful attention should be paid to heating the developing and blank solutions under the same conditions. Hard glass test-tubes of the same size, about 16 mm × 160 mm, should be selected and the 20·0-ml level marked. In heating the solutions, test-tubes are dipped vertically in a boiling water bath in such a way that the surface of the contents of the tubes is about 5 mm below the surface of boiling water. There is no need to stopper the tubes.

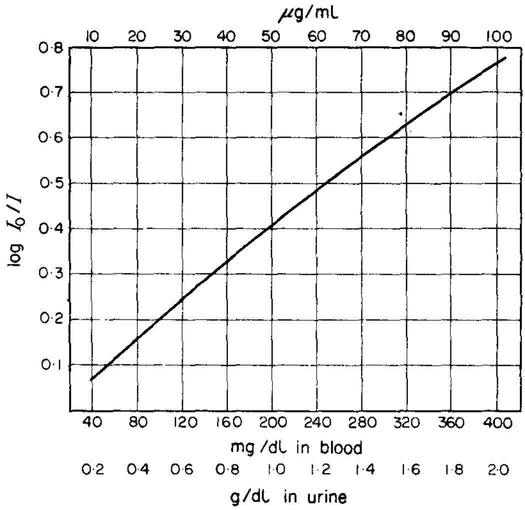

FIG. 3.—Calibration curve.

For treating a large number of samples, it is advisable to use the heating basket shown in Fig. 2. It is easily hand-made by wiring across the top and bottom of a copper gauze basket so that the test-tubes stand vertically in it and equally spaced. This basket, packed with test-tubes, should be dipped in a strongly boiling water bath to the previously mentioned depth, so that the heating is the same for any number of tubes.

Calibration curve

Glucose solution, 100 μg/ml, is prepared by dissolving 100·0 mg of dried glucose (Pharmacopoeia Japonica VI) in 1000 ml of water. This solution is diluted to give 10, 20, 30, 40, 50, 60, 70, 80 and 90 μg/ml solutions.

Three aliquots of 2·00 ml of each solution are pipetted into test-tubes; 1·00-ml of 3 : 6-dinitrophthalic acid solution and 1·00 ml of sodium carbonate solution are successively added, developed and diluted, as described under Procedure. The absorption intensities are read with a reagent blank which is prepared by mixing three aliquots of the reagent blank solution mentioned before. The calibration curve thus drawn up is shown in Fig. 3.

The blood sugar values (mg %) are obtained by multiplying the number of μg/ml by 4, or more conveniently, they are read from a graph.

RESULTS AND DISCUSSION

The calibration curve was reproducible, with successively prepared glucose solutions, with a maximum deviation of ±0·01 in the absorption intensity. This value of deviation meant a maximum error of 5% in 20 μg/ml, 3% in 60 μg/ml, and 2·5% in

100 μg/ml. The stability of 3 : 6-dinitrophthalic acid solution has not yet been determined, but the calibration curve was reproducible with an old solution which had been stored for one month at room temperature in summer. The same result was also obtained with freshly prepared reagent solutions. The developed colour was so stable, that the solution gave the same absorption intensity even when stored at room temperature for three days.

The deproteinising agents had no influence upon the development of colour when tested with glucose solutions. This fact was also confirmed by the examination of known blood sugar values which was carried out by adding known amounts of glucose in blood solution. The results are shown in Table I. The determined value of glucose coincided with the calculated one with a maximum error of ±3 % over a wide range of values.

TABLE I.—EXAMINATION OF KNOWN BLOOD SUGAR VALUES

Initial blood sugar value, *mg/dl**	Glucose added, *mg/dl*	Total glucose calculated, *mg/dl*	Total glucose found, *mg/dl*
85	50	135	134, 135
	100	185	186, 187
	150	235	235, 239
	200	285	284, 288
	250	335	336, 338
88	50	138	138, 142
	100	188	185, 185
	150	238	240, 243
	200	288	293, 295
	250	338	335, 340

* This value was checked by titration with ferricyanide.

The results of parallel tests with a modified Hagedorn's method on deproteinised blood solutions are shown in Table II. In Hagedorn's original method,[7] the deproteinisation of blood was carried out by zinc sulphate and sodium hydroxide, but in this experiment it was carried out with Somogyi's reagents, as described under Procedure, to decrease errors other than the colour developing or titrating error. The individual blood sugar value was in good agreement by the two methods.

TABLE II.—PARALLEL TESTS WITH A MODIFIED HAGEDORN'S METHOD

Blood number	Present method, *mg/dl*	Hagedorn's Method, *mg/dl*
1	95, 96, 97	97, 99, 99
2	97, 98, 100	99, 99, 101
3	104, 106, 106	105, 108, 110
4	118, 120, 120	120, 122
5	124, 125, 126	125, 125

The present method of determination is simple to carry out with a large number of samples, gives reliable results, and may be suitable for blood sugar tests in a clinical laboratory.

DETERMINATION OF URINE SUGAR

Urine sugar is determined in the same way as the determination of blood sugar, except that the deproteinising operation is omitted.

Procedure:

0·100 ml of urine is diluted with sufficient water to measure 20·0 ml. 2·00 ml of the solution is pipetted into a developing test-tube, 1·00 ml of 3 : 6-dinitrophthalic acid solution and 1·00 ml of sodium carbonate solution, as described under Reagents, are successively added, and treated in the same way as in the determination of blood sugar. The urine sugar value (g/dl) is obtained by multiplying the number of μg/ml by 0·02, and is entered as in Fig. 3.

TABLE III.—EXAMINATION OF KNOWN URINE SUGAR VALUES

Initial urine sugar value, *g/dl*	Glucose added, *g/dl*	Total glucose calculated, *g/dl*	Total glucose found, *g/dl*			
0·06	0·40	0·46	0·45,	0·46,	0·46,	0·46
	0·80	0·86	0·85,	0·85,	0·86,	0·87
	1·20	1·26	1·24,	1·25,	1·25,	1·25
	1·50	1·56	1·53,	1·54,	1·54,	1·56
	1·80	1·86	1·83,	1·84,	1·85,	1·85

In this determination, the sample was so dilute that any preliminary treatment of urine was usually unnecessary, except for blood urine. This conclusion was proved by the fact that other substances which might exist in urine gave no interference in the colour reaction i.e. 0·01 ml of 5% albumin, 1% creatine, 1% creatinine, 1% acetone and 1% ethyl acetoacetate each showed only negligible absorption at 450 mμ, when heated with the developing solutions.

The results of examination of known urine sugar values are shown in Table III. The found values coincided with the calculated one with a maximum error of ±2·2%.

Zusammenfassung—Eine neue, kolorimetrische Methode zur Bestimmung von Zucker in Blut und Urin wurde ausgearbeitet. 3,6-Dinitrophthalsäure wird als farbbildendes Reagenz verwendet.

Résumé—Les auteurs ont élaboré une nouvelle méthode colorimétrique de dosage du sucre dans le sang et dans l'urine, utilisant l'acide 3,6-dinitrophtalique comme agent de développement coloré.

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UMBELLIKOMPLEXON UND XANTHOKOMPLEXON

EIN BEITRAG ZUR KENNTNIS KOMPLEXOMETRISCHER FLUORESZENSINDIKATOREN

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Zusammenfassung—Es wird über die Synthese zweier dem Calcein analoger komplexometrischer Fluoreszenzindikatoren, "Umbellikomplexon" und "Xanthokomplexon" berichtet. In einer Tabelle werden Fluoreszenz und Absorptionsmaxima dieser Indikatoren in Abhängigkeit vom pH und dem Zusatz von Kationen angegeben. Mit ihrer Hilfe lässt sich die analytische Verwendbarkeit der gebildeten Indikatorkomplexe abschätzen.

Es werden durch Versuche gestützte Erklärungen für die wichstigsten Fluoreszenzerscheinungen an diesen Indikatoren gegeben: (1) die Bildung teils fluoreszierender teils nicht fluoreszierender Komplexe hängt von der durch verschiedene Elektronenkonfiguration der Kationen bedingten unterschiedlichen Kopplung mit dem mesomeren System des Fluorophors ab; (2) die Fluoreszenslöschung der freien Indikatoren beim Übergang von pH 10 nach pH 12 beruht in einer durch Protolyse bedingten Änderung des Schwingungszustandes des Komplexonrestes im Indikatormolekül und dadurch veränderter Energieableitung aus dem Fluorophor.

Die störende Fluoreszenz der genannten Indikatoren, die höhere Na^+-Konzentrationen bei pH-Werten über 12 verursachen, kann durch Erwärmen der Lösungen stark vermindert werden, ohne merkliche Veränderung des Verhaltens der Ca-Komplexe der Indikatoren.

EINLEITUNG

VERANLASST durch die Mitteilungen von D. H. Wilkins über "metalfluorechromic indicators"[1,2] sei hier über einige unserer Untersuchungen auf diesem Gebiet berichtet.[3,4*] Seitdem das von H. Diehl und J. L. Ellingboe[5] synthetisierte" Calcein"[6] als komplexometrischer *Fluoreszenz*-Indikator erkannt wurde,[3,7] bestand ein Interesse an weiteren Vertretern dieser Indikatorklasse.

Als Ausgangsmaterial wählten wir 4-Methylumbelliferon und 3,6-Dihydroxyxanthon. Diese wurden in essigsauer-wässrigem Medium mit Paraformaldehyd und Iminodiessigsäure umgesetzt. Die beim Methylumbelliferon geplante Einführung *eines* Komplexonrestes gelang ohne Schwierigkeit. Beim Dihydroxyxanthon hingegen misslang überraschenderweise die Einführung *zweier* Komplexonreste, es wurde nur ein *Mono*komplexon erhalten. Die so gewonnenen "Umbellikomplexon" (UK) und "Xanthokomplexon" (XK), von denen ersteres möglicherweise identisch mit Wilkins' "Calcein Blue"[2] ist, sind farblose, in Wasser, Aceton und Äthanol schwerlösliche Substanzen. In Pufferlösungen vom pH 6 bis 10 sind sie mit stark blauer Fluoreszens leicht löslich; nur bei hohen Konzentrationen besitzen die Lösungen blassgelbe Farbe. In KOH-Lösungen mit pH-Werten über 12 lösen sie sich leicht ohne jede Fluoreszenz.

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[*] Vortrag in Lund, 28. Mai 1958, *Über Calcein und verwandte Farbstoffe;* Vortrag in Stockholm, 20. August 1959, *Über komplexometrische Fluoreszenzindikatoren;* beide in schwedischer Sprache.

KOMPLEXBILDUNG DER INDIKATOREN

Tabelle I zeigt die Ergebnisse von Fluoreszenz- und Absorptionsmessungen an UK und XK bei Zusatz verschiedener Kationen. Von einer Diskussion der Ergebnisse sei abgesehen, nur darauf hingewiesen, dass im Allgemeinen Kationen mit gefüllten Elektronenniveaus fluoreszierende und solche mit nicht gefüllten Niveaus nichtfluoreszierende Komplexe bilden. Einige Kationen bilden in den gewählten Milieus gar keine Komplexe. Die stark unterschiedlichen Fluoreszenzeigenschaften verschiedener Komplexe ermöglichen einfache Kationenverdrängungsversuche zur Abschätzung der relativen scheinbaren Stabilität der Komplexe und somit eine rasche Orientierung, ob ein bestimmter Komplex in einem bestimmten Milieu analytische Bedeutung haben kann oder nicht.

TABELLE I.—FLUORESZENZ UND ABSORPTIONSMAXIMA DER INDIKATORKOMPLEXE

	0·1*M* Borax (pH etwa 9–9·5)				0·5*N* KOH (pH etwa 13)			
	UK		XK		UK		XK	
Indikator mit Zusatz von	I_f	$\lambda_{\max}$ mμ	I_f	$\lambda_{\max}$ mμ	I_f	$\lambda_{\max}$ mμ	I_f	$\lambda_{\max}$ mμ
Mg^{2+}	75	353	70	365	10	365	10	373
Ca^{2+}	95	358	80	368	80	358	80	368
Sr^{2+}	105	361	90		95	363	90	
Ba^{2+}	105	359	85		100	364	100	
Cr^{3+}	80	359	70	368	5	367	5	373
Mn^{2+}	5	354	5	365	5		5	
*Fe^{2+}	5		5		5		5	
Co^{2+}	5		5		15	355	20	
Ni^{2+}	5		5		5	358	5	
Cu^{2+}	5	349	5	366	5	349	5	369
Zn^{2+}	50	347	60	363	30		50	370
Cd^{2+}	70	353	75	366	70		40	368
Hg^{2+}	5	363	5		5		5	
Pb^{2+}	15		20		35	361	40	
Bi^{3+}	5		15		5	366	5	
Freier Indikator	80	359	75	368	5	366	5	373

* Es wurde Fe(II)-Salz zugesetzt; es trat jedoch immer teilweise Oxydation beim Mischen auf, daher ist die Oxydationsstufe im Indikatorkomplex ungewiss.

Fluoreszenzstandard: eine gesättigte Lösung von 4-Methylumbelliferon in 0,2*M* K-acetat, mit dem selben Lösungsmittel auf das 5-fache Volum verdünnt; deren Fluoreszenzintensität (I_f) gleichgesetzt mit 20 Einheiten.

Messwerte: Die maximale Fehlerbreite der Fluoreszenzintensitäten liegt bei etwa ±5 Einheiten. Alle Messwerte wurden auf die nächste 5er-Einheit aufgerundet; der Wert 5 bedeutet einen beliebigen Wert zwischen 0 und 5. Die maximale Fehlerbreite der Absorptionsmaxima liegt bei etwa ±1 mμ.

FLUORESZENZEIGENSCHAFTEN DER KOMPLEXE

Zwei Erscheinungen an den Indikatoren bedürfen der Erklärung. Erstens: warum verschwindet bei den freien Indikatoren die Fluoreszenz bei pH-Werten über 12 und bei ihren Stammsubstanzen nicht; und zweitens: warum fluoresziert ein Teil der Komplexe und ein anderer nicht?

Für letztere Erscheinung gibt Wilkins[1] eine Erklärung. Hier dürfte das Entscheidende die unterschiedliche Einwirkung der im Komplex gebundenen Kationen auf das π-Elektronensystem des Fluorophors sein, wobei die Kontaktstelle zwischen beiden der Phenolsauerstoff ist. Hierbei hat die Tatsache Bedeutung, dass die alkalische Hydrolyse des Pyranringes im UK durch Komplexbildung beschleunigt wird, und dass dabei ein deutlicher Unterschied zwischen fluoreszierenden (Na, Ca) und nichtfluoreszierenden (Ni, Co) Komplexen besteht, letztere werden viel schneller verseift.

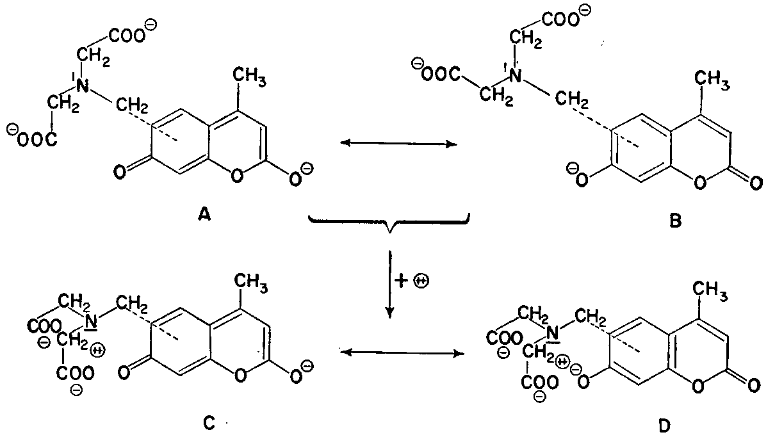

ABB. 1.

Abb. 1 mag dies erklären. Oberhalb pH 12 liegt UK als mesomeres Ion vor, das durch die Strukturen A und B beschrieben wird. Nur aus B kann es alkalisch hydrolysiert werden, nur dort kann sich ein OH^--Ion an die C=O-Bindung im Pyranring anlagern. Wird ein Komplex gebildet, so kann dieser mit den Strukturen C und D beschrieben werden. Wird dieser schneller hydrolysiert als das freie UK, so besagt das, dass im Komplex D gegenüber C mehr betont ist, als im freien UK B gegenüber A. M.a.W. heisst das, dass im Komplex ein Zug auf das π-Elektronensystem in Richtung auf den Phenolsauerstoff ausgeübt wird, der um so stärker ist, je schneller die Hydrolyse des Komplexes vor sich geht.

Geschieht nun die Fluoreszenzlöschung in einem Komplex durch die Störung des mesomeren Systems an sich, oder durch rasche Energieableitung aus dem angeregten System über die Kationen, die ja in den fraglichen Fällen besonders fest mit dem mesomeren System verkoppelt sind? Da die Absorptionsspektra im Vergleich der fluoreszierenden mit den nicht fluoreszierenden Komplexen keine besonderen Mesomeriestörungen ausweisen, wird man Letzteres annehmen dürfen. Das deckt sich damit, dass Kationen dieses Types mitunter die Fluoreszenz Lösungen einiger Substanzen löschen, ohne an diese chemisch gebunden zu sein.

Von einer speziellen Formulierung der Unterschiede der Komplexe sei abgesehen (etwa "ionisch-kovalent" oder Bindung über "äusseres resp. inneres d-Niveau"). Auch scheint die von Wilkins[1] gegebene Formulierung eines speziellen Beweises zu bedürfen; die Formel für den bei pH 13 stabilen, fluoreszierenden Ca-Komplex des Calceins (Fig. 1b bei Wilkins) erscheint ungewöhnlich, allgemein pflegen Phenolprotonen bei pH 13 abdissoziiert zu sein.

FLUORESZENSEIGENSCHAFTEN DER FREIEN INDIKATOREN

Die wesentliche Frage der Fluoreszenzlöschung der freien Indikatoren in stark alkalischem Medium hat Wilkins nicht diskutiert. Kürzlich ist von H. Musso und

H. G. Matthies ein Beispiel der Substituenteneinwirkung auf einen Fluorophor bei den Orceinfarbstoffen beschrieben worden; die Autoren bedienen sich zur Erklärung ihrer Befunde der Arbeiten von G. Kortüm und G. Dreesen[9] wie von G. Oster und Y. Nishijima;[10] die gegebene Erklärung kann auch auf unseren Fall angewendet werden:

Voraussetzung für das Auftreten von Fluoreszenz ist, dass die Lebensdauer eines angeregten Zustandes nicht durch irgendeine andere Energieableitung unter 10^{-8} sek verkürzt wird; beim 4-Methylumbelliferon zB ist diese Bedingung offensichtlich erfüllt. Beim UK im Zustand A–B (Abb. 1) dagegen ist über die mit dem Kern hyperkonjugierte —CH_2-Gruppe eine Energieableitung durch eine Torsionsschwingung um die Bindungsrichtung zum Kern möglich. Durch seine Masse und wohl auch durch Wasserstoffbrücken zum Lösungsmittel* verleiht der an der —CH_2-Gruppe hängende Iminodiessigsäurerest dieser Schwingung ein grosses Trägheitsmoment. Dadurch wird die reziproke Torsionsfrequenz recht klein und die mittlere Lebensdauer des angeregten Zustandes verkürzt sich mit ihr, mit Fluoreszenzlöschung als Folge.

Unterdrückt man die Torsionsschwingung des Restes, so findet keine Energieableitung statt, und die Fluoreszenz sollte wieder auftreten. So geschieht das, wenn zB der Rest bei Bildung von Chelatkomplexen (etwa wie C—D in Abb. 1) mit solchen Kationen arretiert wird, die selbst keine Energie ableiten; analog wirkt die Addition eines Protons an den Stickstoff (Übergang in den schwach alkalischen Bereich) mit Bildung einer Wasserstoffbrücke zum Phenolsauerstoff.

Konsequenterweise müsste auch jede andere Art der Arretierung des Restes Fluoreszenz hervorrufen, zB hinreichend grosse Viskosität des Mediums. Tatsächlich genügt schon die Lösung von UK im Zustand A–B in 80% igem Glyzerin bei ZT, um deutliche Fluoreszenz hervorzurufen, die beim Abkühlen noch zunimmt. Genau dieselbe Erscheinung zeigen auch Calcein und XK, die Richtigkeit der diskutierten Anschauung beweisend.

Aus dieser Anschauung folgt, dass Indikatoren des diskutierten Types auch in der unchelierten Form nur innerhalb bestimmter Viskositäts- bzw. Temperaturbereiche ohne "indigene Restfluoreszenz" existieren und verwendet werden können.

TEMPERATURABHÄNGIGKEIT DER "NATRIUMFLUORESZENZ"

Schon F. Körbl, F. Vydra und R. Přibil[11] haben darauf hingewiesen, dass Calceinlösungen vom pH 12 und grösser bei höherem Na^+-Gehalt eine deutliche bis starke Fluoreszenz zeigen, bedingt durch die Bildung eines Na-Komplexes. Dadurch kann bei manchen Titrationen, zB des Ca^{2+} neben Mg^{2+}, die Bestimmung des Endpunktes erschwert oder unmöglich werden, da oft die Anwesenheit von Na^+ nicht zu vermeiden ist.

Temperaturerhöhung sollte die Dissoziation des schwachen Na-Komplexes fördern, zugleich sollte auch die Torsionsschwingung der Reste im Calcein begünstigt werden: beide Effekte sollten eine Herabsetzung der "Natrium-Fluoreszens" des Calceins bewirken. Tatsächlich verschwindet beim Erwärmen stark alkalischer Calcein- oder XK-Lösungen höheren Na^+-Gehaltes auf etwa 80° der grössere Teil der Fluoreszenz; die Schärfe des Umschlages der Ca-Komplexe gegen ÄDTE wird bei

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* Wäre es nur die Masse des Restes allein, die das Trägheitsmoment verursacht, so müsste zB auch bei Hexylderivaten des Umbelliferons oder Fluoreszeins eine Fluoreszenzlöschung auftreten können; das ist aber nicht der Fall.

diesem Erwärmen nicht merklich beeinflusst. Damit dürfte eine praktisch wichtige Hilfe beim Titrieren mit den genannten Indikatoren in stark Na^+-haltigen Lösungen gegeben sein.

VERSUCHSTELL

Apparaturen

Die Fluoreszenzmessungen wurden mit einem Spektrophotometer Beckman Modell B und einem selbstgebauten Prismaeinsatz durchgeführt. Dieser lässt das monochromatisierte Licht im rechten Winkel zur Einfallsrichtung der Photozelle auf eine 1 cm-Kuvette fallen; die Photozelle misst dann die Summe des Fluoreszenzlichtes. Gemessen wurde bei der jeweils am stärksten aktivierenden Wellenlänge; diese wird neben dem Absorptionsmaximum des Indikators auch stark von der Spektralcharakteristik von Lichtquelle und Photozelle bestimmt; für UK und XK lag sie durchweg im Bereich von 380 bis 405 mμ.

Die Messungen der Absorptionsspektra wurden mit einem Spektrophotometer Beckman Modell DK-2 durchgeführt.

Fluoreszenzmessungen (Tabelle 1)

Zu 5 ml 0,05% ig UK bzw 0,02% ig XK wurden 0,5 ml 0,02M ÄDTE und 2 ml 0,02M Kationsalzlösung gegeben, dann mit 0,1M Borax bzw 0,5N KOH auf 25 ml aufgefüllt und filtriert. Die Messung geschah 4 bis 6 Minuten nach dem Borax- bzw KOH-Zusatz. Allgemein wurden Perchlorate, in wenigen Fällen Nitrate oder Chloride verwendet.

Absorptionsmaxima (Tabelle 1)

Zu 2,5 ml 0,02% ig XK bzw 2 ml 0·05% ig UK wurden 0,5 ml ÄDTE 0,05M und 5 ml 0,02M Kationsalzlösung gegeben, dann mit 0,1M Borax bzw 0,5N KOH aufgefüllt und filtriert. Die Messung geschah 4 bis 6 Minuten nach dem Borax- bzw KOH-Zusatz.

Alkalische hydrolyse von UK und seinen Komplexen

Die Hydrolyse des Na- und des Ca-Komplexes in 0,5N NaOH wurde durch Messung der Fluoreszenzintensität verfolgt (UK-Konzentration 0,1%, analog den sonstigen Fluoreszenzmessungen mit entsprechendem Ca^{2+}-Überschuss, beim Na-Komplex kein weiterer Na^+-Zusatz); die Halbwertszeiten für diese ergaben sich beim Ca-Komplex zu etwa 37 und beim Na-Komplex zu etwa 47 Minuten.

Die Hydrolyse des freien UK und seiner Komplexe mit Co^{2+} und Ni^{2+} in 0,5N KOH wurde durch Messung der Extinktion beim Absorptionsmaximum verfolgt (Bedingungen wie oben bei den Absorptionsmaxima); die Halbwertszeiten für diese ergaben sich beim freien UK zu etwa 80, beim Ni-Komplex zu etwa 7,5 und beim Co-Komplex zu etwa 6 Minuten.

In allen Messreihen, ausgenommen die des Ca-Komplexes in NaOH, liessen sich die Logarithmen des Fluoreszenzintensität bzw der Extinktion gegen die Zeit als Gerade auftragen.

Fluoreszens von Calcein, UK und XK in Glyzerin

Eine Spatelspitze Indikator und eine Spatelspitze ÄDTE werden in 10 ml 0,5N KOH gelöst und die Lösung geteilt; der eine Teil wird mit 4 Teilen Wasser verdünnt: keine Fluoreszenz; der andere Teil wird mit 4 Teilen Glyzerin verdünnt: deutliche Fluoreszenz, die beim Einstellen in ein Kältebad von —10° noch zunimmt.

Fluoreszenzlöschung beim Erwärmen der Na-Komplexe des Calceins und des XK

A: Eine Spatelspitze Indikator und eine Spatelspitze ÄDTE werden in 40 ml 0,5N NaOH gelöst, mit Wasser auf 100 ml verdünnt und geteilt. Die eine Lösung wird im Wasserbad auf etwa 80° erwärmt: Vergleich mit der kalten Lösung erweist Verschwinden des grösseren Teiles der Fluoreszenz, die beim langsamen Erkalten wiederkehrt. Zusatz eines Überschusses von 0,02M Ca-perchlorat zur warmen Lösung bewirkt prächtige Fluoreszenz; tropfenweiser Zusatz von 0,02M ÄDTE lässt diese mit scharfem Umschlag wieder verschwinden.

B: Eine Spatelspitze Indikator und eine Spatelspitze ÄDTE werden in 50 ml 0,5N KOH gelöst, mit Wasser auf 150 m verdünnt und dreigeteilt; ein Teil verbleibt so, in den beiden anderen werden etwa 10% NaCl aufgelöst: starke Fluoreszenz in diesen. Einer dieser Teile wird im Wasserbad auf etwa 80° erwärmt: Vergleich mit der kalten NaCl-Lösung erweist erhebliche Fluoreszenzminderung.

Aufeinanderfolgender Zusatz von Ca-perchlorat und ÄDTE wie oben gibt ebenfalls einen Fluoreszenzumschlag, doch nicht gleich deutlich erkennbar.

Dank gebührt Fil. lic. P. O. Bethge für reges Interesse und freundschaftliche Förderung der Arbeit, den Herren Dozenten B. Lindberg und H. Musso (Göttingen) für anregende Diskussionen, wie Fräulein A. Håkansson und Herrn L. Cronquist für Hilfe bei den Synthesen und Messungen.

Summary—The syntheses of "Umbellikomplexon" and "Xanthokomplexon", two fluorescent indicators for complexometry analogous to "Calcein", are reported. A table shows the dependence of the fluorescence and absorption maxima of these indicators on pH and added cations. With these results the possibility of analytical application of the indicator complexes which are formed can be estimated.

Supported by experiments, explanations are given for the most important fluorescence phenomena of these indicators. (1) The formation of fluorescing and non-fluorescing complexes is caused by different coupling between the mesomeric system of the fluorophore and the cations, depending on the different electron configuration of the latter. (2) The fluorescence quenching of the free indicators during the change from pH 10 to pH 12 depends on a protolysis which changes the oscillation state of the complexone residue of the indicator, followed by a change of the energy dissipation from the fluorophor.

The background fluorescence of the indicators mentioned, caused by high Na^+ ion concentrations at pH 12 and higher, is diminished by heating the solutions, without notable change in the behaviour of the Ca-indicator complexes.

Résumé—L'auteur décrit les synthèses de l'"umbellicomplexon" et du "xanthocomplexon", deux indicateurs fluorescents analogues à la "calcéine". Une table montre comment la fluorescence et les maxima d'absorption de ces indicateurs dépendent du pH et des cations ajoutés. Grâce à ces résultats, on peut estimer la possibilité d'application analytique des complexes de l'indicateur qui sont formés.

Des explications, en accord avec l'expérience, sont données pour les phénomènes de fluorescence les plus importants révélés par ces indicateurs. (1) La formation de fluorescéine et de complexe non fluorescents est due à un couplage différent entre le système mésomère du fluorophore et les cations, dépendant des configurations électroniques différentes de ces derniers. (2) La disparition de la fluorescence des indicateurs libres pendant une variation de pH de 10 à 12 dépend d'une protolyse qui change l'état d'oscillation du résidu complexon de l'indicateur, suivie par un changement de dissipation de l'énergie à partir du fluorophore, On diminue la fluorescence résiduelle de ces indicateurs, due à de fortes concentrations d'ions Na^+ à pH $\geqslant$ 12 en chauffant les solutions; en même temps il n'y a pas de changement notable du comportement des complexes Ca-indicateur.

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THE ISOLATION OF PLATINUM METALS FROM PARTIALLY REFINED CONCENTRATES

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Summary—A new procedure has been developed which effects the dissolution of large or small amounts of complex platinum metal concentrates and permits the application of a variety of methods for the isolation of each platinum metal. A group of standard separations and determinations has been applied successfully and the application of a new separation of rhodium from iridium has been described.

THE present research was undertaken to provide a method of dissolution of platinum metals concentrates which could be applied to large scale operations as well as to analytical processes. It was necessary also to devise methods of subsequent isolation which would lend themselves to the precipitation of both large and small amounts of platinum metals. The procedure described below, while essentially in analytical form, may be thus extended.

INTRODUCTION

The degree of difficulty associated with the isolation of platinum metals from various types of concentrates is dependent upon the method of dissolution, which in turn is determined by the complexity of the material. For concentrates containing little or none of the more insoluble platinum metals the problem of dissolution is a simple one, and one or more treatments with mixtures of mineral acids is usually sufficient. The concentrate discussed below was a by-product of an electrolytic refining process and contained some twenty-five elements in addition to about 25% of platinum metals with the exception of osmium. The principal base metals content in percentages was: nickel 6·45; tin 4·86; silicon oxide 4·10; copper 3·20; lead 1·67; chromium 1·00 and iron 0·87.

The methods of dissolution available were: (1) fusion with lead or zinc followed by selective dissolution with acids and finally fusion with sodium peroxide (2) chlorination at various temperatures in the presence of sodium chloride, (3) the sealed-tube chlorination described by Wickers, Schlecht and Gordon.[1,2]

All of these methods were tried and rejected; the fusion with lead or zinc introduced further impurities, and failed to produce an entirely soluble residue; the chlorination introduced the problem of collecting volatile deposits, and resulted in the formation of an insoluble allotrope of ruthenium;[3] the sealed-tube method was limited to small amounts of concentrate, and all modifications tried failed to achieve complete dissolution.

Preliminary experiments with sodium carbonate fusions suggested the possibility of low temperature sintering. The final process involved an intimate mixing of concentrate and sodium carbonate, heating to about 700°, and subsequent leaching with water and acid. The dissolution resulted in a residue of 2–3% of the original sample consisting mainly of silica and very small amounts of platinum metals. This residue was readily dissolved by fusion with sodium peroxide, and while this was an inconvenience, the method on the whole was a considerable improvement over all other methods tried, since weights of samples required for either analytical or refining purposes could be used with very little contamination from either a porcelain or an iron container. There was also the considerable advantage that the sintered mass was coherent and could be taken from the vessel as a solid, dry body. Subsequent to dissolution of the sinter and fusion of the small residue the aqueous solution may be treated by various conventional methods to isolate the platinum metals. For those concentrates which contained sulphur it was found advantageous to remove this interference by prior treatment with hydrogen. For analytical purposes 1-g samples provided appropriate amounts of platinum metals.

EXPERIMENTAL

Apparatus and reagents

Large cation-exchange column of Dowex 50(X × 8) resin 30 cm in depth and 22 cm in diameter with a draining tube 0·4 cm in diameter.

Small cation-exchange column 4 cm in depth, 1 cm in diameter with a draining tube 4 mm in diameter.

Copper powder, freshly prepared by reducing analytical-grade copper oxide powder with hydrogen at 500°.

Procedure

Reduction in hydrogen. A one-gram sample of concentrate was weighed directly into a silica boat which was then placed in a Vycor tube. Hydrogen was passed through at the rate of a few bubbles per second while the temperature was slowly increased to 450°. To reduce silver chloride this temperature was maintained for 1 hour, following which the temperature was raised to 600°. Heating was continued for about 2 hours to remove the hydrogen sulphide completely. The loss in weight of the sample was of the order of 25%. The reduced sample was cooled, transferred to a 150-ml beaker, and leached on the steam bath with 25 ml of 1 : 4 nitric acid for 2 hours. The mixture was filtered through Whatman No. 42 filter paper and the insoluble **residue 1** (Fig. 1) was washed with dilute nitric acid. The **filtrate 1a** was treated to precipitate the silver chloride which was filtered to provide **filtrate 1b** and then dissolved in ammonia and re-precipitated to provide **filtrate 1c**. The combined filtrates **1b** and **1c** were added to **filtrate 2a** obtained from the *aqua regia* treatment of residue **1**. This residue was washed with dilute nitric acid from the paper into the leaching beaker. The paper was separately destroyed with fuming nitric acid and a few drops of 30% hydrogen peroxide, and the contents were added to the leaching beaker. Twenty ml of *aqua regia* were added, and the mixture was digested on the steam bath for 4 hours. The dark red solution was diluted, filtered through Whatman No. 42 paper and washed with dilute hydrochloric acid. The *aqua regia* filtrate **2a**, combined with filtrates **1b** and **1c**, was evaporated on the steam bath and treated with hydrochloric acid to remove the nitric acid. The liquid was transferred to a 600-ml beaker, diluted with 400 ml water, and the pH adjusted to 1·5 to precipitate meta-stannic acid, which was then coagulated on the steam bath and filtered through a porcelain filter-crucible to provide filtrate **2b**. Since a spectrographic examination revealed small amounts of platinum metal in the tin hydroxide the latter was dissolved with hydrochloric acid, the solution was evaporated to a small volume and re-precipitated as before to provide sufficiently purified stannic acid and a filtrate **2c**, which together with filtrate **2b** were combined to provide part of the sample solution which was later added to the solutions **3a** and **4a**, obtained from residue **2**. The weight of the latter represented a reduction of about 80% and it contained principally platinum, ruthenium, iridium, rhodium, silicon, iron, nickel, chromium and titanium. The gold and palladium content was largely removed by the *aqua regia* treatment of residue **1**. For residue **2**, the optimum sintering temperatures were 700–730°. During the reaction the mixture contracted from the wall and only the bottom layer was in contact with the crucible. Nickel crucibles provided the advantage of non-melting temperatures as high as 790°, and consequently a shorter reaction time. To produce the sinter, about 1 g of powdered sodium carbonate was placed in the bottom of the crucible. The residue plus carbonate in the ratio 1 : 20 was ground and mixed carefully in an agate mortar and transferred to the crucible on the top of the bottom layer. Another portion of about 1 g of carbonate was ground in the mortar to take up any remaining traces of samples and then placed on top of the mixture.

When porcelain crucibles were used the mixture was sintered in a muffle furnace at about 710° for 3 hours, and for nickel crucibles the temperature was 780–790° and the reaction time about 2 hours. After cooling, the compact material was easily loosened from the bottom of the crucible with a spatula and placed in a 600-ml beaker. Dissolution of the sintered product in water was slow but was hastened with dilute hydrochloric acid. The beaker was tightly covered during this operation. Subsequent to neutralisation, 100 ml of hydrochloric acid were added and the beaker was placed on the steam bath for about 2 hours. When cool the dark red solution was filtered through Whatman No. 42 filter paper to provide filtrate **3a** and residue **3** which was washed with water. The filtration was sometimes slow because of precipitated silica. The residue **3** now represented about 3% of the original sample and spectrographic examination showed principally silica. This insoluble material was fused at about 700° in a nickel crucible with 2 g of sodium hydroxide for 15 minutes. The few black particles dissolved in the hydrochloric solution and this, on filtering, provided filtrate **4a**. The platinum metals sample solution now consisted of filtrates **2b**, **2c**, **3a**, and **4a**.

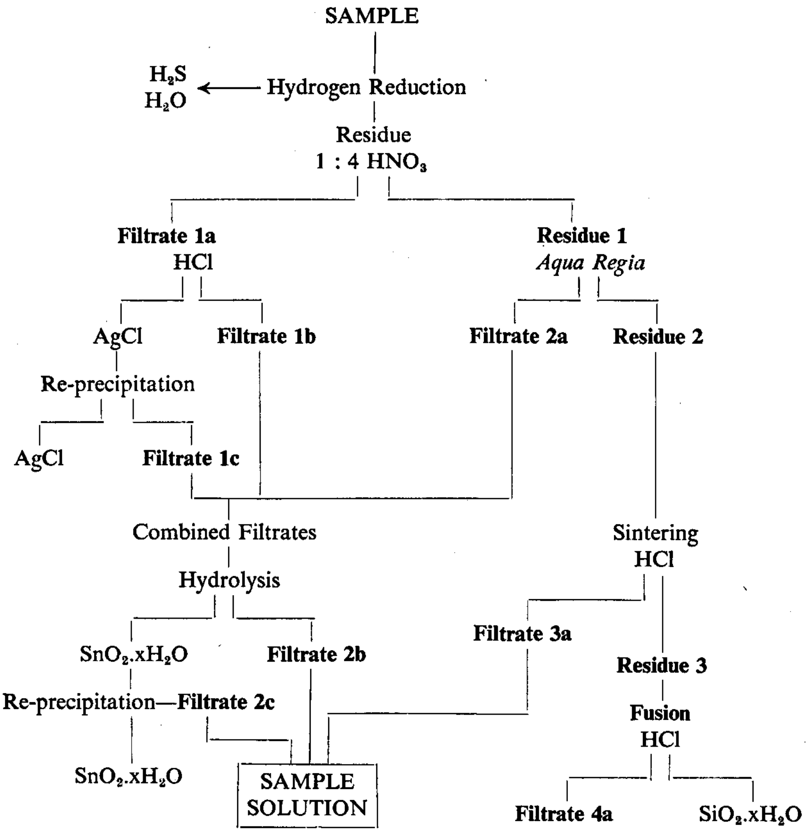

FIG. 1.—Flowsheet

Separation and determination of ruthenium

Ten ml of concentrated sulphuric acid were added to the sample solution and the liquid was evaporated to a small volume. The solution was transferred to the distilling flask[4] and the distillation was carried out with sodium bromate.

The distillate was collected in 1 : 1 hydrochloric acid containing about 3% hydrogen peroxide. The solutions in the four receivers were transferred to a 600-ml beaker, evaporated nearly to dryness in the presence of sodium chloride, filtered and diluted to 250 ml in a volumetric flask. Aliquots of 25 ml were taken, and ruthenium was determined gravimetrically with thionalide according to the procedure of Beamish and coworkers.[5]

Separation of gold and platinum from palladium, rhodium, iridium and base metals

Following the distillation of ruthenium, gold and platinum were separated from palladium, rhodium, iridium and base metals by applying the Gilchrist bromate-hydrolysis procedure.[6] Since the precipitated hydroxides were found by spectrographic examination to be contaminated with gold and platinum a re-precipitation was necessary. To avoid the large amount of hydroxides, the second hydrolysis was carried out after the base metals had been removed from the solution by cation-exchange resin as described below.

The solution in the distilling flask was transferred to a 600-ml beaker, evaporated on the steam bath in presence of hydrochloric acid, the salts were dissolved in water and the solution was diluted to about 200 ml. The hydrolytic precipitation was then applied, but sodium hydroxide solution was used instead of sodium carbonate solution and the pH was controlled by a Beckman pH-meter. Sodium hydroxide was used in order to avoid the formation of gas. The precipitate settled fast and was readily filtered. The precipitate was washed from the paper into the beaker used for the hydrolytic precipitation. The remaining traces on the filter paper were dissolved with hydrochloric acid and washed with water. The whole precipitate was then dissolved in hydrochloric acid and reserved for the separation of the base metals from palladium, rhodium and iridium. The filtrate, containing gold and platinum, was combined with the filtrate after the second hydrolytic precipitation described below.

Separation of base metals from palladium, rhodium and iridium

Subsequent to dissolution of the hydroxides the solution was evaporated nearly to dryness, and diluted with water to 200 ml. The pH of the solution was adjusted to 1·5. The solution was passed through the cation-exchange column at a rate of 1 drop per second.[7,8] The resin was washed with 400 ml of water and the effluent evaporated to about 150 ml, and a second hydrolysis was carried out. It was found very difficult to dissolve this precipitate completely on the filter paper with hydrochloric acid, and therefore this precipitate was filtered through a porcelain filter-crucible as recommended by Gilchrist.[6]

The filtrate was added to the filtrate from the first hydrolysis precipitation and reserved for determination of gold and platinum.

Determination of gold and platinum

The combined filtrates were evaporated to dryness several times in the presence of hydrochloric acid to decompose the sodium bromate. The salts were then dissolved in water, the solution filtered and diluted to about 250 ml. Gold was precipitated with hydroquinone according to the procedure by Beamish and Seath[9] for precipitation of gold in the presence of tellurium. The precious metals concentrate contained 0·87% of tellurium which was found to accompany gold and platinum. The presence of tellurium added considerably to the difficulty of determining platinum. Tellurium is a quantitative reducing agent for platinum and was so used by Westland and Beamish[10] for separation of platinum and palladium from rhodium and iridium. Precipitants for platinum such as zinc, magnesium, hydrogen sulphide and thiophenol similarly precipitate tellurium.

Westland and Beamish[10] separated tellurium from platinum by evaporation of tellurium in hydrogen gas at high temperature. This method was adopted successfully. Platinum was precipitated with thiophenol in the solution after filtration of the gold.[11] The precipitate was filtered through Whatman No. 42 filter paper. The paper was placed in a tared weighing crucible, and was charred at low temperature. The crucible was transferred to a combustion tube and heated at 750° for 0·5 hour in a stream of hydrogen. The paper was finally burned by heating in air. The crucible was once more placed in the combustion tube and the platinum was reduced for twenty minutes.

Determination of palladium

The precipitate of the hydrated oxides of palladium, rhodium and iridium after the second hydrolytic precipitation was dissolved in concentrated hydrochloric acid. After evaporation to near dryness in the presence of sodium chloride, 3 ml of hydrochloric acid were added and the solution was diluted to 200 ml. Two hundred mg of the sodium salt of dimethylglyoxime were dissolved in 1% hydrochloric acid, filtered and added to the solution for precipitation of palladium. After standing 1 hour at room temperature, the solution was filtered through a porcelain filter-crucible, the precipitate was washed with water and dried at 110° for 2 hours.

Separation of rhodium and iridium

Three methods for separating rhodium from iridium have been reported. With one rhodium is precipitated by titanium^{III} chloride,[12] and before precipitation of iridium the excess of titanium is removed by cupferron. This method was rejected because of the mechanical difficulties in freeing iridium from the bulky titanium complex. The second method described by Westland and Beamish[10] involved the selective reduction of rhodium by tellurium, all of the latter being subsequently removed by a distillation. This procedure proved difficult with large samples. The third procedure, used only for small samples, and reported by Berman and McBryde,[13] required an anion-exchanger from which iridium was removed with great difficulty.

It seemed desirable to develop a new separation of rhodium from iridium which would be applicable to large samples, and which would not involve complex techniques in subsequent purifications of the separated metals. This new method, described briefly below, has been submitted for publication by Tertipis[14] and involves the reduction of rhodium by copper, which metal is then separated by a cation-exchanger.

For the separation of rhodium from iridium, the filtrate from the palladium precipitation was evaporated to dryness on a steam bath and the organic matter was oxidised by fuming with 30% hydrogen peroxide. After removal of the nitric acid by hydrochloric acid, the salts were dissolved in water, the solution was filtered and was diluted to 100 ml in a volumetric flask. Aliquots of 25 ml were used, and the pH was adjusted to 1·0 with hydrochloric acid. The solution was heated nearly to boiling, 0·3 g of copper powder was added, and the mixture was heated to slow boiling with the beaker tightly covered. The liquid was stirred with a glass rod about every second minute, and after 15 minutes of slow boiling an additional 0·1 g of copper was added. The mixture was slowly boiled for another 5 minutes, and, after cooling, was decanted through 7-cm Whatman No. 42 filter paper and washed about ten times with distilled water. The filtrate of 70-ml volume was evaporated to small volume in presence of sodium chloride, and was diluted to about 30 ml. The pH was adjusted to 1·5 and the solution was then passed through the small cation-exchange column to separate the dissolved copper from iridium. The column was washed with 100 ml of water, and iridium was determined in the effluent, by using the bromate hydrolysis procedure

The filter paper with the copper–rhodium residue was destroyed with fuming nitric acid and a few drops of 30% hydrogen peroxide. Ten ml of *aqua regia* were added to the original beaker to dissolve adhering copper and rhodium. After destruction of the paper, the resulting solution was added to the *aqua regia* solution, and the mixture was treated with hydrochloric acid on the steam bath to remove the nitric acid. The resulting salt was dissolved with a few drops of hydrochloric acid and water and filtered. The insoluble material was dissolved, after the paper was destroyed, with sulphuric and nitric acids, by heating the sulphuric solution strongly on the hot plate. The sulphuric acid was then fumed off, and the rhodium sulphate was converted to chloride, with sodium chloride and hydrochloric acid; this small amount of rhodium chloride was then transferred to the initial copper–rhodium solution which was then diluted to 100 ml with water, adjusted to pH 1·5 and passed through the large cationic column.[8] The column was washed with 400 ml of water, and the effluent was evaporated to about 150 ml on a steam bath. The rhodium was then determined gravimetrically by thiobarbituric acid.[11]

The complete method of separation is represented schematically in Fig. 1.

CONCLUSION

It should be noted that, with the exception of the new separation of rhodium from iridium, each of the above analytical methods is an established classical procedure, permitting easily applied methods of ensuring high purity; furthermore, these and other separations may be used on a scale comparable to that required for refining. There is also an advantage in that the isolated metal in solution may be recovered by the various large-scale precipitating reagents such as ammonium chloride, etc. The procedures described above, applied to the concentrate, produced the results recorded in Table I. It is of interest to compare the values in Table I with those recorded by the donor (Falconbridge Nickel Mines Limited, Metallurgical Laboratories, Richvale, Ontario,) of the concentrate, whose methods were purely analytical and included spectrophotometric and spectrographic procedures. These were as follows: silver 20·01%, gold 0·25, platinum 1·36, palladium 1·72, ruthenium 4·72, rhodium 5·65, iridium 2·80.

TABLE I.—THE RECOVERY OF THE PRECIOUS METALS FROM ONE GRAM OF THE PLATINUM METALS CONCENTRATE

Silver *mg*	Gold *mg*	Platinum *mg*	Palladium *mg*	Ruthenium *mg*	Rhodium *mg* *	Iridium *mg* *
198·54	2·51	12·22	17·27	4·71	14·07	7·00
196·40	2·84	12·06	17·15	4·68	13·99	7·06
198·77	2·70		17·02	4·75	14·02	6·95
199·35	2·45		17·19	4·72	13·95	6·89
					13·78	6·98
					13·88	6·93
19·8%	0·26%	1·21%	1·72%	4·72%	5·56%	2·78%

* For the rhodium and iridium sample the 1-gram concentrate was made up to 100 ml from which 25 ml were taken for analysis.

Acknowledgement—The authors are indebted to the Falconbridge Nickel Mines for financial support and leave of absence to H. Zachariasen.

Zusammenfassung—Eine neue Methode wurde entwickelt um grosse oder auch kleine Mengen komplexer Platinmetal-konzentrate zu lösen. Die neue Methode gestattet die Anwendung verschiedener Methoden zur Isolierung der einzelnen Platinmetalle. Eine Reihe von Standardtrennungen und Bestimmungen wurde erfolgreich angewendet. Die Verwendung einer neuen Trennungsmethode für Rhodium von Iridium wurde beschrieben[14].

Résumé—Les auteurs ont développé un nouveau procédé qui produit la dissolution de quantités faibles ou importantes de complexes de métaux de la mine de platine, les concentre et permet l'application de plusieurs méthodes pour l'isolement de chaque métal. On a appliqué avec succès un groupe de séparations standard et de dosages et on a décrit l'application d'une nouvelle séparation du rhodium et de l'iridium.[14]

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THE DETERMINATION OF SILVER AND THALLIUM IN ROCKS BY NEUTRON-ACTIVATION ANALYSIS

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Summary—Neutron-activation analysis has been applied to the determination of silver and thallium in rocks. Samples of powdered rocks have been irradiated in the Harwell Pile BEPO. After irradiation, radiochemical separations using carrier chemistry have been based on precipitation, electrodeposition, and solvent extraction. Radiochemically pure silver and thallium have been finally precipitated and counted as the iodate and chromate, respectively.

Samples containing as little as 0·03 p.p.m. silver and 0·04 p.p.m. thallium have been analysed. The rocks which have been examined include the two international standards G1 and W1 and also samples from the Insch Mass, Aberdeenshire, Scotland.

INTRODUCTION

SILVER is classified geochemically as a chalcophile element, and relatively little information is available on its occurrence in igneous rocks.[1] Thallium shows both lithophile and chalcophile properties, and the distribution of thallium in igneous rocks has been studied quite thoroughly. The geochemistry of thallium has been reviewed recently by Shaw.[2]

The crustal abundance of silver appears to be about 0·02 p.p.m.[1] and that of thallium has been quoted as 1·3 p.p.m.[2] It follows that the accurate analysis of these elements in rocks demands the use of a method giving high sensitivity. Previous workers have generally used special spectrochemical procedures. For example, Goldschmidt and co-workers[1] employed dry assay in conjunction with emission spectrography to obtain sufficient sensitivity for the determination of silver in rocks. Similarly, Shaw[3] has employed a special double-arc spectrographic technique for thallium, giving a precision of ±20 per cent and an ultimate sensitivity of 0·05 p.p.m. Tl. In addition, the combined use of ion exchange enrichment and spectrochemical analysis for the determination of trace constituents in rocks is currently being developed by Edge, Brooks, Ahrens and Amdurer.[4] These types of procedure may give rise to relatively large errors, and it was decided to investigate the possibility of determining silver and thallium in rocks by neutron-activation analysis.

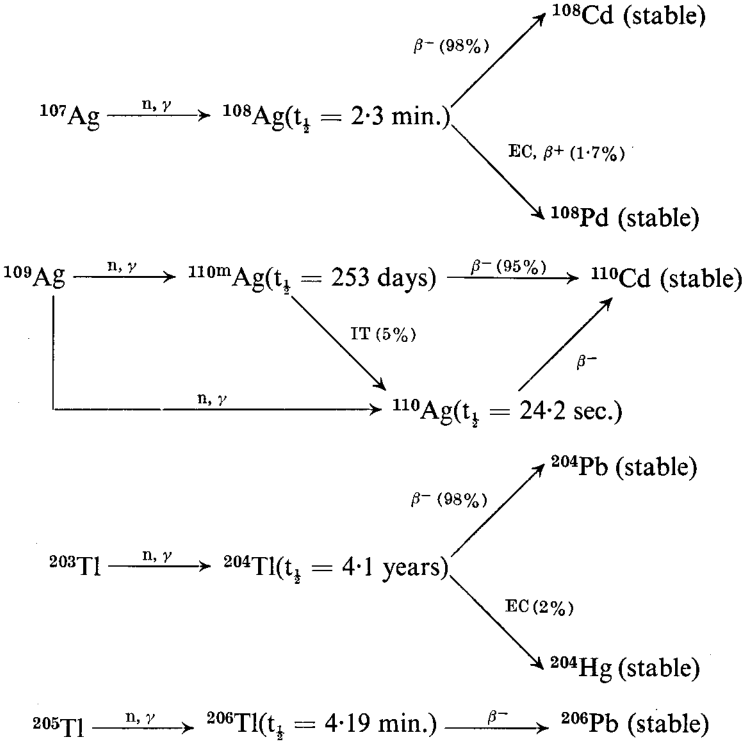
The principles of radioactivation analysis have been extensively reviewed[5–9] and will not be discussed here. The method avoids various possible sources of error inherent in emission and mass spectroscopic procedures, and also offers important advantages over chemical methods for the determination of microgram and submicrogram quantities.

With the availability of high flux Atomic Piles, neutron-activation analysis has been developed to provide the ultimate in practical sensitivity for many elements. The method is not exceptionally sensitive for the determination of silver and thallium. However, with a neutron flux of 10^{12} neutrons/cm^2/sec available in the Harwell Pile

BEPO, it should be possible, under ideal conditions, to determine about 0·005 p.p.m. Ag and 0·01 p.p.m. Tl in a 1-g sample of rock. Better sensitivity is attainable if the Harwell Pile DIDO is used for activation.

NEUTRON ACTIVATION OF SILVER AND THALLIUM

Naturally occurring silver consists of two isotopes, ^{107}Ag (per cent abundance, θ, = 51·35%) and ^{109}Ag (θ = 48·65%). Thallium also exists as two stable isotopes, ^{203}Tl (θ = 29·50%) and ^{205}Tl (θ = 70·50%). On irradiation with neutrons of thermal energies, silver and thallium give rise to radionuclides by the following nuclear reactions:



Isotopic thermal neutron activation cross sections, σ, for the nuclear reactions[10] are—

^{107}Ag(n, γ)^{108}Ag	σ = 44 barns
^{109}Ag(n, γ)^{110m}Ag	σ = 2·8 barns
^{109}Ag(n, γ)^{110}Ag	σ = 110 barns
^{203}Tl(n, γ)^{204}Tl	σ = 8 barns
^{205}Tl(n, γ)^{206}Tl	σ = 0·10 barns

The radionuclides 253-day ^{110m}Ag–^{110}Ag and 4·1-year ^{204}Tl were used in the present study, owing to the short half-lives of the other radioactive species. The decay schemes for ^{110m}Ag– ^{110}Ag and ^{204}Tl are shown in Fig. 1.[11]

For rock samples dealt with in this paper, a one month irradiation in BEPO was adequate.

EXPERIMENTAL

Irradiation

Samples of the powdered rocks, about 1 g, were accurately weighed and sealed in 6-mm internal-diameter silica irradiation tubes. In order to avoid errors due to self-shielding, standards were prepared by the addition of known small quantities (a few μg) of silver and thallium to analytical samples. This was done by adding aliquots of dilute standard solutions of silver and thallium to weighed samples of powdered rock in silica irradiation tubes. The solutions were allowed to soak into the rock, then carefully evaporated to dryness, after which the tubes were sealed. Samples and standards were packed together in 3 in. × 1 in. aluminium cans and sent to the Atomic Energy Research Establishment, Harwell, for irradiation.

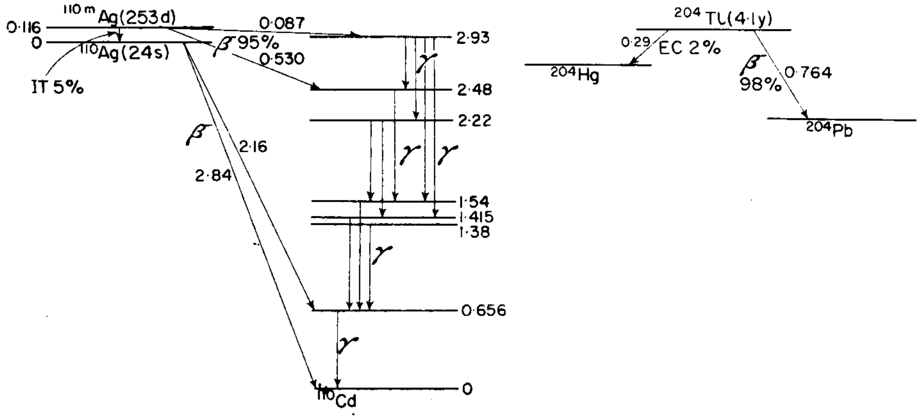


FIG. 1.—Decay schemes for ^{110m}Ag–^{110}Ag and for ^{204}Tl. Energies are in MeV.

The preparation of samples and standards was undertaken in a room distinct from the laboratories, and considerable precautions were taken to avoid any contamination.

Radiochemical separation

Following delivery from Harwell after irradiation, the samples and standards were assayed radiochemically for ^{110m}Ag–^{110}Ag and ^{204}Tl. The rock samples were dissolved by digesting with hydrofluoric acid and fuming with perchloric acid. Alkali or potassium bisulphate fusion could not be employed to render the rock samples soluble, as this would have led to extensive loss of thallium by volatilisation.[12]

Silver and thallium were initially separated from other elements by precipitation of the chlorides. The thallium was then separated from the bulk of the silver by hot-water extraction.

The silver residue was purified by ferric hydroxide scavenging and silver sulphide precipitation, both of which were performed in ammoniacal solution. The silver was further separated by electrolysis,[13] and was finally converted to the iodate, in which form it was counted.[14]

The thallium extracted by hot water, was purified by precipitation of the chromate and monoiodide. Solvent extraction of the trichloride served as an excellent further decontamination step.[15,16] Thallium$^{\mathrm{I}}$ was finally converted to the chromate, in which form it was counted.

Reagents

Ag carrier: 10 mg Ag/ml (added as $AgNO_3$ in very dilute HNO_3)–standardised.
Tl$^{\mathrm{I}}$ carrier: 10 mg Tl/ml (added as $TlNO_3$ in very dilute HNO_3)–standardised.
Fe$^{\mathrm{III}}$ carrier: 10 mg Fe/ml (added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl).
Pb$^{\mathrm{II}}$ carrier: 10 mg Pb/ml (added as $Pb(NO_3)_2$ in very dilute HNO_3).
La carrier: 10 mg La/ml (added as $La(NO_3)_3 \cdot 6H_2O$ in very dilute HNO_3).
HF: 40%.
$HClO_4$: 9*M*.
HNO_3: conc.

Reagents (cont).

HNO_3: 6*M*.
HCl: 6*M*.
HCl: 4*M*.
HCl: 1*M*.
Cyanide plating solution: mix 7 ml of 3*M* NaCN with 1 ml of 5*M* NaOH.
H_2SO_4: conc.
H_2SO_4: 1*N*.
KIO_3: saturated solution.
NaOH: 6*M*.
NaOH: 3*M*.
NH_4OH: conc.
NH_4OH: 6*M*.
$(NH_4)_2S$: saturated solution.
$Na_2CrO_4 \cdot 4H_2O$: 10%.
$Na_2S_2O_5$: solid.
KI: 0·5*M*.
H_2O_2: 30%.
SO_2: siphon.
Ether.
Ethyl alcohol: 95%.
Methyl alcohol: absolute.
Manoxol OT: 0·1% in water.

Preparation and standardisation of carriers

Silver. Dissolve 15·75 g of $AgNO_3$ in a minimum amount of H_2O, add a few drops of HNO_3, and dilute the solution to 1 litre.

Pipette exactly 5 ml of the carrier solution into a 50-ml centrifuge tube and dilute to 20 ml with H_2O. Add 1 ml of saturated KIO_3 solution and stir to coagulate the precipitate which forms. Add an additional drop of KIO_3 to test for completeness of precipitation. Filter the precipitate through a weighed sintered-glass crucible of porosity 3 or 4. Wash the precipitate with 5 ml of 95 per cent ethyl alcohol and dry in an oven at 110° for 15 min. Cool and weigh as $AgIO_3$.

Thallium. Dissolve 13·04 g of $TlNO_3$ in H_2O, add a few drops of HNO_3, and dilute the solution to 1 litre.

Pipette exactly 5 ml of the carrier solution into a 125-ml conical flask. Make the solution alkaline with conc. NH_4OH. Add 5 ml of 10% $Na_2CrO_4 \cdot 4H_2O$ solution to precipitate Tl_2CrO_4. Bring to the boil and permit the precipitate to stand for about 12 h, then filter through a weighed sintered-glass crucible of porosity 4. Wash the precipitate with 10 ml of H_2O, then with 10 ml of 95% ethyl alcohol. Dry at 110° for 0·5 h. Cool and weigh as Tl_2CrO_4.

Radiochemical separation procedure

Step 1. Remove the silica irradiation tubes from the can, open them at the constriction, and transfer the solid samples to 60-ml platinum crucibles. Wash out the tubes with a little warm 6*M* HNO_3 and transfer the washings quantitatively to the crucibles. To a sample in a platinum crucible add 2 ml of standard Ag carrier and 2 ml of standard Tl^I carrier. Cover loosely with a platinum lid, and gently warm for a few minutes.

Step 2. Add 10 ml of 40% HF, cover the crucible with the platinum lid, and digest on a steam-bath until the sample is completely dissolved. Add 3 ml of 9*M* $HClO_4$ and 2 ml of 16*M* HNO_3 and heat the mixture till white fumes of $HClO_4$ begin to be given off, taking care to avoid spattering. Replace the cover loosely, and continue to heat for about 5 min at a temperature such that the $HClO_4$ fumes moderately, but does not rapidly evaporate. Heat for 5–10 min longer, adding 1 ml of 9*M* $HClO_4$. Finally evaporate carefully almost to dryness (*Note a*).

Step 3. Transfer the residue wih 10 ml of H_2O to a 50-ml centrifuge tube. Pass SO_2 through the hot solution. Boil off excess SO_2, add 10 ml of 6*M* HNO_3 and cool. To the cold solution add a few drops of Manoxol OT solution (*Note b*), then 6*M* HCl, drop by drop, until precipitation is complete. Centrifuge and discard the supernate. Wash the precipitate thoroughly three times with

10-ml portions of boiling water. Centrifuge and retain the washings for *thallium determination* and the AgCl residue for *silver determination.*

Step 4. *Determination of silver.* Dissolve the AgCl in 2 ml of conc. NH_4OH (*Note c*). Dilute to 20 ml with H_2O and add 1 ml of Fe^{III} carrier. Centrifuge, transfer the supernate to a clean 50-ml centrifuge tube, and discard the precipitate.

Step 5. To the solution add 1 ml of saturated $(NH_4)_2S$ solution. Stir vigorously and centrifuge. Discard the supernate.

Step 6. Dissolve the Ag_2S precipitate by heating with 1 ml of conc. HNO_3. Dilute to 20 ml with H_2O, centrifuge and discard any S residue.

Step 7. To the solution add a few drops of Manoxol OT solution and heat to boiling. Add 6*M* HCl, drop by drop, until precipitation of AgCl is complete. Heat until the AgCl has coagulated. Centrifuge, and discard the supernate.

Step 8. Dissolve the AgCl in 8 ml of cyanide plating solution (*Note d*). Mix the solution thoroughly, transfer to a Pregl micro-electrolysis apparatus and electrolyse at 4 volts for 15 min. When electrolysis is complete, remove the electrodes and wash the cathode with H_2O from a wash bottle for 1 min.

Step 9. Dissolve the Ag completely off the cathode with conc. HNO_3 and transfer the solution to a clean 50-ml centrifuge tube. Add 10 ml of H_2O. Repeat Steps 7 and 8.

Step 10. Dissolve the Ag completely off the cathode with conc. HNO_3 and transfer the solution to a clean 50-ml centrifuge tube. Make the solution alkaline with 6*M* NaOH, and add 3 drops in excess. Centrifuge the Ag_2O precipitate and discard the supernate. Dissolve the Ag_2O in 4 drops of conc. H_2SO_4 and evaporate to dryness (*Note e*). Cool.

Step 11. Add 20 ml of H_2O and boil until a clear solution is obtained, then add 1 ml of saturated KIO_3 solution. Centrifuge and discard the supernate.

Step 12. Dissolve the $AgIO_3$ precipitate in 4 drops of conc. NH_4OH. Centrifuge, transfer the supernate to a clean 50-ml centrifuge tube.

Step 13. Add 3 drops of conc. H_2SO_4 to the solution. Centrifuge the $AgIO_3$ precipitate and wash twice with H_2O and once with 5 ml of 95% ethyl alcohol.

Step 14. Slurry the precipitate with 95% ethyl alcohol on to a weighed aluminium counting tray (A.E.R.E. Cat. no. 4-3/1068), by using a transfer pipette. Make sure that the distribution of precipitate on the tray is uniform. Dry at 110° for 15 min and weigh to establish the chemical yield (20 mg Ag $\equiv$ 52·43 mg $AgIO_3$).

Step 15. *Determination of thallium.* To the hot water extract from Step 3 add 1 ml of Pb^{II} carrier and 10% $Na_2CrO_4 \cdot 4H_2O$ solution, dropwise, till precipitation of yellow Tl_2CrO_4 and $PbCrO_4$ is complete. Centrifuge, and discard the supernate.

Step 16. Warm the mixed chromate precipitate with 3*M* NaOH to dissolve the $PbCrO_4$. Centrifuge and discard the supernate.

Step 17. Wash the Tl_2CrO_4 residue with water and dissolve by warming with 6*M* HCl. The resultant solution is yellow-green in colour. Add solid $Na_2S_2O_5$ in small amounts until the solution assumes a distinctly green colour.

Step 18. After all action has ceased, add 0·5*M* KI dropwise until precipitation of Tl^I is complete. Centrifuge and discard the supernate.

Step 19. Wash the precipitate with 10 ml of 1*N* H_2SO_4, and dissolve by gentle heating with 10 ml of 4*M* HCl containing 6 drops of 30% H_2O_2.

Step 20. Extract the thallium by agitating with 10 ml of ether saturated with 4*M* HCl. Separate the ether phase and wash it 3 times with 10-ml portions of 4*M* HCl saturated with ether. Then mix the ether phase with 10 ml of 1*N* H_2SO_4, and place on a water bath until the ether is completely evaporated.

Step 21. Reduce the Tl^{III} to Tl^{I} by bubbling SO_2 for a few min through the hot solution.

Step 22. Make up to 30 ml with H_2O and precipitate Tl^I by the addition of a slight excess of 0·5*M* KI. Cool, centrifuge and discard the supernate.

Step 23. To the precipitate add 4 drops of La carrier and 1 ml of 6*M* HNO_3. Heat until all I_2 colour has disappeared. Dilute with H_2O to 20 ml. Warm the solution, pass SO_2 for a few moments to ensure complete reduction to Tl^I, and make basic by the dropwise addition of conc. NH_4OH. Add 1 ml of NH_4OH in excess. Centrifuge, transfer the supernate to a clean 50-ml centrifuge tube, and discard the precipitate of $La(OH)_3$.

Step 24. To the supernate add 5 ml of 10% $Na_2CrO_4 \cdot 4H_2O$ solution. Allow to stand 5 to 10 min to permit the Tl_2CrO_4 precipitate to coagulate. Wash the precipitate with 5 ml of H_2O, then with two 5-ml portions of methyl alcohol. Slurry the precipitate uniformly on to a weighed aluminium counting tray (A.E.R.E. Cat. no. 4-3/1068). Dry at 110° for 10 min and weigh to determine the chemical yield (20 mg Tl $\equiv$ 25·68 mg Tl_2CrO_4).

Notes

(*a*) Steps 1 and 2 should be performed in an efficient fume-cupboard.

(*b*) The addition of Manoxol OT helps to coagulate the precipitate and to prevent its adherence to the walls of the tube.

(*c*) A little heating may be necessary.

(*d*) See *Reagents.*

(*e*) It is not necessary to remove the last traces of H_2SO_4 on the walls of the tube.

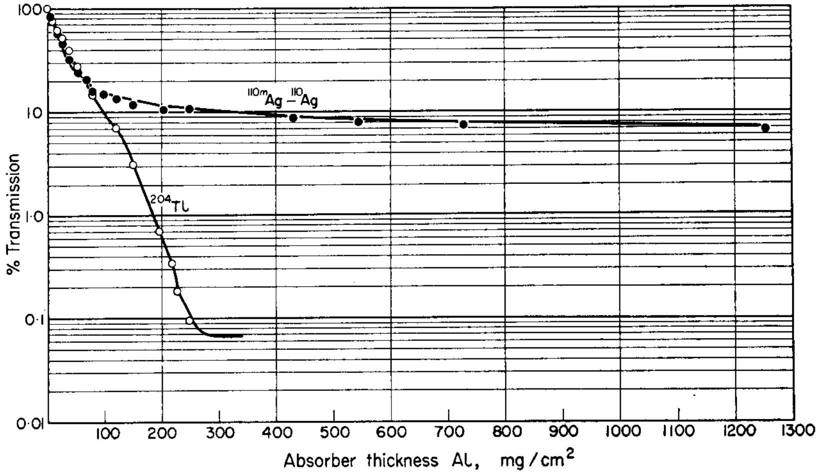


FIG. 2.—Aluminium absorption curves of ^{110m}Ag–^{110}Ag and ^{204}Tl. The full curves are for purified tracers (supplied by the Radiochemical Centre, Amersham) coprecipitated with silver iodate and thallous chromate. The recorded points are for final precipitates from the analysis of a rock sample.

Counting of the isolated silver iodate and thallous chromate precipitates

In the present work the final precipitates of $AgIO_3$ and Tl_2CrO_4 were counted under a thin end-window Geiger-Müller counter (EHM 2/5), with conventional associated electronic equipment. All measured activities were corrected for paralysis, background, and chemical yield. Self-absorption correction curves indicated that no correction for self-absorption needed to be made for the range of weights of precipitates obtained in the radiochemical procedure.

A check of radiochemical purity was obtained by measuring standard aluminium absorption curves of final precipitates, and comparing them with corresponding curves from purified ^{110m}Ag–^{110}Ag and ^{204}Tl tracers[17] (Fig. 2.)

A further check on the reliability of the procedure was obtained by analysing samples of a given rock, using standards consisting of the same rock with different added amounts of silver and thallium. Plots of corrected activity, due to the added silver or thallium in the series of standards, against the corresponding weights of added silver or thallium should then be straight lines passing through the origin. Typical graphs obtained are shown in Fig. 3.

RESULTS

In Table I are shown results of analyses of silver and thallium in the standard granite Gl from Westerley, Rhode Island, and in the standard diabase W1 from Centreville, Virginia.[18] Uniform specimens of these rocks have been widely distributed by the U.S. Geological Survey as standards for both major and minor constituents in igneous rocks.

Table II records the results obtained for the silver and thallium contents of a series of rocks supplied by Dr. J. R. Butler, Department of Geochemistry, Imperial College, London. The arrangement corresponds to the geological differentiation succession of the rocks in the Insch Mass (mostly gabbro), Aberdeenshire.

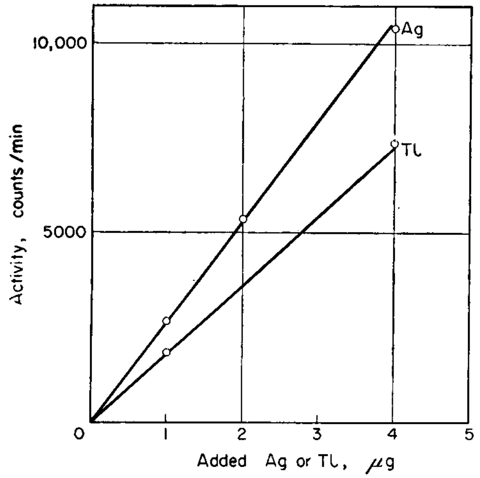


FIG. 3.—Activity due to added silver and thallium in neutron-irradiated standards plotted against the weight of added silver and thallium. Each point is the average of two measurements.

POSSIBLE INTERFERING ELEMENTS

In neutron-activation analysis the possibility that radionuclides of the elements being determined may arise by other nuclear processes than the ones under consideration, must always be borne in mind. Hence, apart from the n, γ reaction with ^{109}Ag, ^{110m}Ag may possibly be produced by the following reactions—

$$^{110}\text{Cd}(\text{n, p})^{110\text{m}}\text{Ag}$$
$$^{113}\text{In}(\text{n}, \alpha)^{110\text{m}}\text{Ag}$$

Similarly ^{204}Tl could be formed from lead by the nuclear process—

$$^{204}\text{Pb}(\text{n, p})^{204}\text{Tl}$$

To confirm that such interferences were of no consequence in the present work, samples of pure CdO, In_2O_3, and PbO were irradiated together with pure silver and thallium standards. The "apparent" silver contents of the CdO and In_2O_3 and the "apparent" thallium content of the PbO were then determined by the radiochemical procedure described above. The results showed that if a rock contained 0·15 p.p.m.* of cadmium and 0·11 p.p.m.* of indium, the maximum spurious silver content would be only 6×10^{-6} p.p.m. Similarly for a rock containing 16 p.p.m.* of lead, the maximum spurious thallium content would be *c.*10^{-6} p.p.m. Errors introduced by the

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* These are average abundances of these elements in igneous rocks. The figures for Cd and Pb are from Rankama and Sahama[20] and the figure for In is from Shaw[2].

TABLE I.—SILVER AND THALLIUM ANALYSES OF THE STANDARD GRANITE G1 AND STANDARD DIABASE W1

G1		W1	
Silver content, *p.p.m.*	Thallium content, *p.p.m.*	Silver content, *p.p.m.*	Thallium content, *p.p.m.*
0·047	1·3	0·055	0·15
0·046	1·1	0·055	0·17
0·048	1·2	0·058	0·17
0·036	1·4	0·058	0·18
0·038	1·0	0·057	0·17
0·037	1·5	0·058	0·16
0·044	1·0		
0·042	1·5		
0·043	1·4		
av. 0·042	av. 1·3	av. 0·057	av. 0·17

Values of 1·3 and 0·1 p.p.m. have been obtained by the ion-exchange-spectrographic technique[4] for the thallium contents of G1 and W1, respectively[19].

TABLE II.—SILVER AND THALLIUM IN ROCKS OF THE INSCH MASS, ABERDEENSHIRE

Sample No. (Dept. of Geology, Imperial College, London)	Rock	Location	Silver found, *p.p.m.*	Thallium found, *p.p.m.*
3722(H63)	Peridotite	W. Slope of Hill of Barra	0·030 0·028 0·030 0·028	1·03 1·06 1·04 1·04
3724(H67)	Pyroxenitic peridotite	W. Slope of Hill of Barra	0·086 0·078	
3732(H55)	Olivine gabbro	N. E. top of Gallow Hill, Leslie	0·037 0·041 0·038 0·041	0·047 0·049 0·046 0·048
3645(H107)	Syenogabbro	S. slope of Gallow Hill	0·44 0·46 0·47 0·43	0·046 0·045 0·047 0·045
3731(H51)	Syenite	S. W. slope of Gallow Hill	0·040 0·032 0·039 0·038 0·040 0·036 0·033	0·31 0·28 0·26 0·26 0·34 0·26 0·31

secondary nuclear reactions are therefore quite negligible for all the samples that have been examined. The presence of significant amounts of radionuclides of silver and thallium other than ^{110m}Ag–^{110}Ag and ^{204}Tl, respectively, would have been recognised from the absorption curve measurements described earlier.

ADDENDUM

Since completion of the work described in this paper, Hamaguchi and Kuroda[21] have published results on the silver content of igneous rocks and have calculated the crustal abundance as 0·08 p.p.m. These investigators employed an analytical procedure involving chemical enrichment followed by spectrochemical analysis.[22]

In addition, Ehmann and Huizenga[23] have recently determined thallium, together with other elements, in stone meteorites by neutron-activation. Their radiochemical procedure has utilised anion-exchange.

Zusammenfassung—Neutronen-Aktivierungs-Analyse wurde zur Bestimmung von Silber und Thallium in Gesteinen angewendet. Proben von 1 Gramm gepulverten Gesteins wurden im Harwell-Reaktor BEPO bestrahlt. Nach der Bestrahlung wurden radiochemische Trennungsoperationen durchgeführt, die sich auf Fällung, Elektrodeposition und Solventextraktion basierten und mit Trägersubstanzen arbeiteten. Radiochemisch reines Silber und Thallium wurden letztlich gefällt und die Zählung an Silberjodat und Thalliumchromat durchgeführt. Proben mit nur 0·03 Teilen Silber und 0·04 Teilen Thallium per Million Teilen Gestein wurden analysiert. Unter den analysierten Proben befanden sich die beiden internationalen Standarde G1 und W1 sowie Proben von Insch Mass, Aberdeenshire, Schottland.

Résumé—Les auteurs ont appliqué l'analyse par activation des neutrons au dosage de l'argent et du thallium dans les roches. Ils ont irradié des échantillons de 1 g de roches pulvérisées dans la pile BEPO de Harwell. Après irradiation, les séparations radiochimiques utilisant la chimie des entraineurs ont été basées sur la précipitation le dépôt électrolytique et l'extraction par solvent. Finalement l'argent et le thallium radiochimiquement purs ont été précipités et dosés par comptage respectivement à l'état d'iodate et de chromate.

On a analysé des échantillons contenant des quantités aussi faibles que 0,03 p.p.m. d'argent et 0,04 p.p.m. de thallium. Les roches qui ont été examinées comprenaient les deux "standard internationaux" G1 et W1, et aussi des échantillons provenant de Insch Mass, Aberdeenshire, Ecosse.

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THE ANALYSIS OF BERYLLIUM AND BERYLLIUM OXIDE—I

THE DETERMINATION OF IRON

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Summary—The importance of beryllium and beryllium oxide to the atomic energy programme has necessitated the development of accurate methods of chemical analysis for the determination of metallic impurities. A method is presented for separating iron by extraction with tri-*n*-octylphosphine oxide followed by determination with 1:10-phenanthroline. The method is accurate to ±3% or ±3 micrograms of iron, whichever is greater. The accuracy and sensitivity could be increased by appropriate choice of sample weight, volume of extract, and/or cell length. Of the 68 elements investigated, 61 do not interfere in 10-mg amounts. No interference is caused by 5 mg of silicon, 1 mg of antimony, gallium, molybdenum, or tungsten, or 0.1 mg of tellurium or uranium. Only gallium, tellurium and silicon interfere without producing a warning turbidity in the coloured solution.

INTRODUCTION

SINCE beryllium and beryllium oxide are becoming increasingly important to the atomic energy programme, a need exists for accurate methods for the determination of metallic impurities in these materials. With few exceptions, it is desirable from the standpoint of time and economy to perform these analyses spectrographically. However, because of the difficulty of accurately evaluating spectrographic analyses with a varying matrix, chemical methods are necessary for comparison. They are also necessary when very accurate results are required. An extensive research programme has been undertaken to develop and investigate methods for determining trace elements in beryllium and beryllium oxide. The following points have served as a guide for the development and application of these methods.

(1) A number of grades of beryllium oxide are received by our department. Therefore, it is desirable, although not absolutely essential, that the methods of analysis be applicable to samples containing up to 1 per cent of metallic impurities, regardless of kind or combination.

(2) The methods should be applicable to samples weighing at least 1 gram so that reasonable sensitivities may be obtained.

(3) Commonly occurring elements should not interfere in milligram quantities unless

(*a*) their presence in interfering amounts is easily apparent, or
(*b*) some simple provision is made for their removal which will not cause interference by another element.

(4) The methods must be applicable to the determination of an element in the presence of considerable amounts of other elements which might be expected to be

associated with it, such as the determination of niobium in the presence of tantalum, or the determination of molybdenum in the presence of tungsten.

Methods which fulfil these qualifications will give results such that a considerable degree of certainty can be attached to the accuracy of the reported values. Synergistic effects have not, in general, been considered during the development of the methods. The term synergistic is used here and in following papers to indicate a total effect greater or less than the sum of two or more effects taken independently.

Probably the most popular method for determining iron colorimetrically is by means of 1:10-phenanthroline. However, a number of elements interfere to a greater or lesser extent.[1] An excellent way of separating iron^{III} from some of these interfering elements, before complexing with 1:10-phenanthroline, is by extraction from hydrochloric acid solution into a solution of tri-*n*-octylphosphine oxide in *cyclo*hexane.[2–4] A further separation to remove those interfering elements which are extracted is desirable. A method has been developed which is almost specific for iron. Only a few elements interfere at the 10-mg level and of these elements only gallium, tellurium, and silicon interfere without producing a warning turbidity in the coloured solution. The method is accurate to $\pm 3\%$ or ± 3 micrograms of iron, whichever is greater.

EXPERIMENTAL

Apparatus

Cary Model 14 Spectrophotometer, 1-cm and 2-cm cells.
International Clinical Centrifuge, 15-ml glass-stoppered centrifuge tubes.

Reagents

Standard iron solution: dissolve 8.6 g of ferric ammonium sulphate in approximately 150 ml of 1*M* sulphuric acid. Dilute to 500 ml. Standardise this solution and dilute an aliquot to obtain a solution containing 20 μg of iron per ml.

Tri-n-octylphosphine oxide (TOPO), 0.01*M*, in *cyclo*hexane.
TOPO, 0.1*M*, in chloroform.
1:10-*phenanthroline*, 3% (w/v), in *iso*propyl alcohol.
Hydroquinone, 3% (w/v), in *iso*propyl alcohol. Prepare fresh daily.
Isopropyl alcohol.
Sulphuric acid, 3*M* and 6*M*.
Hydrochloric acid, sp. gr. 1.19.
Bromine water, saturated solution.
Citric acid.

Dissolution of samples

Transfer an appropriate sample (up to 1 g) of beryllium to a 150-ml beaker. Cover with a watch glass. Add 20 ml of 6*M* hydrochloric acid dropwise. The reaction is very vigorous. When the reaction subsides, heat to dissolve and evaporate to about 5 ml. If a black residue remains, wash down the sides of the beaker with distilled water and continue heating. If the residue does not dissolve completely, filter through No. 50 Whatman filter paper and wash the residue with water. Analyses of the residues from two samples of beryllium metal are shown in Table I. If the residue is to be analysed, transfer the filter paper and contents to the original beaker, dry, char, and ignite at 500° until the paper has been completely ashed. Pulverise the ash and fuse with 1 g of potassium bisulphate. Cool and add 10 ml of sulphuric acid. Heat to dissolve the fused mass. Cool and wash down the sides of the beaker with a minimum amount of distilled water. Add approximately seven drops of hydrofluoric acid, 1 ml of hydrochloric acid dropwise and 1 ml of nitric acid dropwise. Heat to fumes of sulphur trioxide. Cool and add to the filtrate. Evaporate to about 30 ml.

Transfer an appropriate sample (up to 1 g) of beryllium oxide to a 150-ml beaker. Add 30 ml of 6*M* sulphuric acid and heat until the sample is completely dissolved. Evaporate to about 15 ml.

Procedure

Transfer the sample, containing about 100 micrograms of iron, to a 125-ml separatory funnel. (Use a 250-ml separatory funnel if fusion of the insoluble residue from beryllium metal was necessary.) Add 1 g of citric acid.* Dilute with water or hydrochloric acid to obtain a solution which is $6M$ with respect to hydrochloric acid. Add 4 drops of bromine water (or sufficient to impart a yellow colour to the organic phase after the iron is extracted.) Add 25 ml of $0.01M$ TOPO in *cyclo*hexane, stopper and shake for 2 minutes. Allow the layers to separate, and draw off and discard the aqueous phase completely by draining the organic phase into the stopcock. Stopper the funnel, invert, and allow the drop of organic phase to return to the funnel. If sulphuric acid was present during the extraction, add 30 ml of $6M$ hydrochloric acid. Shake for 1 minute and discard the acid wash. Add 30 ml of $3M$ sulphuric acid, stopper and shake for 2 minutes. Transfer the aqueous phase to a second 125-ml separatory funnel. Wash the organic phase with 10 ml of $3M$ sulphuric acid, shake for 30 seconds, and add the washings to the second funnel. Care must be taken not to transfer any of the organic phase to the second funnel. (If necessary, the aqueous phase may be washed several times with a solution of $0.1M$ TOPO in chloroform† to remove excessive amounts of hafnium, indium, tungsten, or zirconium. This is called the "modified" procedure in Table II.) Add 40 ml of hydrochloric acid to the second funnel and mix. Add exactly 10 ml of $0.01M$ TOPO, stopper, and shake for 2 minutes. Allow the layers to separate, and draw off and discard the aqueous phase. Transfer the organic phase to a 15-ml centrifuge tube and centrifuge for 1 minute (to remove water droplets). Transfer a 3-ml portion of the organic extract to each of two 25-ml volumetric flasks containing about 15 ml of *iso*propyl alcohol. Add 1 ml of hydroquinone solution to each flask. Add 2 ml of 1:10-phenanthroline solution to one flask only. Dilute the solutions in both flasks to the mark with *iso*propyl alcohol and mix well. Allow to stand 2 hours for full colour development and measure the absorbance of the solution containing the 1:10-phenanthroline versus the other solution at 510 mμ in 2-cm cells. Determine the iron concentration by reference to a standard curve obtained by carrying known amounts of iron through the above procedure. A blank and standard should, of course, be carried through the whole procedure. If the absorbance of the unknown exceeds that on the standard curve, the unknown may be diluted with an appropriate amount of *iso*propyl alcohol.

TABLE I. SPECTROGRAPHIC ANALYSES OF RESIDUES FROM NBL BERYLLIUM METAL[a]

Sample No.	Impurities, μg										
	Ni	Cr	Fe	Al	Ti	Mo	Cu	Ag	Zr	Mg	Mn
NBL-88	0.7	3	3	1.5	0.15	0.7	3	0.07	1.5	0.7	0.15
NBL-85	0.3	0.7	1.5	0.3	0.15	0.15	3	0.07	0.01	0.7	0.15

[a] The major constituents of both residues were Be, Si, and C. The residues were obtained from 1-g samples.

Extraction of the iron^{III}-chloride complex

Ross and White[3] have reported that 99% of 10 mg of Fe^{III} is extracted with TOPO from $7M$ hydrochloric acid at aqueous/organic phase ratios of 20. With smaller amounts of iron this percentage should be noticeably higher. The presence of sulphuric acid, at least up to $3M$, has no measurable effect on the distribution coefficient. We have found that iron is completely extracted in 1½ minutes.

Measurement of the iron^{II}-1:10-phenanthroline complex

The absorbance spectrum and the wavelength of maximum absorbance of the complex in *cyclo*hexane are essentially identical with those in the aqueous phase. The molar absorptivity is similar

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* Citric acid was added to prevent precipitation of tungsten when the effects of impurities were determined.

† Chloroform is used in order that the washings may be carried out without transferring the solutions to another separatory funnel.

TABLE II. THE EFFECT OF OTHER ELEMENTS ON THE DETERMINATION OF IRON

Element added	*mg*	Relative error, %[a]		Remarks
		Direct method	Modified[b] method	
Al	10	<3		
$\mathrm{Sb^{III}}$	10	6[c]	<3	No Br_2 added
$\mathrm{Sb^{V}}$	5	d		Br_2 added to $\mathrm{Sb^{III}}$
	1	<3		Br_2 added to $\mathrm{Sb^{III}}$
$\mathrm{As^{III}}$, Ba, Be	10	<3		[e]
Bi	10	<3		2 ml 1:10-phenanthroline added
B, Br, Cd, Ca	10	<3		[e]
$\mathrm{Ce^{III}}$	10	<3		10 mg $\mathrm{Ce^{IV}}$, 5 mg $\mathrm{Sn^{II}}$
$\mathrm{Ce^{IV}}$, $\mathrm{Cr^{III}}$, $\mathrm{Cr^{VI}}$ Cs, Co, Cu, Dy, Er, $\mathrm{Eu^{III}}$	10	<3		[e]
F	100	<3		Added as HF
Gd	10	<3		
Ga	5	−70		Consumes TOPO. Additional 1:10-phenanthroline has no effect
	1	<3		
Ge	10	<3		
Au	10	<3		2 ml 1:10-phenanthroline added
Hf	10	d	<3	Added as fluoride solution
	5	<3		
Ho	10	<3		
In	10	d		
	5	<3		
I, $\mathrm{Ir^{IV}}$, La, Pb, Li, Lu, Mg, $\mathrm{Mn^{II}}$, $\mathrm{Mn^{VII}}$, $\mathrm{Hg^{II}}$	10	<3		[e]
Mo	5	d		
	1	<3		
Nd, Ni	10	<3		[e]
Nb	10	<3		Added as fluoride solution
$\mathrm{Pd^{II}}$	10	<3		
P	100	<3		Added as PO_4^{3-}
$\mathrm{Pt^{IV}}$, K, Pr, $\mathrm{Re^{VII}}$, $\mathrm{Rh^{III}}$, Rb, Sm, Sc, $\mathrm{Se^{IV}}$	10	<3		[e]
Si	10	−8		Large ppt. when TOPO added
	5	<3		
Na, Sr	10	<3		[e]
Ta	10	<3		Added as fluoride solution
$\mathrm{Te^{IV}}$	5	−40		Consumes TOPO. Additional 1:10-phenanthroline has no effect.
	1	−16		
	0.1	<3		
Tb, $\mathrm{Tl^{I}}$, Th, Tm, Sn, Ti	10	<3		[e]
W	5	d	+8[c]	
	1	<3		
$\mathrm{U^{VI}}$	1	c		
	0.1	<3		
V, Yb, Zn	10	<3		[e]
Zr	10	d	+6[c]	Added as fluoride solution
	5	+6[c]	<3	

[a] 101 μg Fe added, 2-cm cells

[b] Three washes of the $3M$ H_2SO_4 solution with 25 ml of $0.1M$ TOPO in $CHCl_3$

[c] Slightly turbid in coloured solution

[d] Very turbid in coloured solution

[e] The effect of 10 mg of each element determined independently.

TABLE III. DETERMINATION OF IRON IN OXIDES

Sample	Fe added, μg	Fe found, μg	% Recovery
1 gram BeO	0	18,16,17	—
1 gram BeO	101	118	100
1 gram BeO	101	117	99
1 gram BeO	101	116	98
1 gram BeO	101	114	96
1 gram BeO + 1 mg each of Al, B, Ca, Cr^{III}, Mn^{II}, Ni, Si, Co, Li, Cd, Cu, Ti^{III}, Ba, and Sr, and 10 mg each of Mg and Na	101	120	102
1 gram BeO + 1 mg each of Al, B, Ca, Cr^{III}, Mn^{II}, Ni, Si, Co, Li, Cd, Cu, Ti^{III}, Ba, and Sr, and 10 mg each of Mg and Na	101	119	101
1 gram BeO + 1 mg each of Al, B, Ca, Cr^{III}, Mn^{II}, Ni, Si, Co, Li, Cd, Cu, Ti^{III}, Ba, and Sr, and 10 mg each of Mg and Na	101	115	97
1.3 gram Y_2O_3	0	0	—
1.3 gram Y_2O_3 + 100 μg each of Zn, Ca, Mg, Sn^{II}, Al, Mn^{II}, V^{V}, Pb, Ba, Cd, B, Si, Li, K, Be, Dy, Ho, Tb, Yb, Co, Ni, Mo, Cr^{VI}, W, Nb; 200 μg Cu, 400 μg Ta, 4 mg Ti^{III}, 5 mg F, and 10 mg Zr	202	196[a]	97
1.3 gram Y_2O_3 + 100 μg each of Zn, Ca, Mg, Sn^{II}, Al, Mn^{II}, V^{V}, Pb, Ba, Cd, B, Si, Li, K, Be, Dy, Ho, Tb, Yb, Co, Ni, Mo, Cr^{VI}, W, Nb; 200 μg Cu, 400 μg Ta, 4 mg Ti^{III}, 5 mg F, and 10 mg Zr	202	198[a]	98

[a] 1-cm cells

to that obtained with an aqueous phase. The absorbance is a linear function of iron concentration at least to 2 ppm and the colour is stable indefinitely.

Effect of other elements

The effect of other elements on the determination of iron by this procedure is shown in Table II. The recovery of iron in the presence of mixtures of elements, and the application of the method to beryllium oxide and yttrium oxide are shown in Table III. Sufficient bromine water was added to ensure the presence of iron in the ferric state. Since nitric and perchloric acids tend to prevent

TABLE IV. ANALYSIS OF NEW BRUNSWICK STANDARDS[a]

Sample No.	Fe found, *ppm*	Average	Nominal value
Be 85	390, 400	395	400
86	1310, 1320, 1410, 1310, 1400	1350	1400
87	1640, 1640, 1740, 1640	1670	1700
88	2510, 2500	2505	2500
BeO 72–1	765, 748	756	746
72–2	382, 380	381	386
72–3	192, 194	193	205
72–4	53.8, 56.5	55.2	61.3
72–5	19.7, 20.2	20.0	25.2

[a] Nominal values for beryllium metal are based on chemical analysis

complete colour formation, they should be removed by volatilisation with sulphuric acid. It has been found that the method can be applied to 1-gram samples of nickel or chromium, in addition to beryllium and yttrium, without prior removal of the main constituent.

Application of the method

Results obtained when the method was applied to New Brunswick Laboratory standard samples of beryllium and beryllium oxide are shown in Table IV.

CONCLUSION

Despite the number of manipulations involved, the procedure is relatively rapid and very precise. Increased sensitivity could easily be obtained by using larger samples and/or a greater cell-length than specified in the procedure described, or possibly by substituting 4:7-diphenyl-1:10-phenanthroline for 1:10-phenanthroline.

Zusammenfassung—Die Wichtigkeit von Beryllium und Berylliumoxyd im Zusammenhang mit Atomenergieprojekten machte die Entwicklung von genauen Methoden zur Bestimmung von metallischen Verunreinigungen. Eine Methode zur Abtrennung von Eisen wird mitgeteilt, welche auf der Extraktion mit Tri-n-octylphosphinoxyd beruht. Das extrahierte Eisen wird mit 1:10-Phenanthrolin bestimmt. Die Methode ist innerhalb von ±3% oder ±3 ppm (Mikrogramm per Gramm) genau, abhängig was der grössere Wert ist. Genauigkeit und Empfindlichkeit der Methode können gesteigert werden, durch geeignete Wahl von Probenmenge, Extraktionvolum und/oder Zellänge. Von 68 untersuchten Elementen stören 61 nicht, wenn in Mengen bis zu 10 mg anwesend. Keine Störung ist zu verzeichnen in Anwesenheit von 5 mg Silizium, 1 mg Antimon, Gallium, Molybdän oder Wolfram, sowie 0.1 mg Tellur oder Uran. Lediglich Gallium, Tellur und Silizium stören ohne eine warnende Trübung in der gefärbten Lösung zu erzeugen.

Résumé—L'importance du béryllium et de l'oxyde de béryllium dans le programme de l'énergie atomique a nécessité le développement de méthodes précises d'analyse chimique pour le dosage des impuretés métalliques. Les auteurs présentent une méthode de séparation du fer par extraction avec l'oxyde de tri-n-octylphosphine suivie du dosage avec la 1-10 phénanthroline. La méthode est précise à ±3% prés (limite de sensibilité: 3 p.p.m.).

On pourrait augmenter la précision et la sensibilité par un choix approprié du poids de l'échantillon, du volume du corps extrait, et/ou de la longueur de la cellule. Parmi les 68 éléments étudiés, 61 ne gênent pas pour des quantités de 10 mg. 5 mg de silicium, 1 mg d'antimoine, de gallium, de molybdéne ou de tungsténe ou 0,1 mg de tellure ou d'uranium ne gênent pas. Seuls le gallium, le tellure et le silicium gênent sans produire de trouble avertisseur dans la solution colorée.

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SALTING-OUT CHROMATOGRAPHY—VI

EFFECT OF THE LENGTH OF THE HYDROCARBON CHAIN, THE ELUENT SALT, AND THE CROSSLINKING AND IONIC FORM OF THE RESIN

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Summary—Each increment of CH_2 in the hydrocarbon chain causes a nearly constant rise in the logarithm of C, the distribution ratio. Increases in the crosslinking of Dowex 1 cause increases in C, but increases in the crosslinking of Dowex 50 generally cause decreases in C. With water as eluent, the largest C values are obtained when the counter ion of the resin has the least salting-out ability. The interpretation of these effects and the effect of the eluent salt are discussed.

SALTING-OUT chromatography[1,2,3,4] is the separation of water-soluble non-electrolytes by elution through ion-exchange resins with aqueous salt solutions as eluents. Alcohols,[1] amines,[2] ethers,[3] aldehydes,[4] and ketones[4] may be separated by this technique. A similar technique, solubilisation chromatography, utilises aqueous solutions of organic solvents such as ethanol or acetic acid as eluents and serves to separate water-insoluble non-electrolytes (or weak electrolytes) such as alcohols,[5] phenols,[5] ketones,[6] ethers,[7] carboxylic acids,[7] and aromatic hydrocarbons.[7] The plate theory of chromatography with ion-exchange resins has been discussed in two recent treatises.[8,9]

In this paper, the basic equation[8,9] of the plate theory

$$U^* = V(C + 1) \tag{1}$$

is used to calculate C values. In this equation, U^* is 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. It has been demonstrated that

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

where 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. This equation is analogous to those employed for the determination of k by solubility, distribution, or vapour-pressure methods.[10,11]

This investigation was designed to gain a better insight into the nature of salting-out on ion-exchange resins.

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EXPERIMENTAL

Reagents and resins

Assayed reagent-grade salts were used in preparing the eluents. All carbonyl compounds were of the best grade available. Propanone, butanone, and 2-pentanone were dried and redistilled.

The resins were sulphonated crosslinked polystyrenes (Dowex 50) and crosslinked polystyrenes with quaternary nitrogen atoms attached by methylene bridges (Dowex 1). They were all of 200-400 mesh but varied in nominal crosslinking (% divinylbenzene). The Dowex 50 resins were treated with $4M$ hydrochloric acid until the effluent was free of iron, then washed with water. They were converted to the desired cationic forms by treatment in columns with the appropriate salt or hydroxide solution until the pH values of the influent and effluent were the same, and were finally washed with water. The Dowex 1 resins were conditioned with $3M$ hydrochloric acid and ethanol; water rinses followed each treatment. They were generally converted into the desired anionic form by column treatment with an appropriate salt. In some cases, they were first converted to the hydroxide form, which was then treated with the appropriate acid. The excess of acid was removed with water.

The interstitial volumes of the columns were determined as previously described.[3] A more comprehensive study of interstitial volumes is reported elsewhere.[12]

Elution and analysis

The preparation of the columns and the procedure for elution have been described elsewhere.[4,8] The concentration of ketone in the effluent was determined by oxidation with dichromate[13] or by a modification[4] of the differential pH method.[14]

RESULTS AND DISCUSSION

Effect of crosslinking

Fig. 1 shows the results of eluting mixtures of three ketones through columns of Dowex 1 of different crosslinkages with ammonium sulphate. Table I shows the parameters of equation (2) obtained from an extensive series of elutions of other ketones through resins of various crosslinkages with several concentrations of ammonium sulphate. This table also gives the ratios of the C values of 2-pentanone (C_p) to those of acetone (C_a).

TABLE I.—SALTING-OUT CONSTANTS WITH AMMONIUM SULPHATE

Resin	Propanone		Butanone		2-Pentanone		C_p/C_a	
	$\log C_0$	k	$\log C_0$	k	$\log C_0$	k	H_2O	$2M\,(NH_4)_2SO_4$
Dowex 1-X4	−0.175	0.283	0.000	0.360	0.180	0 440	2.44	4.46
Dowex 1-X8	−0.170	0.318	0.105	0.397	0.405	0.448	3.58	6.53
Dowex 50-X4	0.183	0.272	0.282	0.358	0.345	0.429	1.67	3.66
Dowex 50-X8	0.010	0.312	0.151	0.398	0.295	0.478	1.94	3.91
Dowex 50-X12	−0.030	0.330	0.125	0.397	0.270	0.484	2.03	4.10
Dowex 50-X16	0.045	0.322	0.200	0.385	0.350	0.480	2.06	4.28

These results reveal the following facts: (*a*) As the crosslinking of the anion-exchange resin increases, the distribution ratios increase at first and then appear to level off (Fig. 1). The same general tendency was exhibited, except for a few compounds of low molecular weight, by alcohols,[1] ethers,[3] and other ketones.[4] (*b*) With the cation-exchange resin, the distribution ratios decrease as the crosslinking is increased from 4 to 12% but increase slightly with a further increase in crosslinking. (*c*) The salting-out constant, k, for a given solute is constant within the experimental error for all resins with nominal crosslinkings of 8% or more.[3,8] (*d*) The absorption selectivity, C_p/C_a, increases with increasing crosslinkage.

The absorption of non-electrolytes from aqueous salt solutions can be best understood in terms of the following factors:[15,16] (1) the simple dissolution of the non-electrolyte in the solution within the resin beads; (2) the London dispersion forces between the hydrocarbon portion of the organic solute and the benzene rings and the tetra-alkylammonium groups of the resin; (3) interactions between the dipoles of the solute and the ions of the resin; and (4) the salting-out of the organic compound by the aqueous salt solution into the resin phase. On the other hand, the rejection of non-electrolyte molecules by the resin phase is due to (5) the salting-out of the non-electrolyte by the fixed and counter ions of the resin and (6) steric effects concerned with the size of the uncharged molecule and the interstices of the resin framework.

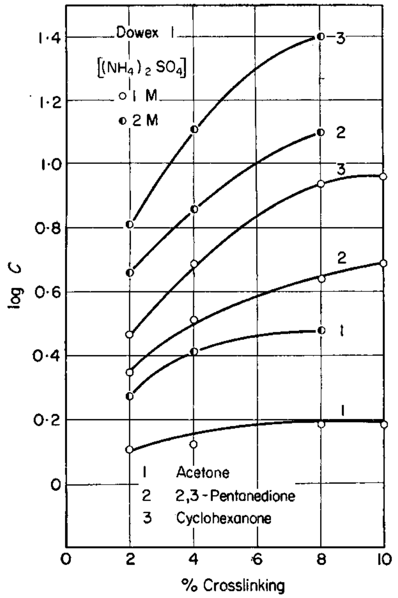

FIG. 1.—The effect of varying the crosslinking on the distribution ratio, C.

Although the magnitude of the foregoing factors has not been evaluated, they can be used for a qualitative explanation of the effect of crosslinking on the distribution ratio. As the crosslinking of the anion exchanger is increased, factors (2) and (3) would lead to increased absorption whereas factors (1), (5), and (6) would result in decreased uptake of non-electrolyte. The increase in selectivity (Table I) with increasing crosslinkage indicates that the London forces probably predominate.

The observation that increasing the crosslinkages of Dowex 50 from 4 to 12% leads to decreased sorption whereas Dowex 1 shows the opposite effect is probably due to the greater salting-out effect of benzenesulphonate ions as compared with benzyltrimethylammonium ions coupled with the increase in the concentration of these ions due to the shrinking of the resin with increasing crosslinkage.

The fact that the salting-out constant, k, is independent of the resin (provided the crosslinking is 8% or more) indicates that this parameter is related solely to the interaction between the salt and organic solute, whereas C_0 in equation (2) is related to the interaction between the resin and the non-electrolyte.

Effect of eluent salt

The effect of the eluent salt on the constants of equation (2) for three ketones and three resins is given in Table II. Again, it is seen that *k* is constant for any given pair of salt and non-electrolyte, regardless of the resin (provided there is at least 8% crosslinking). The discrepancy in the values for magnesium nitrate with propanone is due to the experimental difficulty in the accurate evaluation of very small *C* values.

By virtue of their large *k* values, magnesium and ammonium sulphates are more generally useful in salting-out chromatography than the other salts in Table II. Of these two, ammonium sulphate is the better because of its greater solubility and greater selectivity (difference in log C_0 for any two of the ketones).

TABLE II.—SALTING-OUT PARAMETERS WITH DIFFERENT ELUENT SALTS

Resin	Eluent	Propanone		Butanone		2-Pentanone	
		log C_0	*k*	log C_0	*k*	log C_0	*k*
Dowex 1-X8	NH_4NO_3	0.048	0.035	0.305	0.047	0.605	0.056
Dowex 1-X8	$(NH_4)_2SO_4$	−0.170	0.318	0.105	0.397	0.405	0.448
Dowex 1-X8	$MgSO_4$	−0.185	0.279	0.085	0.378	0.375	0.454
Dowex 1-X8	$Mg(NO_3)_2$	0.057	0.028	0.320	0.064	0.595	0.091
Dowex 50-X8	NH_4NO_3	0.015	0.034	0.155	0.047	0.302	0.058
Dowex 50-X8	$(NH_4)_2SO_4$	0.010	0.312	0.151	0.398	0.295	0.478
Dowex 50-X8	$MgSO_4$	0.083	0.312	0.182	0.408	0.332	0.481
Dowex 50-X8	$Mg(NO_3)_2$	0.085	0.062	0.205	0.089	0.365	0.125
Dowex 50-X12	KCl	0.052	0.109				
Dowex 50-X12	KNO_3	0.055	0.056				
Dowex 50-X12	KI	0.066	0.040				
Dowex 50-X12	$(NH_4)_2SO_4$	−0.300	0.330	0.125	0.397	0.270	0.484

The *k* values of propanone with magnesium sulphate, potassium chloride, potassium nitrate, and potassium iodide determined by classical methods[10] are respectively 0.310, 0.101, 0.041, and 0.020. Except for the last very small value, these check the values obtained by salting-out chromatography (Table II).

If it is assumed that the salting-out constant for a given salt with a given non-electrolyte is equal to the sum of the salting-out contributions of its ions and if the salting-out constant of the nitrate ion is arbitrarily taken as zero,[17] the ionic salting-out constants can be calculated. The values of Table III were calculated thus from the values of Table II for Dowex 50-X8 with the sulphates and nitrates of magnesium and ammonium. The values of $k_{SO_4^{-2}}$ check very well.

TABLE III.—IONIC SALTING-OUT CONSTANTS

Compound	$k_{NH_4^+}$	$k_{Mg^{+2}}$	$k_{SO_4^{-2}}$	
			From $MgSO_4$	From $(NH_4)_2SO_4$
Propanone	0.034	0.062	0.250	0.244
Butanone	0.047	0.089	0.319	0.304
2-Pentanone	0.058	0.125	0.356	0.362

Effect of the ionic form of the resin

Elutions of three ketones were performed with water as the eluent through Dowex 50-X8 in 26 different ionic forms and through Dowex 1-X8 in 18 different ionic forms. The results are summarised in Tables IV and V. The C_0 values of 2-pentanone and of acetone are denoted respectively C_p and C_a in these tables.

TABLE IV.—EFFECT OF THE COUNTER ION OF DOWEX 50-X8

Counter ion	Distribution ratio			$\log (C_p/C_a)$
	Propanone	Butanone	2-Pentanone	
H	1.63	2.25	3.11	0.281
$\mathrm{Mn^{II}}$*	1.40	1.96	2.64	0.285
Bi*	1.40	1.83		
$\mathrm{Ce^{IV}}$	1.37	1.85	2.66	0.287
$\mathrm{Cr^{III}}$*	1.36	1.88	2.63	0.288
Th*	1.34	1.90	2.74	0.311
Cd*	1.33	1.85	2.55	0.281
$\mathrm{Fe^{III}}$*	1.32	1.81	2.62	0.299
Ca	1.30	1.73	2.58	0.296
Cu*	1.30	1.70	2.48	0.279
Al	1.26	1.70	2.57	0.310
$\mathrm{Co^{II}}$*	1.25	1.67	2.40	0.283
Zn*	1.25	1.64	2.38	0.279
Li	1.22	1.52	2.04	0.220
Ba*	1.22	1.69	2.69	0.342
Pb*	1.22	1.62	2.45	0.302
Mg	1.21	1.60	2.31	0.280
$\mathrm{Hg^{II}}$*	1.20	1.68	2.41	0.304
$\mathrm{Ni^{II}}$*	1.20	1.56	2.27	0.275
Sr	1.18	1.60	2.41	0.311
K	1.14	1.47	2.08	0.262
$\mathrm{NH_4}$	1.01	1.41	1.96	0.288
Na	1.00	1.30	1.87	0.272
Ag*	0.92	1.15	1.59	0.247
$\mathrm{(C_2H_5)_4N}$	0.51	0.55	0.62	0.085†
$\mathrm{(CH_3)_4N}$	0.48	0.58	0.64	0.126†
				Mean = 0·284
				Mean deviation = 0.017

* These values were determined by Miss Eva Agnes Smith.
† Excluded from the mean.

It is obvious from these tables that the magnitude of the absorption is markedly dependent on the nature of the counter ion. Other less extensive studies[18,19] have indicated the same effect. Two hypotheses will be considered as possible explanations of these data.

If the ketone is absorbed mainly by simple dissolution in the internal water of the resin, the distribution ratios should be governed by the swelling of the resin in the various forms. A comparison of the C values of Table IV with the available data on the uptake of water[20,21,22] by various ionic forms of Dowex 50 indicates that this hypothesis is untenable.

TABLE V.—EFFECT OF THE COUNTER ION OF DOWEX 1-X8

Counter ion	Distribution ratio			$\log (C_p/C_a)$
	Propanone	Butanone	2-Pentanone	
Iodide	2.04	5.50	16.43	0.92
Thiocyanate	1.39	3.11	7.39	0.74
Bromide	1.15	2.42	5.36	0.67
Nitrate	1.14	2.11	4.09	0.56
Formate*	1.00	1.66	3.56	0.55
Oxalate	0.95	1.76	3.64	0.59
Citrate	0.96	1.55	2.62	0.43
Chloride	0.91	1.66	3.26	0.55
Hydroxide	0.88	1.42	2.81	0.50
Benzoate*	0.85	1.28	2.51	0.47
Salicylate	0.77	1.64	3.62	0.69
Fluoride	0.77	1.47	3.10	0.60
Acetate	0.71	1.33	2.58	0.56
Sulphate	0.70	1.28	2.51	0.57
n-Butyrate*	0.66	1.29	2.56	0.59
n-Caproate*	0.65	1.11	2.20	0.53
Adipate*	0.63	1.27	2.51	0.61
Phosphate	0.64	1.12	2.18	0.53

* These values were determined by Miss Eva Agnes Smith.

On the other hand, if the salting-out by the counter ions is the main factor the values of C in Tables IV and V should be parallel with those obtained by classical salting-out methods. According to Long and McDevit,[10] the salting-out ability of cations (per equivalent) toward acetone decreases in the order

$$Na^+ > K^+ > Mg^{2+} > Li^+$$

This checks the order of these cations in Table IV. Similarly, Long and McDevit place the anions in the order

$$SO_4^{2-} > Cl^- > NO_3^- > Br^- > I^-$$

which checks the order of Table V except for the reversal of nitrate and bromide. It is concluded, therefore, that the chief factor in the effect of the counter ion is its salting-out ability, those ions with the least salting-out ability imparting the greatest sorption power to the resin.

On the basis of this hypothesis, however, one glaring anomaly exists. The tetra-alkylammonium ions have negative salting-out properties; hence they should impart the greatest sorptive ability to Dowex 50, whereas, in fact, they stand at the bottom of Table IV. This discrepancy may be explained by assuming that these large ions are oriented close to the benzene rings of the resin and thus interfere with the normal attractive forces between the aromatic nuclei and the organic solutes.

Effect of the length of the hydrocarbon chain

Fig. 2 indicates that the addition of a CH_2 group to a 2-alkanone causes a nearly constant increment in the C_0 value with various cationic forms of Dowex 50. Fig. 3 indicates the peculiar behaviour of the tetraethylammonium ion in this regard, also that the anion-exchanger behaves differently from the cation-exchanger.

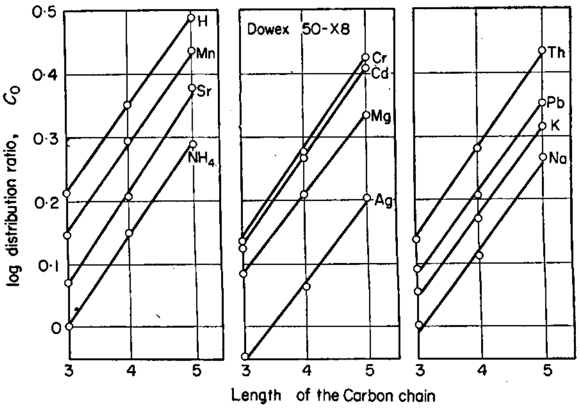

FIG. 2.—The distribution ratios, C_0, of 2-alkanones with various cationic forms of Dowex 50 as a function of the length of the carbon chain.

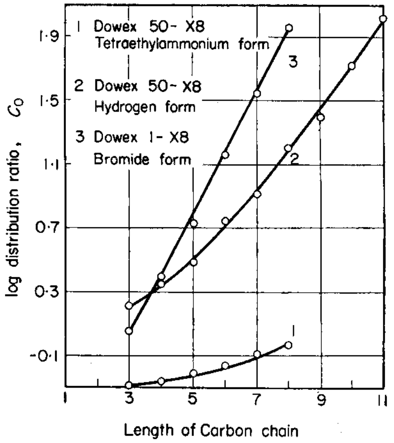

FIG. 3.—The distribution ratios, C_0, of 2-alkanones as a function of the length of the carbon chain.

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Zusammenfassung—Jedes Inkrement von CH_2 in einer Kohlenwasserstoffkette bewirkt einen nahezu konstanten Anstieg in Log *C* (*C* der Verteilungs koeffizient). Anstieg des Vernetzungsgrades von Dowex 1 bewirkt Anstieg in *C*, während bei Dowex 50 ein Abstieg in *C* zu verzeichnen ist. Mit Wasser als Eluant werden die grössten *C*-Werte erhalten, wenn das Gegenion des Harzes die geringste Aussalzfähigkeit aufweist. Eine Interpretation dieser Effekte wird zur Diskussion gestellt.

Résumé—Chaque augmentation de CH_2 dans une chaîne hydrocarbonée provoque une augmentation à peu près constante du logarithme de *C*, le coefficient de partage. Des accroissements du degré de pontage de la Dowex 1 provoquent des accroissements de *C*, mais des accroissements du degré de pontage de la Dowex 50 provoquent généralement des décroissances de *C*. Avec l'eau comme éluant, on obtient les plus grandes valeurs de *C* quand l'ion dans la résine a le plus faible pouvoir d'exclusion. L'interprétation de ces effets et l'effet du sel éluant sont discutés.

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PRELIMINARY COMMUNICATIONS

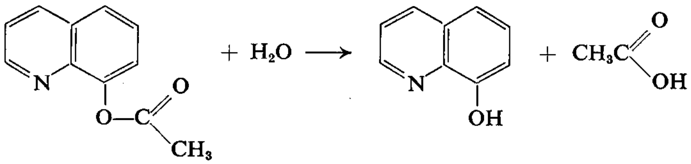
The precipitation of metal 8-hydroxyquinolates from homogeneous solution—I

Preparation of 8-acetoxyquinoline

(*Received* 24 *February* 1960)

INTRODUCTION

No method has apparently been reported for the precipitation of a metal ion from homogeneous solution by the generation of 8-hydroxyquinoline from a parent reagent such as an ester. Although aluminium 8-hydroxyquinolinate has been precipitated from homogeneous solution, this was accomplished by raising the pH of an acid soluton containing 8-hydroxyquinoline through the hydrolysis of urea.[1] This paper describes a convenient method for the preparation of the ester, 8-acetoxyquinoline, which serves as an excellent source reagent for the generation of 8-hydroxyquinoline, thus:



It has been found in preliminary experiments with many metal ions that the use of 8-acetoxyquinoline results in the formation of large, well-developed, and readily filterable crystals as compared to conventional precipitation with 8-hydroxyquinoline.

The preparation of 8-acetoxyquinoline has been reported previously by several investigators. In 1882, Skraup[2] prepared this compound by reacting 8-hydroxyquinoline with sodium acetate and an excess of acetic anhydride. He hydrolyzed the excess acetic anhydride with water, neutralized the solution with sodium carbonate, and extracted the oil that separated out with ether. He distilled the dried ether extract and obtained 8-acetoxyquinoline as a colourless oily liquid (b.p. 280°) which would neither solidify upon long standing at room temperature nor upon cooling to −20°. Borsche and Groth[3] reported the preparation of solid 8-acetoxyquinoline (m.p. 56 to 57°) but did not furnish any details of the method of synthesis. Dimroth[4] reacted 8-hydroxyquinoline with acetic anhydride and upon cooling the reaction mixture an addition product precipitated from which solid 8-acetoxyquinoline (m.p. 55.5 to 56.5°) was subsequently obtained. Although Browning[5] also reportedly prepared 8-acetoxyquinoline, this seems unlikely because the melting point of the solid he obtained was 75 to 76° which is quite close to that of 8-hydroxyquinoline (76°).

In the present method of preparation, acetic anhydride reacts with 8-hydroxyquinoline, the 8-acetoxyquinoline is subsequently distilled, and after solidification, purified by recrystallization from a mixture of *iso*propyl ether and *n*-heptane to give a crystalline product with a m.p. at 56.2 to 56.5°.

EXPERIMENTAL

Reagents

Reagent grade 8-hydroxyquinoline was obtained from the Matheson, Coleman, and Bell Division of the Matheson Company, Norwood, Ohio. Reagent grade acetic anhydride was obtained from the Mallinckrodt Chemical Work, New York, New York.

Preparation and purification

Seventy-seven and one-half grams (0.69 mole) of 8-hydroxyquinoline were placed in a 500 ml Claisen flask. Then 200 ml (2.1 mole) of acetic anhydride were added and the mixture heated. An amber-coloured solution formed, which upon further heating changed until it was almost colourless.

The acetic acid by-product and the excess acetic anhydride were distilled from the reaction mixture at atmospheric pressure. The boiling range of the distillate was from 125° to 145°. The liquid remaining in the flask was then subjected to a reduced-pressure distillation. The product, which was a viscous, light yellow liquid that solidified after a few hours, distilled over between 195° and 205° at 35 mm Hg pressure. The crude 8-acetoxyquinoline (>90% yield) was dissolved in the smallest possible amount of *iso*propyl ether at room temperature and the solution was diluted with *n*-heptane. The solution was filtered at room temperature and then cooled to −78° in a dry ice-acetone bath. The slurry that was obtained was quickly filtered through a Buchner funnel and the white solid precipitate was then dried in the air at room temperature.

Properties

The melting point of 8-acetoxyquinoline was found to be 56.2° to 56.5° after two recrystallizations from the *n*-heptane-*iso*propyl ether mixture; further recrystallization did not alter the melting point.

Two samples of the 8-acetoxyquinoline, prepared and purified as described previously, were analyzed for carbon, nitrogen, and hydrogen content. The results of these analyses are presented in Table I.

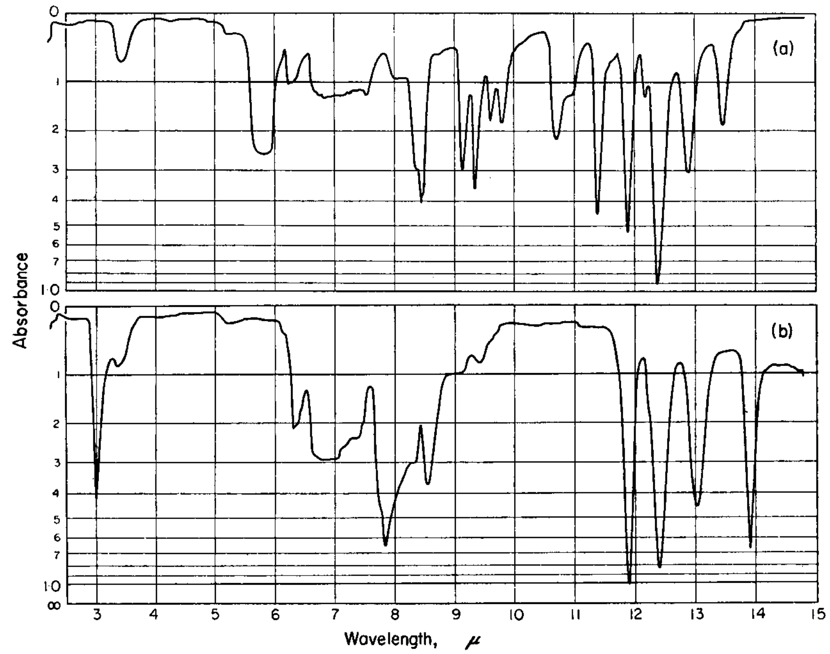


FIG. 1. Infra-red absorption spectra
(a) Upper spectrum: 8-acetoxyquinoline
(b) Lower spectrum: 8-hydroxyquinoline

Infrared spectra of 10% (by weight) solutions of 8-acetoxyquinoline and 8-hydroxyquinoline in acetone were obtained with a Perkin Elmer (Model 137) Infra-red Spectrophotometer. In each case, the solution path lengths were 0.094 mm in sodium chloride cells. The spectra are shown in Fig. 1. It should be observed that the characteristic absorption bands in the spectrum of 8-hydroxyquinoline at 3.0, 7.8, and 13.9 microns are completely absent from the spectrum of 8-acetoxyquinoline.

8-Acetoxyquinoline was added to acetate-buffered aqueous solutions of several ions, namely, Mg^{II}, Al^{III}, Zn^{II}, UO_2^{II}, Th^{IV}, Fe^{III}, Cu^{II}, Co^{II}, Ni^{II}, Pb^{II}, Mn^{II}, and Cd^{II}, and was found to precipitate the corresponding 8-hydroxyquinolinates from homogeneous solution. The hydrolysis reaction appeared to proceed more rapidly in basic solution than in neutral or acid solution. Substitution of other groups for the acetyl group of 8-acetoxyquinoline can be expected to give compounds with other hydrolysis rates as desired. The results will subsequently be reported in full in TALANTA.

TABLE I.—RESULTS OF CARBON, NITROGEN. AND HYDROGEN ANALYSIS

	Found	Theoretical
% Carbon	70.3 70.4	70.5
% Nitrogen	7.5 7.6	7.5
% Hydrogen	4.5 4.6	4.9
% Oxygen (By Difference)	17.7 17.4	17.1

Acknowledgement—The authors acknowledge the partial assistance of the United States Atomic Energy Commission in supporting the investigation described herein under contract AT(11-1)-582.

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Summary—The reagent, 8-acetoxyquinoline, has been found to be useful for the precipitation from homogeneous solution of metal 8-hydroxyquinolates. A convenient method for the preparation of the reagent in crystalline form is described.

Zusammenfassung—8-Acetoxychinolin wurde als geeignetes Reagens zur Fällung von Metalloxinaten aus homogener Lösung gefunden. Eine einfache Methode zur Darstellung des Reagenses in kristallisierter Form wurd beschrieben.

Résumé—Les auteurs ont trouvé que le réactif, la 8-acetoxyquinoliné était utile pour la précipitation en solution homogène de 8-hydroxyquinolates métalliques. Une méthode convenable de préparation du réactif sous forme cristalline est décrite.

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N : N : N′ : N′-Tetracarboxymethyl derivatives of some benzidines as metallofluorescent indicators

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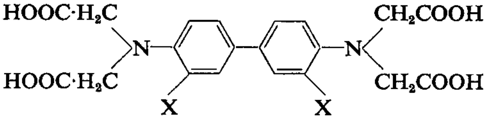
WE have found that metallofluorescent complexans are formed when the 3 : 3′-disubstituted derivatives of benzidine are condensed with chloroacetate. The structure of these complexans is believed to be



The three complexans which proved of interest were *o*-dianisidine-N:N:N′:N′-tetraacetic acid (X = OMe), *o*-diphenetidine-N:N:N′:N′-tetraacetic acid (X = OEt), and benzidine-3:3′-dicarboxylic acid-N:N:N′:N′-tetraacetic acid (X = CO_2H). The first two compounds fluoresce in pH *c*.4 to *c*.10 solutions, the maximum fluorescence being at pH 5·5 to 6·0, and the last compound in solutions greater than pH8, the maximum fluorescence being in caustic soda solution. The fluorescence of the alkoxyl derivatives is quenched by copper^{II} and mercury ^{II} ions and that of the dicarboxyl derivative by calcium ions. The reactions form a suitable basis for the detection of the visual end-point by employing the appearance (or disappearance in a back-titration) of fluorescence in the EDTA titration. A very sharp end-point is obtained with the first two indicators in the copper^{II}-EDTA titration in pH 4 to 10 solutions; in the direct titration of mercury^{II} with EDTA in slightly acid solution the end-point is not quite so sharp. Calcium can be titrated with EDTA in alkaline solution using benzidine-3:3′-dicarboxylic acid-N:N:N′:N′-tetraacetic acid as indicator. As with calcein[1], a residual fluorescence occurs on the "non-fluorescent" side of the end-point probably due to the presence of unchanged benzidine-3:3′-dicarboxylic acid; the purification of this complexan is now being studied. This effect impairs the sharpness of the end-point.

The fluorescence shown by these complexans is very intense and only a very minute amount of the indicator is required; the indicator blanks are negligible. In fact 0·035 μg of copper^{II} quenches the fluorescence of the two alkoxyl derivatives at a dilution limit of 1 in 2 × 10^6.

EXPERIMENTAL

The indicators were prepared in the form of their sodium salts. Aqueous solutions of these salts deteriorate to some extent, and it is more convenient to use the indicators as solid mixtures with an inert salt such as sodium chloride or potassium nitrate in the ratio of 1 : 100.

Titration of copper^{II} with EDTA

The type of apparatus employed in the titration has been described by Belcher and Nutten[2]; the ultra-violet source was a Mazda mercury vapour electric discharge lamp-type MBW/U, 230–240 volts, 125 watts. Ten ml of 0·02*M* copper^{II} solution were pipetted into a 250-ml conical flask and diluted with water, and the buffer solution and indicator were added. The titration was done in a darkened room with the contents in the flask exposed to the ultra-violet source. The solution was titrated with 0·02*M* EDTA to the appearance of fluorescence.

An average titre of 10·06 ± 0·02 ml of 0·02*M* EDTA was obtained using *o*-dianisidine-and-*o*-diphenetidine-N:N:N′:N′-tetraacetic acids at a pH range of 4 to 10, as against a titre of 10·05 ± 0·01 using Fast Sulphon Black as visual indicator[3].

The end-point in the reverse titration was equally sharp, being marked by the disappearance of fluorescence. The following metal ions can be determined by titrating an excess of EDTA with copper^{II}—Bi^{3+}, Fe^{2+}, Fe^{3+}, In^{3+}, Ni^{2+}, Pb^{2+}, Th^{4+}, Tl^{3+}, V^{4+} and Zr^{4+}.

Titration of calcium with EDTA

The following results were obtained using benzidine-3:3′-dicarboxylic acid-N:N:N′:N′-tetraacetic acid with three buffer solutions indicated below. The titration was standardised using Acid Alizarin Black SN indicator and diethylamine buffer solution[4].

10 ml 0·02*M* Ca^{2+} ≡ 10·01 ± 0·01 ml 0·02*M* EDTA.

Buffer	EDTA, *ml*
5*N* NaOH	10·02, 10·03, 10·02
Et_2NH	10·02, 10·02, 10·02
NH_3-NH_4Cl	10·04, 10·04, 10·03

The sharpest end-points were obtained in caustic soda solution. The end-point was improved somewhat when phenolphthalein was present; this also gave an indication as to whether sufficient caustic soda was present. A large excess of the latter must be avoided as this would cause percipitation of the calcium.

The synthesis and properties of the complexans of other derivatives of benzidine and related compounds are under investigation.

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Summary—Metallofluorescent indicators are formed by condensing 3:3′-disubstituted derivatives of benzidine with chloroacetate. These complexes can be used as indicators in titration of EDTA with, *e.g.*, copper^{II}. In consequence, a wide range of metal ions can be determined by back-titrating an excess of EDTA with copper^{II} solution, using the disappearance of fluorescence of these complexans as indicators.

Zusammenfassung—Fluorescierende Metallindicatoren werden erhalten, wenn man 3,3′-substituierte Derivate des Benzindins mit Chloressigsäure kondensiert. Diese Verbindungen können als Indicatoren in ÄDTE-Titrationen, z.B. von Kupfer(II), verwendet werden. Folglich kann ein weiter Bereich von Metallionen bestimmt werden, indem man einen Überschuss von ÄDTE mit Kupfermasslösung zurücktitriert, bis die Löschung der Fluorescenz den Endpunkt anzeigt.

Résumé—Les indicateurs métallofluorescents sont formés par condensation des dérivés 3-3′ disubstitués de la benzidine avec du chloracétate. Ces complexes peuvent etre utilisés comme indicateurs dans le titrage de l'EDTA par le cuivre II, par exemple. Ainsi, une grande série d'ions métalliques peuvent être dosés par titrage en retour d'un excès d'EDTA par une solution de cuivre II en utilisant comme méthode indicatrice la disparition de la fluorescence de ces complexes indicateurs.

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SHORT COMMUNICATION

Further comments on metalfluorechromic indicators

(*Received* 23 *February* 1960)

RECENTLY Körbl and Svoboda[1] have criticised the term "metalfluorechromic indicators" and the mechanism proposed by Wilkins[2] to explain the reversal of the indicator and the blocking reactions which take place with certain metal ions and various indicators. In light of this criticism further comments are necessary regarding the mechanisms proposed by Wilkins[2] and by Körbl, *et al.*[1,3] as well as the terminology involved in classifying these indicators.

Semantics can be an interesting subject but becomes particularly difficult when the discussion involves translations from one language to another. If one were to break down the terms "metalfluorechromic indicator" and "metallochromic indicator" into their integral parts, it is apparent that it is the "chromic" portion of the term which causes the difference of opinion. The term "chromic" signifies colour and there is nothing expressed or implied in this term regarding a change in colour. Thus the term "metallochromic" is an adjective and it is the noun "indicator" which implies that a change in colour is under consideration. In all common usage e.g., "hypsochromic shift," "bathochromic change," a noun is necessary to indicate that a change of colour is taking place. The term "metallochromic indicators" has received wide-spread usage and a further description of these compounds appears unnecessary. The term "metalfluorechromic indicator" was proposed because of the many similarities to metallochromic indicators, however, the fluorescent properties are rather unique and merit special designation. Calcein with ultra-violet light as the sole source of illumination is a one-colour (fluorescent) indicator and the colour change is from green to absence of colour. To preclude this phenomenon from being classified as a colour change would be analogous to stating that the red to colourless transition of phenolphthalein is not a colour change. The fact that the green colour is a result of emitted radiation is not a legitimate basis for excluding this phenomenon from being discussed as a change of colour. For example, one speaks freely of the yellow colour of the sodium flame.

The mechanism proposed by Wilkins[2] was suggested as a means of explaining the unusual differences which various cations exhibited in their reactions with these indicators. The normal complex and the reversal complex received limited discussion, whereas the blocking reaction was only mentioned as being explicable by a comparable mechanism. It was noted that the phenomena were being studied and would be reported at a later date. In view of the criticism and alternative proposal by Körbl and Svoboda[1], it appears appropriate to continue the discussion of the reactions of these indicators at this time.

The basis of this mechanism is the possibility of the formation of two geometrically different chelates with the fluorechromic indicator. These configurations are illustrated in Fig. 1.

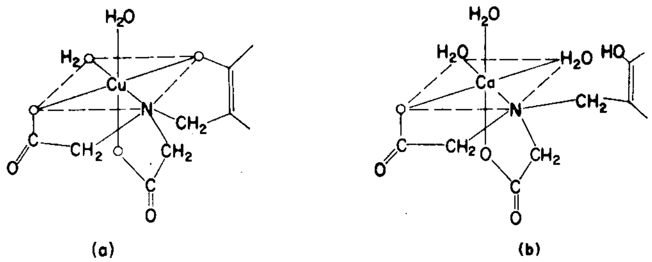


FIG. 1.

The "normal complex" would have the structure shown in Fig. 1a. Experimentally the "normal complex" is demonstrated by the quenching of the fluorescence of free Calcein at a pH of 7 for example. The phenomenon observed is that co-ordination of the indicator anion with copper forces the indicator anion to assume an electronic configuration which would normally exist in a more alkaline region. Calcein does not fluoresce at a high pH (above 12). In my opinion the bond between the copper and the phenolic oxygen would be predominantly covalent in character, contrary to the opinion of Körbl and Svoboda.[1] This assumption is based on the ease of extraction of many chelates with a copper-phenolic oxygen bond into non-polar solvents.[4] If the bond were predominantly ionic, such chelates would not be so soluble in non-polar solvents.[5]

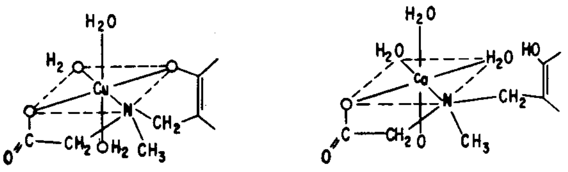
There is good reason to expect the configuration shown in Fig. 1a to be formed in a stepwise fashion. In fact one would expect the configuration shown in Fig. 1b to be one of the steps. The fact that such a stepwise formation probably exists is aptly demonstrated by the work of Schwarzenbach[6] and is not inconsistent with the "normal complex." These experiments are also consistent with the "indicator-reversal complex" and the "blocking reaction."

The "indicator-reversal complex" is demonstrated experimentally by adjusting the pH of a solution of Calcein to such a high value that the free indicator no longer fluoresces. The addition of calcium to this solution results in a green fluorescence. The portion of the indicator molecule responsible for the emission of fluorescent radiation has assumed the electronic configuration of a form which normally exists in a more acid region. It should be noted that this is the opposite from the normal reaction and was the reason for the term "indicator-reversal complex." Here again one would expect stepwise formation but the observable step would be the configuration illustrated in Fig. 1b and the indicator reverses the normal sequence of events and exhibits the characteristics of a more acid species instead of a more alkaline species.

The statement was made that, "In no case has an element been found which will take part in both types of complex types of complex formation."[2] With the compounds and metal ions studied, we have not as yet found an element which *demonstrates* both reactions. It appears possible with certain metal ions in combination with an appropriate univalent anion to prevent (or delay) the formation of the "normal complex" (Fig. 1a), but to allow the stepwise formation as far as the configuration shown in Fig. 1b. The experiments indicate the formation of an indicator-reversal complex but the pH range at which the experiments must be carried out gives one reason to suspect that a hydroxide precipitate may be present. The adsorption of the non-fluorescing anion on a precipitate frequently results in fluorescence. The statement, however, should not be construed to say that no such element and indicator will ever be found. Such a combination may exist although it is highly unlikely that such is the case in view of the probable bonding; and the experiments presented by Körbl and Svoboda[1] certainly are not a suitable example of such a case. They have given the example of the reactions of calcium with Phenolphthalein Complexone. Their argument is that at a pH of 10 the addition of calcium to a solution of Phenolphthalein Complexone results in a colour change from colourless to red and at a higher pH the change is from red to colourless. Körbl and Svoboda have overlooked the fact that the colour changes for Phenolphthalein Complexone in these pH ranges are colourless to red and back to colourless. This is probably better known by the fact that phenolphthalein as an acid base indicator goes colourless in more alkaline solutions. Therefore the more logical interpretation in the example they have presented is that in this instance the same kind of complex is formed in both cases. An example of such a case, of course, must be restricted to a given cation and a single indicator. There are many examples when a cation forms a normal complex with one indicator and a reversal-complex with another.

Some further evidence may be presented by examining some indicators in which the chelating functional group is modified. One of these which has been prepared and will be described in the literature shortly is N-methyl Calcein, a condensation product of N-methyl glycine, formaldehyde and fluorescein. The chelating portion of the indicator is illustrated in Fig. 2 to show the two types of complexes.

It should be noted that one of the chelating ligands has been removed. In the case of the normal complex the possible number of chelate rings involving the metal ion and an indicator molecule has been reduced from three to two whereas with the indicator-reversal complex the reduction is from two to one. The cases in which the normal complexes are involved show subtle but useful changes. In those cases where indicator-reversal complexes are formed the changes are drastic. One would expect this since a change from three to two rings would not be expected to alter characteristics nearly so much as a change from two to one. N-Methyl Calcein is useful for titrations where the normal complex is involved. For example in copper titrations sharp end-points are obtained, and it is apparent that a stable complex is formed. The addition of calcium to a solution of this indicator in the high pH range results in a slight increase in fluorescence but the titration with EDTA leaves much to be desired.



a b

FIG. 2.

The blocking reactions[7] which sometimes occur also fit into the mechanism proposed by Wilkins.[2] In this case the structure is illustrated in Fig. 1b. The structure is identical to the indicator-reversal complex. The difference between the two is that in the case of the blocking reaction we generally are working in a region in which the indicator, by virtue of the pH, is already in the electronic configuration to which it would be reversed by the formation of a reversal-complex. In general one would expect that the examples shown by Körbl and Přibil[7] would show indicator-reversal complexes at higher pH values: in fact they mention that the blocking of the indicator (Phenolphthalein Complexone) resulted in the disappearance of the original pink colour. If a cation is occupying the co-ordination sites as shown in Fig. 1b and exhibits a blocking reaction, the cation added, which prefers to co-ordinate with the phenolic oxygen, finds nothing available in order to form a chelate ring with this phenolic oxygen.

If one is to entertain the proposal of Körbl and Svoboda[1] one must also take into account the various conclusions which must be drawn from their theory. First it is necessary to demonstrate that copper forms the normal complex with Calcein in the upper pH region (above 12) as well as in the lower ranges where the free indicator fluoresces. This can be done by the following experiment. Adjust a solution of Calcein with a $1M$ solution of potassium hydroxide until the indicator no longer fluoresces. Now add a few drops of a $0.03M$ calcium solution. It will be noted that the solution now fluoresces (indicator-reversal complex). To this solution add a few drops of a $0.03M$ copper solution and it will be observed that the fluorescence is immediately quenched. The copper ions have displaced the calcium from the indicator-metal ion complex and a non-fluorescing (normal) complex is formed. The experiment could have been performed without calcium but then the solution would not have fluoresced either before or after the addition of copper and no conclusions could have been drawn. Under the conditions specified it is apparent that copper forms a complex with the indicator and that the complex is non-fluorescing.

A consideration of the elements which cause fluorescence in the strongly alkaline solutions, in comparison to copper, which does not, results in some highly improbable conclusions.

For example, consider that calcium, lithium, and sodium cause fluorescence at a high pH. According to the mechanism of Körbl and Svoboda[1] these elements have formed a covalent bond with the phenolic oxygen. Under the same conditions copper does not cause fluorescence, therefore one would be forced to conclude that it does not form a covalent bond with the phenolic oxygen. The bond is not covalent, but is ionic (according to Körbl and Svoboda[1]) and the picture is complete. One is faced with the rather unpleasant position of stating that the electropositive elements are formed covalent bonds and that the transition elements are forming ionic bonds, and the conditions are somewhat analogous to that of the Mikado[8] with his cloth untrue, a twisted cue and elliptical billiard balls.

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Summary—The mechanism previously proposed for the behaviour of metalfluorechromic indicators is further discussed, and criticisms of Körbl and Svoboda are answered.

Zusammenfassung—Der fruher bereits beschriebene Mechanismus über das Funktionieren fluorescierender Metalliondicatoren wird weiter diskutiert und auf die Kritik von Körbl und Svoboda erwidert.

Résumé—Le mécanisme précédemment proposé pour le comportement des indicateurs métallofluorochromiques est à nouveau discuté, et l'auteur répond aux critiques de Körbl et Svoboda.

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Talanta, 1960, Vol. 4, pp. 84 to 86. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The following meetings have been arranged

Wednesday and *Thursday* 20 and 21 *April* 1960: **Society of Chemical Industry, Agriculture Group.** Church House, Westminster, London, S.W.1. Symposium on *Advances in the Chemical Analysis of Fertilisers, Soils and Plants.* Further information may be obtained from Dr. P. W. Arnold, Hon. Secretary, Agriculture Group, Society of Chemical Industry, Rothamsted Experimental Station, Harpenden, Herts., England.

Thursday and *Friday* 21 and 22 *April* 1960: **Fertiliser Society: Society for Analytical Chemistry.** Symposium on *Fertiliser Analysis.* Church House, Westminster, London, S.W.1. Those wishing to register should apply as soon as possible to the Secretary, The Fertiliser Society, 44, Russell Square, London, W.C.1. A registration fee of £1 will be charged to cover the cost of preprints, which will be sent to those who have registered and remitted the registration fee before the meeting. The proceedings of the Symposium will be published subsequently in a single volume, and those wishing to purchase copies should ask to be advised on publication.

Tuesday 26 *April* 1960: **Society for Analytical Chemistry,** Midlands Section. *The Analytical Chemistry of Titanium and Zirconium:* Mr. W. T. Elwell and Mr. D. F. Wood. The University, Birmingham, 3, England. 6.30 p.m.

Friday 29 *April* 1960: **Society for Analytical Chemistry,** Scottish Section. *Chemical Services on British Railways:* Dr. G. H. Wyatt. Central Hotel, Glasgow, Scotland. 7.15 p.m.

Tuesday and *Wednesday* 3 and 4 *May* 1960: **Society for Analytical Chemistry: Iron and Steel Institute: Institute of Metals.** Symposium on *The Determination of Gases in Metals.* Convocation Hall, Church House, Great Smith Street, London, S.W.1. Those wishing to attend should apply to the Secretary, Iron and Steel Institute, 4, Grosvenor Gardens, London, S.W.1. There is no registration fee, but those wishing to obtain preprints of papers can obtain them by subscribing to the bound volume of the proceedings of the meeting, which is to be published later in the year at a price of 3 guineas.

The fifth Annual General Meeting of the Western Section of the Society for Analytical Chemistry was held on Friday 8 January 1960 in Cabot House, College of Technology, Ashley Down, Bristol, England. Mr. S. Dixon, M.Sc., F.R.I.C., Chairman of the Section was in the Chair.

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

Chairman:	Dr. G. V. James
Vice-Chairman:	Dr. F. H. Pollard
Hon. Secretary-Treasurer:	Dr. T. G. Morris, B.Sc., A.R.C.S., D.I.C., Brockleigh, Clevedon Avenue, Sullay, Glamorgan, S. Wales.

The 25th Annual General Meeting of the Scottish Section of the Society for Analytical Chemistry was held on Friday 29 January 1960 at the Grosvenor Restaurant, Gordon Street, Glasgow, C.1., Scotland. Mr. A. N. Harrow, A.H.-W.C., F.R.I.C. was in the Chair.

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

Chairman:	Mr. A. N. Harrow.
Vice-Chairman:	Mr. A. F. Williams
Hon. Secretary-Treasurer:	Mr. J. Brooks, M.A., A.R.I.C., Nobel Division, Analytical Research Section, Imperial Chemical Industries Limited, Stevenston, Ayrshire, Scotland.

The 35th Annual General Meeting of the North of England Section of the Society for Analytical Chemistry was held at the Nag's Head Hotel, Lloyd Street, Manchester, England on Saturday 30 January 1960. Dr. J. R. EDISBURY was in the Chair.

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

Chairman:	Dr. J. R. EDISBURY
Vice-Chairman:	Mr. J. MARKLAND.
Hon. Secretary-Treasurer:	Mr. B. HULME, Ch. Goldrei, Foucard and Son, Ltd., Brookfield Drive, Liverpool, 9, England.

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The *ORNL Master Analytical Manual* is now available in printed form from the Office of Technical Services, Department of Commerce, Washington, 25, D.C., U.S.A. This is a collection of the analytical methods that are in use in the Analytical Chemistry Division of the Oak Ridge National Laboratory.

Section 1: *Ionic Methods:* $9.00. Section 2: *Radiochemical Methods:* $6.50. Sections 3 and 5: *Spectrographic Methods and Nuclear Analyses:* $4.50. Section 9: *Process Methods:* $9.00. Annual supplements are issued to the Manual: these will also be available from the Office of Technical Service.

The B. S. I. News announces, among others, the following new British Standards:

B.S. 3202: 1959. *Recommendations on laboratory furniture and fittings.* This contains detailed recommendations on the planning and design of laboratories and on the design, material and construction of laboratory furniture and fittings with special reference to laboratory benches, fume extraction systems and piped services. It includes bibliography, index and 31 illustrations. (Price 25s.)

B.S. 3210: 1960. *Methods for the analysis of water-soluble coal-tar dyes permitted for use in foods.* This contains specific methods for the determination of (1) matter volatile at 135°C, (2) matter insoluble in water, (3) di-*iso*propyl ether extract, (4) subsidiary dyes, (5) chloride, (6) sulphate, (7) dye content, (8) copper, arsenic and lead. A limit test for heavy metals (as sulphides) is also included. In some of the methods the details of procedure are varied according to the dye being analysed, and for details of such variations reference is required to the British Standard specification for the individual dyes concerned. (Price 7s 6d.)

B.S. 3211: 1960. *Tartrazine.* This applies to tartrazine for use in the colouring of foodstuffs. Limits are specified for matter volatile at 135°C; matter insoluble in water, di-*iso*propyl ether extract, subsidiary dyes, phenylhydrazine-*p*-sulphonic acid, chloride and sulphate, dye content, copper, arsenic, lead and heavy metals (as sulphides). (Price 3s.)

B.S. 3218: 1960. *Test tubes and boiling tubes.* This specifies length, external diameter, and two alternative wall thicknesses, with tolerances on each, for thirteen sizes of test tubes and boiling tubes made of soda glass or borosilicate glass and suitable for general laboratory use. The material and the finish of the top of the tubes are also specified. (Price 3s.)

The following Standards have been revised:

B.S. 1428: Microchemical Apparatus: Part A 4: 1960. *Halogen and sulphur combustion train (micro-Grote).* This specifies the components of the micro-Grote combustion train including a combustion tube of clear fused quartz, a borosilicate absorption vessel and a small electric heater for use as an alternative to the Bunsen burner. A U-tube is specified instead of a gas-washing bottle, and protective sheaths of nickel sheet instead of wire gauze. Dimensioned drawings and an assembly drawing of the whole train are included, and an innovation is the inclusion of notes outlining the method of use of the apparatus. *B.S. 1428: Parts A1 and A2* are referred to for components standardised for use in the combustion trains specified in those two parts. (Price 4s.)

B.S. 1016: Methods for the analysis and testing of coal and coke: Part 9: 1960. *Phosphorus in coal and coke.* This deals with the determination of phosphorus by the titrimetric or the colorimetric method. In the latter case either hydrazine sulphate or stannous chloride may be used for the reduction. (Price 4s 6d.)

B.S. 1017: Sampling of coal and coke: Part 1: 1960. *Sampling of coal.* Methods of sampling and sample preparation are detailed for coal and are summarised in an appendix. Other appendices describe methods of assessing sampling accuracy, give recommendations on the procedure for sample preparation, and present evidence in support of the principles stated. (Price 25s.)

B.S. 1017: Sampling of coal and coke: Part 2: 1960. *Sampling of coke.* Methods of sampling and sample preparation are detailed for coke and are summarised in an appendix. Other appendices explain the collection and use of statistical data on sampling, and describe methods of sampling for special purposes. (Price 25s.)

B.S. 1428: Microchemical apparatus. Part B2: 1960. *Ammonia distillation apparatus (Markham).* This specifies a steam-jacketed ammonia distillation apparatus of the Markham type and permits, as an alternative, a spherical ground-glass joint connection between the distillation vessel and condenser. The latter is as specified in *B.S. 1948.* Mandatory and recommended dimensions are given on a detailed diagram, and notes on the method of use of the apparatus are included. (Price 3s.)

B.S.I. Publications may be obtained from the B.S.I. Sales Branch, 2, Park Street, London, W.1., England.

Talanta, 1960, Vol. 4, p. 87. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Estimation of small amounts of amines by means of cationite paper. A. Lewandowski and A. Jarczewski. (29 *December* 1959).

2:5-Dihydroxy-*p*-benzoquinone as an analytical reagent for the gravimetric determination of thorium and zirconium. B. D. Jain and S. P. Singhal. (30 *December* 1959).

Spectrophotometric determination of phosphate using lanthanum chloranilate. Kiyoko Hayashi, Taeko Danzuka and Keihei Ueno. (30 *December* 1959).

Determination of ^{131}I, ^{137}Cs and ^{140}Ba in fluid milk by gamma spectroscopy. C. R. Hagee, G. J. Karches and A. S. Goldin. (28 *January* 1960).

The application of the cathode ray polarograph to the analysis of explosives, III. Simultaneous determination of nitroglycerine and dinitroglycol. J. Hetman. (1 *February* 1960).

A self-sampling indicator tube for oxygen. B. E. Dixon and P. R. Kiff. (4 *February* 1960).

Über die Anfänge der kolorimetrische Analyse. F. Szabadváry. (10 *February* 1960).

The photometric determination of alcohols by means of vanadium oxinate. Motoharu Tanaka. (10 *February* 1960).

Determination of lead, cadmium and zinc ions in the presence of large excess of sodium ions by means of the alternating current polarograph. Takeo Takahashi and Hideko Shirai. (10 *February* 1960).

Potentiometrische Untersuchung einiger Fallüngs und Komplexierungsreaktionen des Silbers in stark alkalischem Medium. G. H. Facsko and R. Minges. (15 *February* 1960).

The ultraviolet spectra of some inorganic solids. William H. Waggoner and Moss E. Chambers. (15 *February* 1960).

A polarographic wave for fluoride. C. P. Wallis. (16 *February* 1960).

A new colour reaction for alkali metal ions. F. E. Critchfield and J. P. Johnson. (22 *February* 1960).

Further comments on metalfluorechromic indicators. D. H. Wilkins. (23 *February* 1960).

The precipitation of metal 8-hydroxyquinolates from homogeneous solution, I: Preparation of 8-acetoxyquinoline. Eugene D. Salesin and Louis Gordon. (24 *February* 1960).

New method for "ferrous iron" and "excess oxygen" in rocks, minerals and oxides. C. Oliver Ingamells. (26 *February* 1960).

N:N:N′:N′-Tetracarboxymethyl derivatives of some benzidines as metallofluorescent indicators. R. Belcher, D. I. Rees and W. I. Stephen. (26 *February* 1960).

New redox systems, II: Oxidation of cobalt^{II} with iron^{III} chloride in 1:10-phenanthroline solution. Frantisek Vydra and Rudolf Přibil. (29 *February* 1960).

Untersuchung der Kationensorption aus Komplexanmedium, I: Das Verhalten von Mangan und Erdkalien. Paval Povondra, Rudolf Přibil and Zdenek Sulcek. (29 *February* 1960).

Talanta, 1960, Vol. 4, p. 88. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Optische Daten zur Bestimmung anorganischer Substanzen mit dem Polarisations-mikroskop: Ernst Kordes. Verlag Chemie, Weinheim, 1960. Pp. 192. DM 43.

Crystals and the Polarising Microscope: N. H. Hartshorne and A. Stuart, 3rd Edition. Edward Arnold (Publishers), Ltd., London, 1960. Pp. xv + 557. 80s.

Handbuch der mikrochemischen Methoden, Band I, Teil 2: Waagen und Geräte zur anorganischen Mikro-Gewichtsanalyse: A. A. Benedetti-Pichler und F. Hecht. Springer-Verlag, Wien, 1959. Pp. 307. $19.05.

Proceedings of the International Symposium on Microchemistry. Symposium Publications Division, Pergamon Press Limited, London and New York, 1960. Pp. xxvi + 583. 100s.

The following publications have been received and are available from the Office of Technical Services, Department of Commerce, Washington, 25, D.C., U.S.A.

A Colorimetric Method for Rapid Determination of Traces of Selenium: E. M. Ray. GAT-289. *December* 1959. Pp. 11. $0.50.

Determination of Hydrogen in Solid Hydride Compounds by Use of Induction Heating: R. A. Dunleavy, M. R. Menke and E. W. Rebol. APEX 243. *January* 1956, Re-issue *December* 1959. Pp. 8. $0.50.

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. Summaries will not be required for short or preliminary communications. For other contributions the essential contents of each paper should be briefly recapitulated in a summary at the beginning of the paper. This should be in the language of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

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6. 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.

7. Except in the case of preliminary communications, proofs will be sent to authors for correction when their contribution is first set, but there is rarely time for page proofs also to be sent for checking. This will be done, however, when the amount of alteration makes it advisable.

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MARCH 1960 VOLUME 4 NUMBER 1

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