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TITRIMETRIC DETERMINATION OF SOLUBLE SILICA AS MOLYBDOSILICIC ACID

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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 ($[NH_4]_6Mo_7O_{24}\cdot 4H_2O$, G.R.) in 100 ml of water.

0·04*N ferrous solution:* Dissolve 4 g of ferrous ammonium sulphate ($Fe[NH_4]_2[SO_4]_2\cdot 6H_2O$, 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.

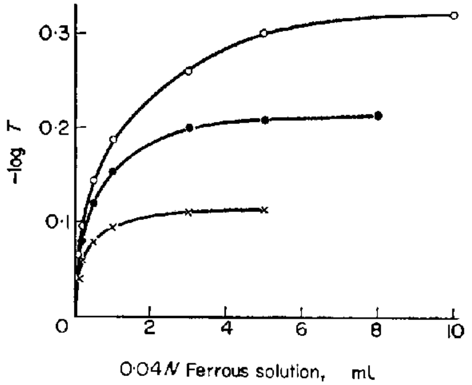

FIG. 1.—Reduction by ferrous ion in sulphuric acid solution.
Factor of ferrous solution: 0·964
SiO_2: ○ 0·126 mg
● 0·084 mg
× 0·042 mg

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

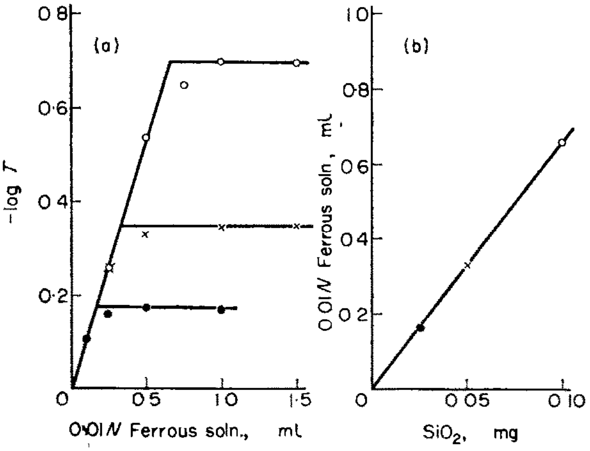

FIG. 2.—Reduction by ferrous ion in oxalic acid solution.
Factor of ferrous solution: 1·008
SiO$_2$: ○ 0·1 mg
× 0·05 mg
● 0·025 mg

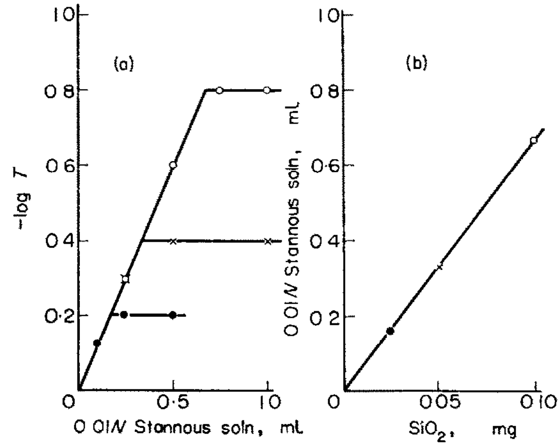

FIG. 3.—Reduction by stannous ion in sulphuric acid solution.
Factor of stannous solution: 1·024
SiO$_2$: ○ 0·1 mg
× 0·05 mg
● 0·025 mg

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 6N 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 0·01N 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.

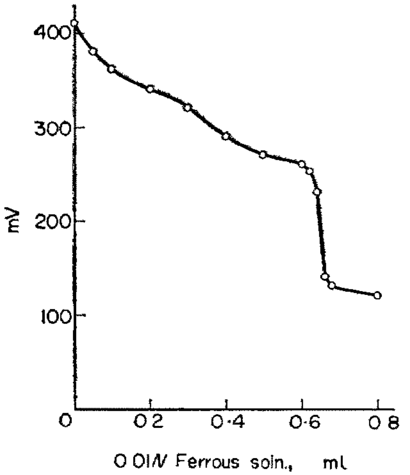

FIG. 4.—Potentiometric titration curve of silicomolybdic acid with 0·01N Fe^{II} solution (f = 1·008) in oxalic acid.

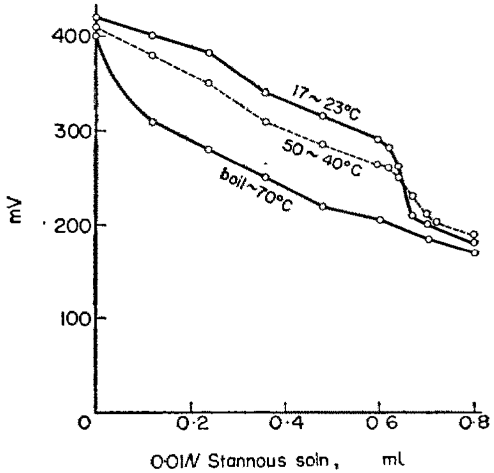

FIG. 5.—Potentiometric titration curves of silicomolybdic acid with 0·01N Sn^{II} solution (f = 1·010) in sulphuric acid.

From the curve, 0·1 mg of silica is equivalent to 0·65 ml of 0·01N 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 6N sulphuric acid and 1 ml of 2·5% ammonium molybdate solution and allowed to stand for several minutes. After adding 5 ml of 6N sulphuric acid and dilution with water to about 25 ml, the solution was titrated with 0·01N 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 0·01N 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°.

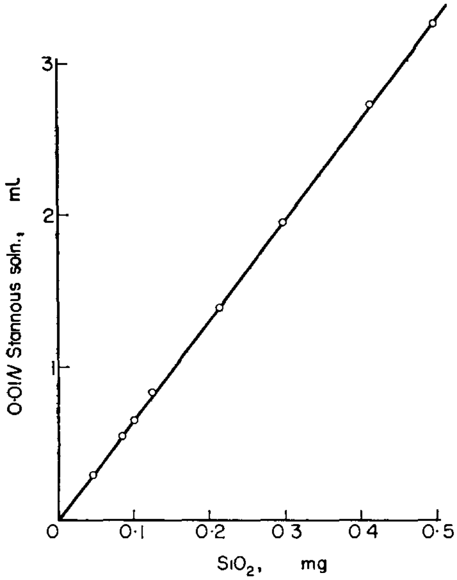

FIG. 6.—Calibration curve for silica in the potentiometry.

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 ~ 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

REFERENCES

[1] D. F. Boltz, Thomas DeVries and M. G. Mellon, *Analyt. Chem.*, 1949, **21**, 563.
[2] J. D. H. Strickland, *J. Amer. Chem. Soc.*, 1952, **74**, 862, 868, 872.
[3] M. A. DeSesa and L. B. Rogers, *Analyt. Chem.*, 1954, **26**, 1278.
[4] R. L. Pecsok and R. M. Parkhurst, *ibid.*, 1955, **27**, 1920.
[5] R. M. Vietsman, *Zavodskaya Lab.*, 1957, **23**, 153, *Chem. Abs.*, 1957, **51**, 17588.
[6] F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, D. van Nostrand Company, Inc., New York, 1949.

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EINE NEUE SCHNELLMETHODE ZUR BESTIMMUNG VON THORIUM

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

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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 $\cong$ 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

LITERATUR

[1] W. R. Schoeller u. A. R. Powell, *The analysis of Minerals and Ores of the Rarer Elements.* Charles Griffin, London, 1955. s. 156–167.

[2] G. W. C. Milner u. J. W. Edwards, *Analyt. Chim. Acta*, 1959, **20**, 1.

[3] H. Flaschka, K. ter Haar u. J. Bazen, *Mikrochim. Acta*, 1953, 345.

[4] J. Fritz u. J. Ford, *Analyt. Chem.*, 1953, **25**, 1640; 1954, **26**, 1206.

[5] V. Suk, M. Malat u. O. Ryba, *Coll. Czech. Chem. Comm.*, 1954, **19**, 679.

[6] C. Bannerjee, *Z. analyt. Chem.*, 1955, **148**, 349.

[7] V. Narayana Rao u. G. Gopala Rao, *ibid.*, 1957, **155**, 334.

[8] R. Přibil u. E. Körös, *Magyar Kém. Folyóirat*, 1958, 64, 55.

[9] R. Přibil u. K. Burger, *ibid.*, 1959, 65, 204.

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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.

REFERENCES

[1] F. Hecht and W. R. Rohrwig, *Monatsh.*, 1929, **53**, 596.
[2] R. Schwarz, *Helv. Chim. Acta.*, 1920, **3**, 330: *Chem. Abs.*, 1921, **15**, 641.
[3] G. Canneri and L. Fernandes, *Gazzetta*, 1924, **54**, 770: *Chem. Abs.*, 1925, **19**, 1389.
[4] L. F. Nilson, *Ber.*, 1882, **15**, 2520.
[5] O. Hauser, *Z. analyt. Chem.*, 1908, **47**, 677: *Chem. Abs.*, 1909, **3**, 406.
[6] P. Ray and M. K. Bose, *Z. analyt. Chem.*, 1933, **95**, 400: *Chem. Abs.*, 1934, **28**, 1625.
[7] W. R. Schoeller and H. W. Webb, *Analyst*, 1933, **58**, 143: *Chem. Abs.*, 1933, **27**, 2110.
[8] P. N. Das Gupta, *J. Indian Chem. Soc.*, 1929, **6**, 777: *Chem. Abs.*, 1930, **24**, 1312.
[9] *Idem*, *J. Indian Chem. Soc.*, 1929, **6**, 763: *Chem. Abs.*, 1930, **24**, 1312.
[10] *Idem*, *Analyst*, 1930, **55**, 154.
[11] W. A. Turner, *Amer. J. Sci.*, 1916, **42**, 109: *Chem. Abs.*, 1916, **10**, 2444.
[12] V. Auger, *Compt. rend.*, 1920, **170**, 995.
[13] J. A. Holladay and T. R. Cunningham, *Trans. Amer. Electrochem. Soc.*, 1923, **43**, 329: *Chem. Abs.*, 1923, **17**, 1768.
[14] E. A. Ostroumov and R. I. Bomshtein, *Zavodskaya Lab.*, 1939, **8**, 558: *Chem. Abs.*, 1940, **34**, 5783.
[15] H. Hovorka and J. Voříšek, *Chem. Listy*, 1940, **34**, 55: *Chem. Abs.*, 1940, **34**, 5783.
[16] H. Hovorka and V. Sykora, *Coll. Czech. Chem. Comm.*, 1938, **10**, 182: *Chem. Abs.*, 1938, **32**, 5723.
[17] E. A. Ostroumov, *Zavodskaya Lab.*, 1937, **6**, 16: *Chem. Abs.*, 1937, **31**, 4616.
[18] G. M. Saxena and T. R. Seshadri, *Proc. Indian Acad. Sci.*, 1958, **47**, 238.
[19] R. Anschütz, *et al.*, *Annalen*, 1909, **367**, 169: *Beilstein*, 1933, **17**, 569.
[20] R. Anschütz *et al.*, *Ber.*, 1903, **36**, 465: *Annalen*, 1909, **367**, 169.
[21] A. Sonn, *Ber.*, 1917, **50**, 1292.
[22] K. H. Bauer and F. Schoder, *Arch Pharm.*, 1921, **259**, 53.
[23] M. A. Stahman, I. Wolff and K. P. Link, *J. Amer. Chem. Soc.*, 1943, **65**, 2285.
[24] H. R. Eisenhauer and K. P. Link, *ibid.*, 1953, **75**, 2044.

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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.

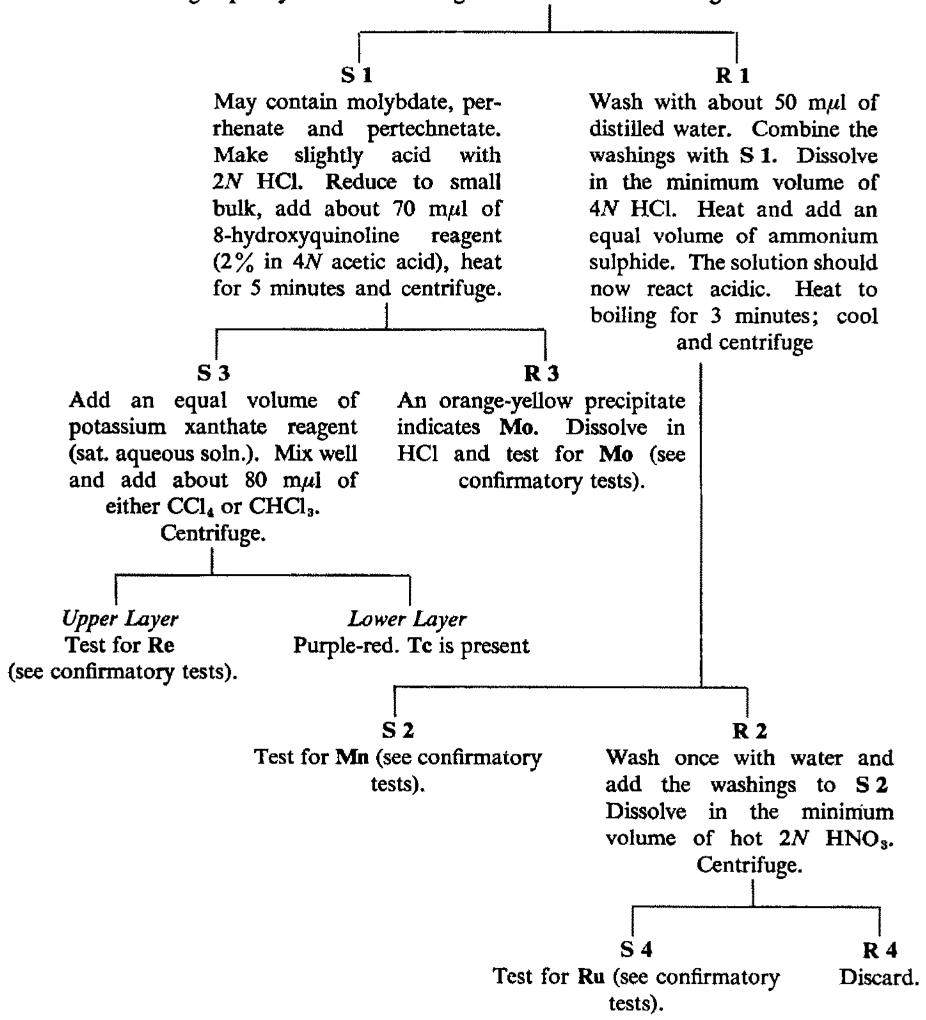
Reagents: 10% sodium hydroxide solution; benzidine, 0·05 g in 100 ml of 10% acetic acid.

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.

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 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.

R 3
An orange-yellow precipitate indicates **Mo**. Dissolve in HCl and test for **Mo** (see confirmatory tests).

Upper Layer
Test for **Re**
(see confirmatory tests).

Lower Layer
Purple-red. **Tc** is present

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.[8] 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 $m\mu l$ of the neutral or slightly acid test solution with about 70 $m\mu l$ 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 $m\mu l$ of 1% $FeCl_3$ solution. Agitate and add sufficient concentrated ammonia to precipitate the iron present. Centrifuge.

R 1

Yellow precipitate

Estimate as under Molybdenum (oxinate, p. 21). Wash once with boiling water and combine the washings with S 1.

S 2

Add 50 $m\mu l$ 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.

R 2

Wash once with water and combine the washings with S 2. Dissolve in the minimum of dil. H_2SO_4. Add 30 $m\mu l$ of 6% H_2O_2. Re-precipitate the ferric hydroxide with concentrated ammonia added in small amounts at a time with stirring. Centrifuge.

S 3

Discard.

R 3

Black precipitate.

Estimate as rhenium sulphide. (p. 22)

S 4

Reduce in bulk. Make just alkaline. Add 70 $m\mu l$ of tetraphenylarsonium chloride reagent (1%). Centrifuge for 7 mins.

R 4

Discard.

S 5

Discard.

R 5

White precipitate

Estimate as tetraphenylarsonium pertechnetate. (p. 22).

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 $m\mu l$ 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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the loan of 1 mg of technetium which was of value in confirming the preliminary results obtained on ultramicro quantities.

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.

REFERENCES

[1] R. J. Magee, I. A. P. Scott and C. L. Wilson, *Talanta*, 1959, **2**, 376.

[2] J. B. Gerlit, *Report to International Conference on the Peaceful Uses of Atomic Energy*, A/Conf. 8/P/671. U.S.S.R., 5th July, 1955. (H.M.S.O.).

[3] R. J. Magee, *Technetium: Comprehensive Analytical Chemistry*, Vol. Ic, Elsevier Publishing Co., Amsterdam, in press.

[4] E. H. Huffman, R. L. Oswalt and L. A. Williams, *J. Inorg. Nuclear Chem.*, 1956, **3**, 49.

[5] M. Nelson, J. K. Foreman and E. Kemp, *Windscale Progress Reports*, A.R.D.C., pp. 77, 101, 121, 147; G. P. Cook and J. Foreman, *ibid.*, IGC., A.R.D.C., p. 223.

[6] F. Jasim, R. J. Magee and C. L. Wilson, *Talanta*, 1959, **2**, 93.

[7] A. A. Benedetti-Pichler, *Introduction to the Microtechnique of Inorganic Analysis*, Wiley and Sons, Inc., New York, 1950.

[8] H. M. El-Badry and C. L. Wilson, *Mikrochemie*, 1952, **40**, 141.

[9] P. E. Wenger and R. Duckert, *Reagents for Qualitative Inorganic Analysis*, Elsevier Publishing Co., Amsterdam, 1948.

[10] F. Feigl, *Spot Tests in Inorganic Analysis*, Elsevier Publishing Co., Amsterdam, 1958.

[11] E. B. Sandell, *Colorimetric Determination of Traces of Metals*, Interscience Publishers, Inc., New York. 1944.

[12] J. H. W. Forsythe, R. J. Magee and C. L. Wilson, *Talanta*, 1959–60, **3**, 324, 330.

[13] H. H. Willard and G. M. Smith, *Ind. Eng. Chem. Anal.*, 1939, **11**, 305.

[14] R. G. W. Hollingshead, *Oxime and its Derivatives*, Vols. I–IV, Butterworths Scientific Publications, 1954–1956.

Talanta, 1960, Vol. 4, pp. 25 to 32. Pergamon Press Ltd. Printed in Northern Ireland

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.

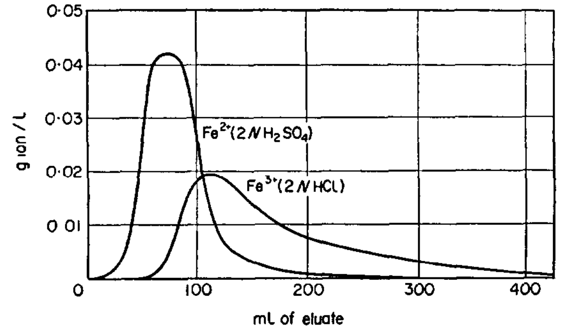

FIG .1.

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) 0·01*N* and 4*N* 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) 0·1*N* 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 4*N* 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 4*N* sulphuric acid and excess acid is washed out with 100 ml of 0·01*N* sulphuric acid.

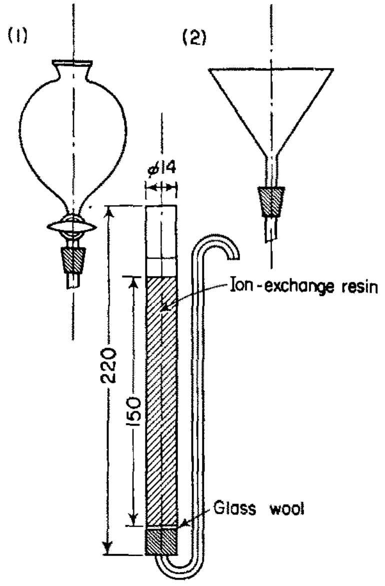

Fig. 2.

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 0·2*N*, 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 0·1*N* 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 0·01*N* sulphuric acid until a small amount of the effluent solution does not bleach 1 ml of 0·01*N* potassium permanganate solution. Iron^{II} ions are then eluted with 200 ml of 4*N* 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$^{\text{II}}$ and tin$^{\text{IV}}$ ions correspond to the appearance of the first traces of ions, while in the case of iron$^{\text{II}}$ 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
$E^{\text{II}}_{\text{tin}}$ (first traces)	0·10	0·06	0·05	0·06
$E^{\text{IV}}_{\text{tin}}$ (first traces)	0·61	0·27	0·11	0·06
$E^{\text{II}}_{\text{iron}}$ (last traces)	0·21	0·21	0·20	0·19

According to the figures tin$^{\text{II}}$ ions can be bound even in a 2N hydrochloric acid medium. On the other hand a higher acid concentration ($>3N$) is needed when tin$^{\text{IV}}$ ions are to be bound. The negligible sorption of iron$^{\text{II}}$ 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$^{\text{IV}}$ 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$^{\text{II}}$ ions is then required, and the oxidimetric determination of iron$^{\text{II}}$ 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 0·1N iron$^{\text{III}}$ chloride can be reduced and eluted in the 3N hydrochloric acid without elution of tin$^{\text{II}}$ ions. At the third reduction, however, tin$^{\text{IV}}$ ions appear in the effluent solution together with iron$^{\text{II}}$ ions. Complete removal of tin$^{\text{II}}$ and tin$^{\text{IV}}$ ions, *i.e.* complete regeneration of the column is a very lengthy process when 0·005N 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$^{\text{II}}$ ions, titration of the latter can again be carried out with 0·1N 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$^{\text{III}}$ ions on an anion-exchange-stannous column

Reagents: (1) 3N hydrochloric acid. (2) Tin$^{\text{II}}$ chloride solution: Dissolve 10 g of crystallised tin$^{\text{II}}$ chloride in 75 ml of 2 + 1 HCl with heating, and make it up to 100 ml. (3) 0·1N cerium$^{\text{IV}}$ sulphate standard solution. (4) Ferroïn indicator solution: Dissolve 1·624 g of *o*-phenanthroline hydrochloride and 0·695 g of iron$^{\text{II}}$ 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) 0·1N 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 0·5N 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.

REFERENCES

[1] H. G. Cassidy, M. Ezrin and J. H. Updegraff, *J. Amer. Chem. Soc.*, 1953, **75**, 1615.
[2] B. Sansoni, *Naturwiss.*, 1952, **39**, 281.
[3] L. Erdey and E. Bodor: *Analyt. Chem.*, 1952, **24**, 418.
[4] W. Fischer, R. Paul and H. J. Abendroth, *Analyt. Chim. Acta.* 1955, **13**, 38.
[5] Y. Yosimo, *Bull. Chem. Soc. Japan*, 1953, **26**, 401.

[6] V. Fleps and J. Inczédy, *Magyar. Kém. Folyóirat*, 1956, **62**, 322.
[7] F. Haber and J. Weiss, *Proc. Roy. Soc. A.*, 1934, **147**, 332.
[8] W. G. Barb, J. H. Basendale, P. Eorge and K. R. Hargrave, *Trans. Faraday Soc.* 1951, **47**, 462.
[9] K. A. Kraus and F. Nelson, *Proc. International Conf. Peaceful Uses of Atomic Energy*, Paper 837, 1956, **7**, 113.
[10] D. Jentzsch, *Z. analyt. Chem.*, 1956, **152**, 134.
[11] D. Jentzsch and I. Pawlik, *Z. analyt. Chem.*, 1955, **146**, 88.
[12] D. Jentzsch, *ibid.*, 1956, **148**, 321.

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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.†

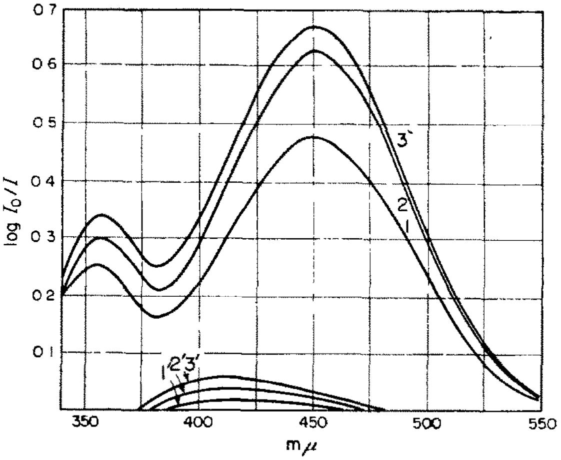

FIG. 1.—Absorption curves for developed and blank solutions.
2 ml of glucose solution, (80 μg/ml) heated with 1 ml of 3:6-dinitrophthalic acid solution and 1 ml of sodium carbonate solution for (1) 5, (2) 10, (3) 15 mins, and diluted to 20 ml. (1'), (2') and (3') are the corresponding blanks.

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.

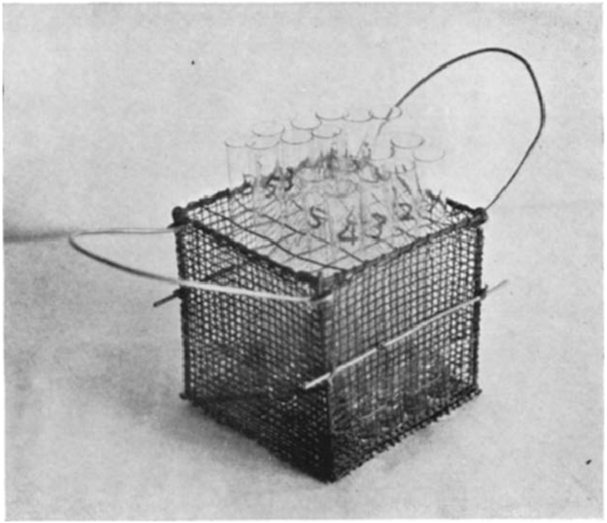

FIG. 2.—Heating basket.

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.

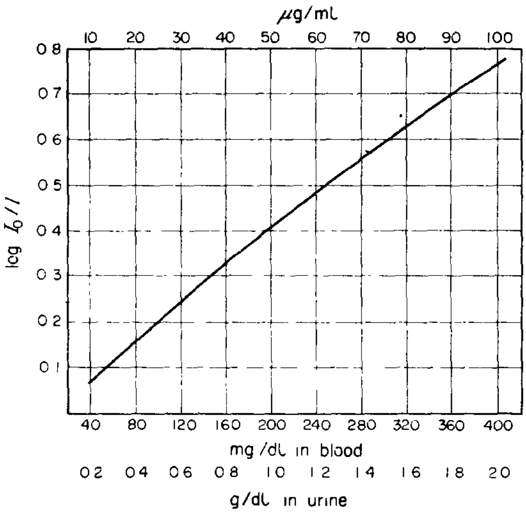

FIG. 3.—Calibration curve.

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.

REFERENCES

[1] T. Momose and A. Inaba, *Chem. Pharm. Bull.* (Tokyo), 1959, **7**, 541.
[2] C. D. Braun, *J. Prakt. Chem.*, 1865, **96**, 411.
[3] J. B. Sumner and V. A. Graham, *J. Biol. Chem.*, 1921, **47**, 5.
[4] E. Borel and H. Deuel, *Helv. Chim. Acta*, 1953, **36**, 801.
[5] T. Momose and M. Torigoe, *Yakugaku Zasshi*, 1951, **71**, 977.
[6] M. Somogyi, *J. Biol. Chem.*, 1945, **160**, 69.
[7] H. C. Hagedorn and B. N. Jensen, *Biochem. Z.*, 1923, **135**, 46.

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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	λ_{max} mμ	I_f	λ_{max} mμ	I_f	λ_{max} mμ	I_f	λ_{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.

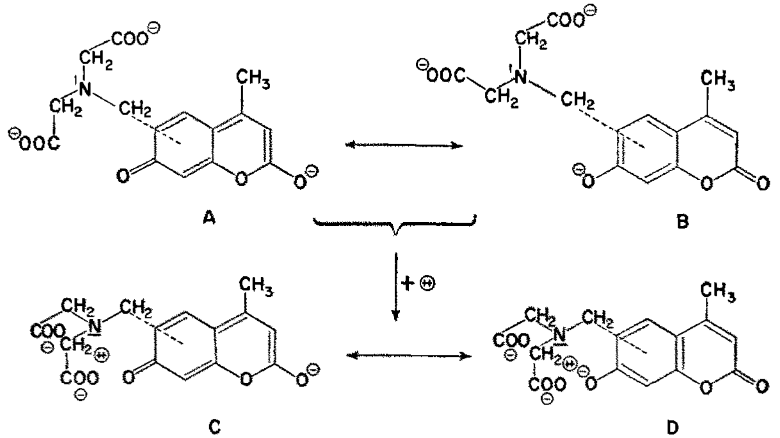

ABB. 1.

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 0,02*M* ÄDTE und 2 ml 0,02*M* Kationsalzlösung gegeben, dann mit 0,1*M* Borax bzw 0,5*N* 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 0,05*M* und 5 ml 0,02*M* Kationsalzlösung gegeben, dann mit 0,1*M* Borax bzw 0,5*N* 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 0,5*N* NaOH wurde durch Messung der Fluoreszenzintensität verfolgt (UK-Konzentration 0,1%, analog den sonstigen Fluoreszenzmessungen mit entsprechendem Ca^{2+}-Uberschuss, 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 0,5*N* 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 0,5*N* 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 0,5*N* 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 0,02*M* Ca-perchlorat zur warmen Lösung bewirkt prächtige Fluoreszenz; tropfenweiser Zusatz von 0,02*M* ÄDTE lässt diese mit scharfem Umschlag wieder verschwinden.

B: Eine Spatelspitze Indikator und eine Spatelspitze ÄDTE werden in 50 ml 0,5*N* 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.

LITERATURVERZEICHNIS

[1] D. H. Wilkins, *Talanta*, 1959, **2**, 277.
[2] *Idem*, *Analyt. Chem.*, 1959, **31**, 39A.
[3] J. H. Eggers, *Svensk Kem. Tidskr.*, 1958, **70**, 332.—Vortragsreferat
[4] *Idem*, *ibid.*, 1959, **71**, 399.—Vortragsreferat
[5] H. Diehl und J. L. Ellingboe, *Analyt. Chem.*, 1956, **28**, 882.
[6] D. F. Hoelzl Wallach, D. M. Surgenor, J. Soderberg und E. Delano, *ibid.*, 1959, **31**, 456.
[7] J. Körbl und F. Vydra, *Chem. Listy.*, 1957, **51**, 1457.
[8] H. Musso und H. G. Matthies, *Naturwiss.*, 1959, **46**, 15.
[9] G. Kortüm und G. Dreesen, *Ber.*, 1951, **84**, 182.
[10] G. Oster und Y. Nishijima, *J. Amer. Chem. Soc.*, 1956, **78**, 1581.
[11] J. Körbl, F. Vydra und R. Přibil, *Talanta*, 1958, **1**, 281.

Talanta, 1960, Vol. 4, pp. 44 to 50. Pergamon Press Ltd. Printed in Northern Ireland

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**.

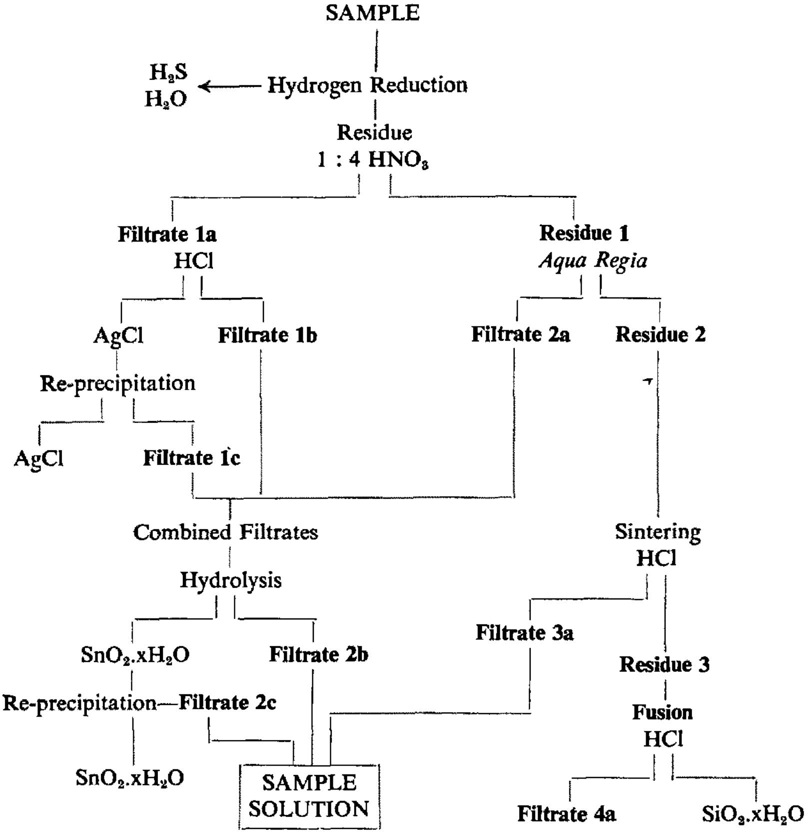

FIG. 1.—Flowsheet

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$^{\text{III}}$ 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]

REFERENCES

[1] E. Wichers, W. G. Schlecht and C. L. Gordon, *J. Res. Nat. Bur. Stand.*, 1944, **33**, 363
[2] C. L. Gordon, W. G. Schlecht and E. Wichers, *ibid.*, 457.
[3] M. Hill and F. E. Beamish, *Analyt. Chem.*, 1958, **30**, 414.
[4] A. D. Westland and F. E. Beamish, *ibid.*, 1954, **26**, 739.
[5] W. F. Roger, F. E. Beamish and D. S. Russel, *Ind. Eng. Chem. Anal.*, 1940, **12**, 561.
[6] R. Gilchrist, *J. Res. Nat. Bur. Stand.*, 1934, **12**, 291.

[7] H. G. Coburn, F. E. Beamish and C. L. Lewis, *Analyt. Chem.*, 1956, **28**, 1297.

[8] A. Marks and F. E. Beamish, *ibid.*, 1958, **30**, 1464.

[9] F. Seath and F. E. Beamish, *Ind. Eng. Chem. Anal.*, 1937, **9**, 373.

[10] A. D. Westland and F. E. Beamish, *Mikrochim. Acta*, 1957, 625.

[11] J. E. Currah, W. A. E. McBryde, A. F. Cruickshank and F. E. Beamish, *Ind. Eng. Chem. Anal.*, 1946, 18, 120.

[12] R. Gilchrist, *J. Res. Nat. Bur. Stand.*, 1932, **9**, 547.

[13] S. S. Berman and W. A. E. McBryde, *Canad. J. Chem.*, 1958, **36**, 845.

[14] G. Tertipis and F. E. Beamish, in press.

Talanta, 1960, Vol. 4, pp. 51 to 60. Pergamon Press Ltd. Printed in Northern Ireland

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.

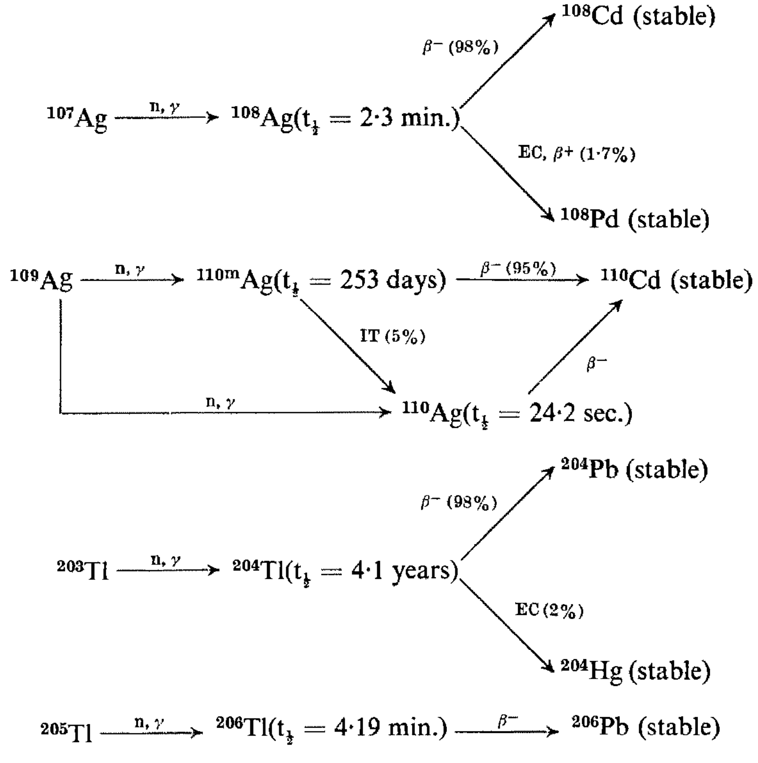
The principles of radioactivation analysis have been extensively reviewed[5–9] and will not be discussed here. The method avoids various possible sources of error inherent in emission and mass spectroscopic procedures, and also offers important advantages over chemical methods for the determination of 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, $= 51{\cdot}35\%$) and ^{109}Ag ($\theta = 48{\cdot}65\%$). Thallium also exists as two stable isotopes, ^{203}Tl ($\theta = 29{\cdot}50\%$) and ^{205}Tl ($\theta = 70{\cdot}50\%$). 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	$\sigma = 44$ barns
^{109}Ag(n, γ)^{110m}Ag	$\sigma = 2{\cdot}8$ barns
^{109}Ag(n, γ)^{110}Ag	$\sigma = 110$ barns
^{203}Tl(n, γ)^{204}Tl	$\sigma = 8$ barns
^{205}Tl(n, γ)^{206}Tl	$\sigma = 0{\cdot}10$ 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.

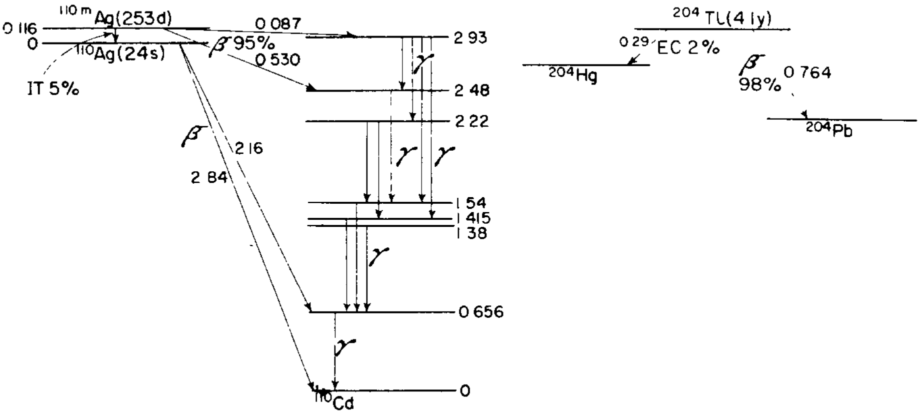


FIG. 1.—Decay schemes for ^{110m}Ag–^{110}Ag and for ^{204}Tl. Energies are in MeV.

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^{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^{I} carrier: 10 mg Tl/ml (added as $TlNO_3$ in very dilute HNO_3)–standardised.
Fe^{III} carrier: 10 mg Fe/ml (added as $FeCl_3\cdot 6H_2O$ in very dilute HCl).
Pb^{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 $6M$ 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 $6M$ 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 $3M$ 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 $6M$ 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 0·5M KI dropwise until precipitation of Tl^I is complete. Centrifuge and discard the supernate.

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

Step 20. Extract the thallium by agitating with 10 ml of ether saturated with $4M$ HCl. Separate the ether phase and wash it 3 times with 10-ml portions of $4M$ HCl saturated with ether. Then mix the ether phase with 10 ml of $1N$ 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 0·5M KI. Cool, centrifuge and discard the supernate.

Step 23. To the precipitate add 4 drops of La carrier and 1 ml of $6M$ 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 ≡ 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.

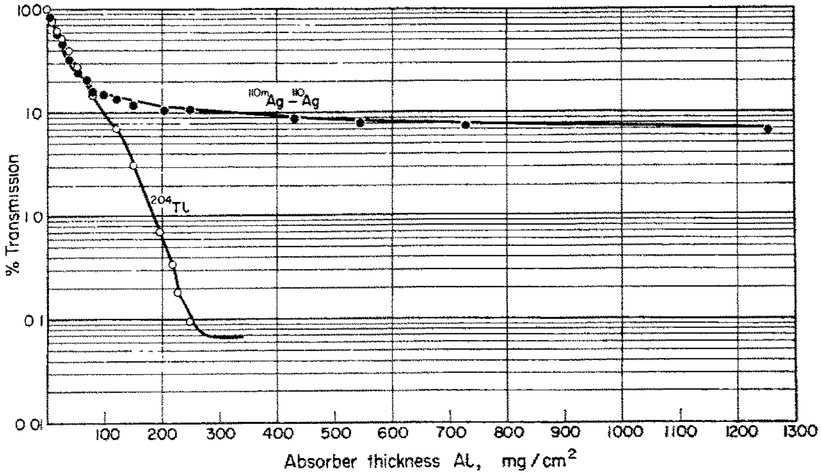


FIG. 2.—Aluminium absorption curves of ^{110m}Ag–^{110}Ag and ^{204}Tl. The full curves are for purified tracers (supplied by the Radiochemical Centre, Amersham) coprecipitated with silver iodate and thallous chromate. The recorded points are for final precipitates from the analysis of a rock sample.

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.

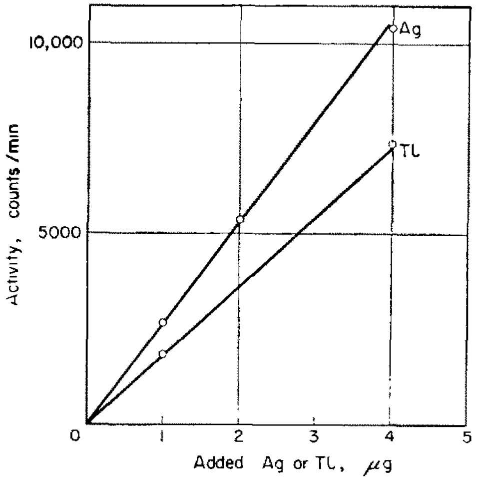


FIG. 3.—Activity due to added silver and thallium in neutron-irradiated standards plotted against the weight of added silver and thallium. Each point is the average of two measurements.

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—

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

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

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

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[8].

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[10].

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	1·03
			0·028	1·06
			0·030	1·04
			0·028	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	0·047
			0·041	0·049
			0·038	0·046
			0·041	0·048
3645(H107)	Syenogabbro	S. slope of Gallow Hill	0·44	0·046
			0·46	0·045
			0·47	0·047
			0·43	0·045
3731(H51)	Syenite	S. W. slope of Gallow Hill	0·040	0·31
			0·032	0·28
			0·039	0·26
			0·038	0·26
			0·040	0·34
			0·036	0·26
			0·033	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.

REFERENCES

[1] V. M. Goldschmidt, *Geochemistry.* Oxford University Press, 1954.
[2] D. M. Shaw, *Progr. Phys. Chem. Earth,* 1957, **2,** 164.
[3] D. M. Shaw, *Geochim. Cosmochim. Acta,* 1952, **2,** 118.
[4] R. A. Edge, R. R. Brooks, L. H. Ahrens and S. Amdurer, *ibid.,* 1959, **15,** 337.
[5] G. E. Boyd, *Analyt. Chem.,* 1949, **21,** 335.
[6] A. A. Smales, *Atomics,* 1953, **4,** 55.
[7] W. W. Meinke, *Science,* 1955, **121,** 177.
[8] R. C. Plumb and J. E. Lewis, *Nucleonics,* 1955, **13,** No. 8, 42.
[9] E. N. Jenkins and A. A. Smales, *Quart. Rev.,* 1956, **10,** 83.
[10] U.S.A.E.C. Neutron Cross Section Advisory Group. U.S. Atomic Energy Commission Document AECU-2040 and supplements.
[11] D. Strominger, J. M. Hollander and G. T. Seaborg, *Rev. Mod. Phys.,* 1958, **30,** 585.
[12] V. I. Kuznetsov and G. V. Myasogedova, *Zhur. priklad Khim.,* 1956, **29,** 1875.
[13] D. N. Sunderman and W. W. Meinke, *Analyt. Chem.,* 1958, **29,** 1578.
[14] D. F. C. Morris and R. A. Killick, *Talanta,* 1959, **3,** 34.
[15] H. Irving and F. J. C. Rossotti, *Analyst,* 1952, **77,** 801.
[16] C. J. Delbecq, L. E. Glendenin and P. H. Yuster, *Analyt. Chem.,* 1953, **25,** 350.

[17] G. Phillips and E. N. Jenkins, A.E.R.E., C/R 1534, 1954.
[18] H. W. Fairbairn *et al.*, *Bull. U.S. Geol. Surv.*, 1951, 980.
[19] L. H. Ahrens, Private communication.
[20] K. Rankama and T. G. Sahama, *Geochemistry*, University of Chicago Press, 1950.
[21] H. Hamaguchi and R. Kuroda, *Geochim. Cosmochim. Acta*, 1959, **17**, 44.
[22] *Idem*, *Nippon Kagaku Zasschi*, 1957, **78**, 1668.
[23] W. D. Ehmann and J. R. Huizenga, *Geochim. Cosmochim. Acta*, 1959, **17**, 125.

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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[8] 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		
Sb^{III}	10	6[c]	<3	No Br_2 added
Sb^{V}	5	d		Br_2 added to Sb^{III}
	1	<3		Br_2 added to Sb^{III}
As^{III}, Ba, Be	10	<3		[e]
Bi	10	<3		2 ml 1:10-phenanthroline added
B, Br, Cd, Ca	10	<3		[e]
Ce^{III}	10	<3		10 mg Ce^{IV}, 5 mg Sn^{II}
Ce^{IV}, Cr^{III}, Cr^{VI} Cs, Co, Cu, Dy, Er, 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, Ir^{IV}, La, Pb, Li, Lu, Mg, Mn^{II}, Mn^{VII}, Hg^{II}	10	<3		[e]
Mo	5	d		
	1	<3		
Nd, Ni	10	<3		[e]
Nb	10	<3		Added as fluoride solution
Pd^{II}	10	<3		
P	100	<3		Added as PO_4^{3-}
Pt^{IV}, K, Pr, Re^{VII}, Rh^{III}, Rb, Sm, Sc, 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
Te^{IV}	5	−40		Consumes TOPO. Additional 1:10-phenanthroline has no effect.
	1	−16		
	0.1	<3		
Tb, Tl^{I}, Th, Tm, Sn, Ti	10	<3		[e]
W	5	d	+8[c]	
	1	<3		
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.

REFERENCES

[1] E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Ed., Interscience Publishers, New York, 1959, pp. 537–542.

[2] W. J. Ross and J. C. White, AEC Project Report ORNL-2382 (1957).

[3] J. C. White, AEC Project Report CF-56-9 (1956).

[4] J. C. White, B. L. McDowell, and A. S. Meyer, Jr., *Spectrophotometric Determination of Iron By Formation and Measurement of the o-Phenanthroline Complex in Organic Media*, presented at The American Chemical Society Southeastern Regional Meeting, Gainesville, Florida, December, 1958.

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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 4*M* 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 3*M* 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.

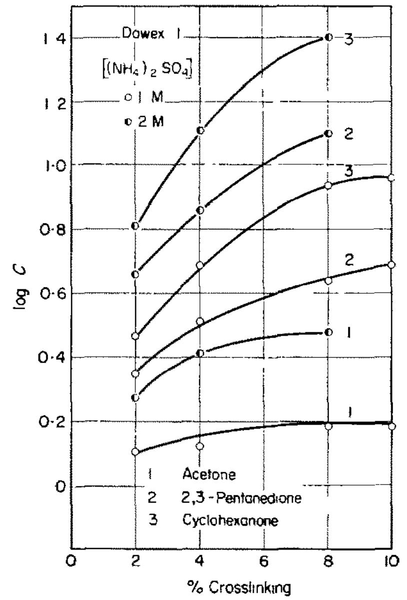

FIG. 1.—The effect of varying the crosslinking on the distribution ratio, C.

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
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
$(C_2H_5)_4N$	0.51	0.55	0.62	0.085†
$(CH_3)_4N$	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.

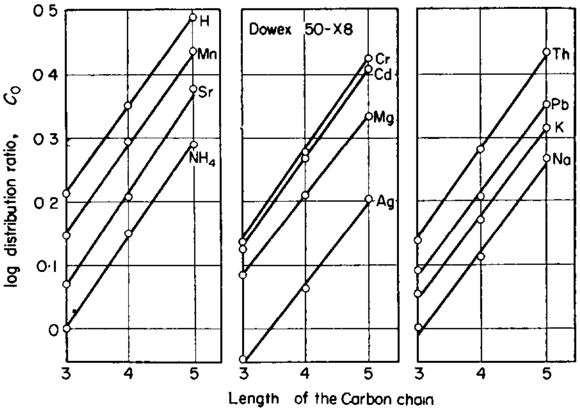

FIG. 2.—The distribution ratios, C_0, of 2-alkanones with various cationic forms of Dowex 50 as a function of the length of the carbon chain.

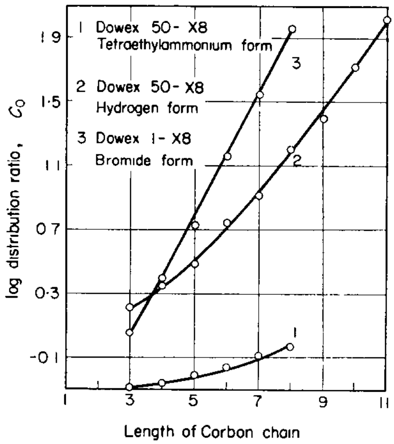

FIG. 3.—The distribution ratios, C_0, of 2-alkanones as a function of the length of the carbon chain.

Acknowledgments—A leave of absence from Upsala College, East Orange, N.J., and a fellowship from the National Science Foundation, which made it possible for one of the authors (A. B.) to co-operate in this investigation, are gratefully acknowledged. Gratitude is also expressed to The Dow Chemical Company for generous financial support and to Miss Eva Agnes Smith for assistance in some of the experimental work.

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.

REFERENCES

[1] R. Sargent and W. Rieman, *J. Phys. Chem.*, 1957, **61**, 354.
[2] *Idem*, *Analyt. Chim. Acta*, 1957, **17**, 408.
[3] *Idem*, *ibid.*, 1958, **18**, 197.
[4] A. Breyer and W. Rieman, *ibid.*, 1958, **18**, 204.
[5] J. Sherma and W. Rieman, *ibid.*, 1958, **18**, 214.
[6] *Idem*, *ibid.*, 1959, **19**, 134.
[7] *Idem*, *ibid.*, 1959, **20**, 357.
[8] W. Rieman and R. Sargent, *Ion Exchange* in *Physical Methods of Chemical Analysis*, Vol. IV, edited by W. G. Berl, Academic Press, New York, N.Y., in press.
[9] W. Rieman and A. Breyer, *Columnar Liquid-Solid Ion-Exchange Processes*, Chapter 35, Part I of *Treatise on Analytical Chemistry*, edited by I. M. Kolthoff and P. J. Elving, Interscience Publishers, New York, N.Y., in press.
[10] F. A. Long and W. F. McDevit, *Chem. Revs.*, 1952, **51**, 119.
[11] F. A. Long and R. L. Bergen, *J. Phys. Chem.*, 1956, **60**, 1131.
[12] G. Manalo, R. Turse, and W. Rieman, *Analyt. Chim. Acta*, 1959, **21**, 383.
[13] R. Sargent and W. Rieman *ibid.*, 1956, **14**, 381.
[14] H. Roe and J. Mitchell, *Analyt. Chem.*, 1951, **23**, 1758.
[15] D. Reichenberg and W. F. Wall, *J. Chem. Soc.*, 1956, 3364.
[16] A. Breyer, *Thesis*, Rutgers, The State University, New Brunswick, N.J., 1958.
[17] E. Larson, *Z. phys. Chem.*, 1931, **153**, 799.
[18] R. M. Wheaton and W. C. Bauman, *Ann. N.Y. Acad. Sci.*, 1953, **57**, 159.
[19] H. Ruckert and O. Samuelson, *Svensk. Kem. Tid.*, 1954, **64**, 337.
[20] O. D. Bonner, *J. Phys. Chem.*, 1954, **58**, 318.
[21] O. D. Bonner and L. L. Smith, *ibid.*, 1957 **61**, 329.
[22] O. D. Bonner, *ibid.*, 1958, **62**, 250.

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PRELIMINARY COMMUNICATIONS

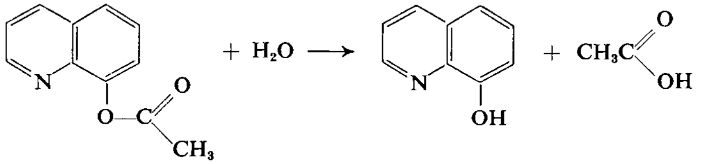
The precipitation of metal 8-hydroxyquinolates from homogeneous solution—I

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.

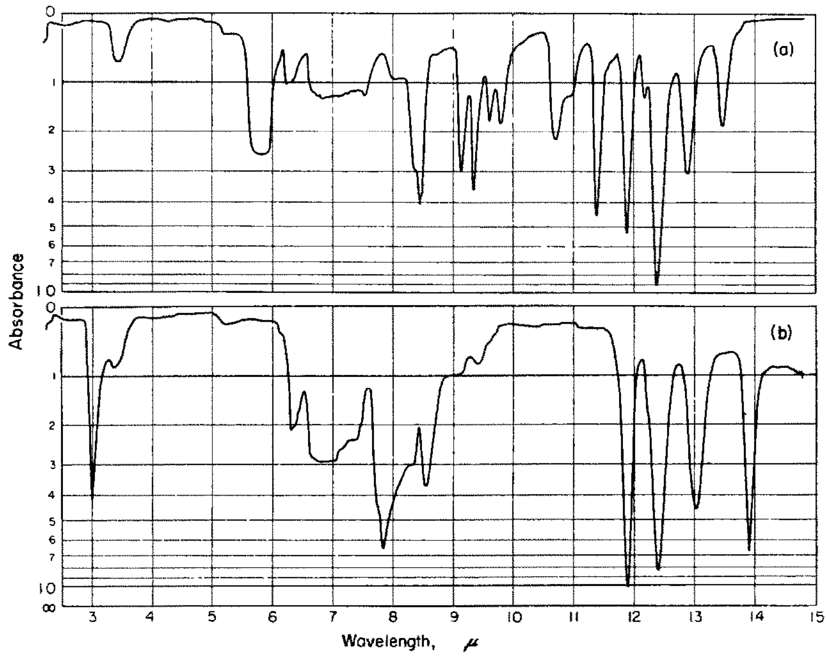


Fig. 1. Infra-red absorption spectra
(a) Upper spectrum: 8-acetoxyquinoline
(b) Lower spectrum: 8-hydroxyquinoline

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

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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 cris'talline est décrite.

REFERENCES

[1] E. L. Bickerdike and H. H. Willard, *Analyt. Chem.*, 1952, **24**, 1026.
[2] H. Skraup, *Monatsh.*, 1882, **3**, 540.
[3] W. Borsche and H. Groth, *Ann.*, 1941, **549**, 238.
[4] O. Dimroth, *ibid.*, 1926, **446**, 119.
[5] C. H. Browning, *Proc. Roy. Soc.*, 1922, [B] **93**, 345.

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

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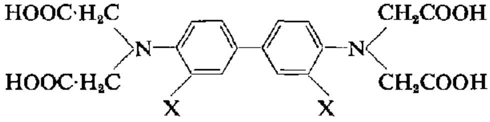
We have found that metallofluorescent complexans are formed when the 3:3′-disubstituted derivatives of benzidine are condensed with chloroacetate. The structure of these complexans is believed to be



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.

REFERENCES

[1] J. Körbl and F. Vydra, *Chem. Listy*, 1959, **51**, 1457; *Coll. Czech. Chem. Comm.*, 1958, **23**, 622.
[2] R. Belcher and A. J. Nutten, *Quantitative Inorganic Analysis*, 2nd Edition, Butterworths Scientific Publications, London, 1960.
[3] R. Belcher, R. A. Close and T. S. West, *Chem. & Ind.*, 1647, 1957.
[4] *Idem*, *Chemist-Analyst*, 1958, **47**, 2.

Talanta, 1960, Vol. 4, pp. 80 to 83. Pergamon Press Ltd. Printed in Northern Ireland

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.

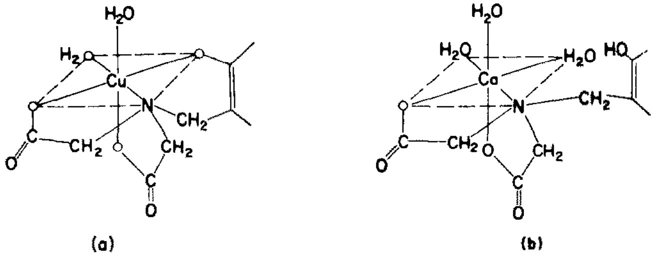


FIG. 1.

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]

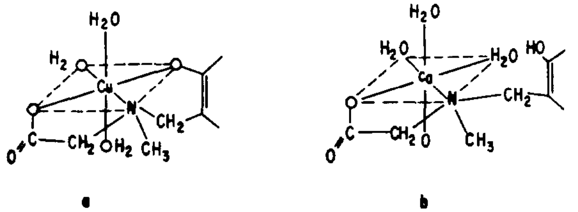
There is good reason to expect the configuration shown in Fig. 1a to be formed in a stepwise fashion. In fact one would expect the configuration shown in Fig. 1b to be one of the steps. The fact that such a stepwise formation probably exists is aptly demonstrated by the work of Schwarzenbach[6] and is 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 1*M* solution of potassium hydroxide until the indicator no longer fluoresces. Now add a few drops of a 0.03*M* calcium solution. It will be noted that the solution now fluoresces (indicator-reversal complex). To this solution add a few drops of a 0.03*M* 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.

REFERENCES

[1] J. Körbl and V. Svoboda, *Talanta* 1960, **3**, 370.
[2] D. H. Wilkins, *ibid.*, 1958, **2**, 277.
[3] J. Körbl and R. Přibil, Ind. Chemist, 1958, **34**, 677.
[4] G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*, John Wiley and Sons, Inc., New York, 1957.
[5] A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds*, Prentice-Hall, Inc., New York, 1952.
[6] G. Schwarzenbach, G. Anderegg and R. Salmann, *Helv. Chim. Acta*, 1952, **35**, 1785.
[7] J. Körbl and R. Přibil, *Coll. Czech. Chem. Comm.*, 1958, **3**, 1213.
[8] *The Mikado*, W. S. Gilbert and A. S. Sullivan, Chappell and Co., Inc. New York, 1885.

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.

The Committee on Special Classifications of the Special Libraries Association and the Classification Committee of the Cataloging and Classification Section, Resources and Technical Services Division, American Library Association, are co-operating in a continuing project to develop and expand a Loan Collection of library classification schemes originally established by the Special Libraries Association. This Collection covers all fields of science, law, medicine, technology, the social sciences and the humanities.

New libraries or libraries with special collections are constantly asking for classifications—in all areas of knowledge—and it is imperative that the Collection be kept up-to-date through the addition of new schemes or with modernised versions of existing classification schedules. Curators of special collections, special librarians, and those individuals who have developed special classification schemes for specific types of material or for special subjects are invited to contribute a copy of their work to the Collection. Classification schemes should be sent to: Dr. JESSE H. SHERA, Curator, SLA Loan Collection, School of Library Science, Western Reserve University, Cleveland 6, Ohio, U.S.A.

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$^{\text{II}}$ with iron$^{\text{III}}$ 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.

Talanta. 1960. Vol. 4, pp. 89 to 100. Pergamon Press Ltd. Printed in Northern Ireland

ESTIMATION OF EFFICIENCY FOR BUBBLER-TYPE GAS ABSORBERS

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Summary—The behaviour of bubbler-type absorbers is discussed, and used to predict an estimate of absorption efficiency for such absorbers and to indicate the factors which have the greatest effect on efficiency.

GAS analysis methods involving the selective collection of one or more components of a gaseous mixture in a liquid absorbent are subject to error if the absorption efficiency is unknown and may even be limited in feasibility if the efficiency is too low. It is important to be able to predict (or estimate) the efficiency of an absorption system and to control the factors which significantly affect efficiency. While performance data for laboratory-scale absorbers have been reported in the literature, they are not universally applicable and must be interpreted for any situation which is not identical with the original experiment.

The purpose of this paper is to present sufficient generalised information to serve as a basis for predicting the performance and understanding the behavior of bubbler-type absorbers. Bubblers were chosen for discussion because they are the simplest and most commonly used class of absorbers. Much of the general discussion which follows applies to all absorbers, but the design equations were developed for specific application to the case of bubbles rising through liquid.

An extensive general discussion of analytical absorbers is given by Jacobs[1] and performance data (also presented by Jacobs) are given[2] in the American Public Health Association Yearbook, 1939–40. It will be assumed here that these or other sources may be consulted for details of absorber construction and operating procedure. While there are many variations in design, bubbler-type absorbers generally involve the dispersion of gas into the bottom of a reservoir of liquid and withdrawal of the gas above the level of the "aerated" column of liquid.

Dispersion of the gas is obtained either by introduction of a gas jet from a submerged orifice or by introduction of gas through a sintered-glass plate or similar porous medium. Effective gas bubble size is practically independent of orifice (or pore) size when the bubble population is high[3]. This observation is attributed to the coalescence of small bubbles in the vicinity of the dispersion plate. While the bubble diameters are statistically distributed, the distributions measured by Houghton *et al.*[3] are fairly narrow and the average diameters range from 0.35 to 0.45 cm over a wide range of gas velocity.

Because the extent of absorption depends on both the residence time of a bubble in the aerated column of liquid and the bubble velocity relative to the liquid, it is important to have information on these quantities. Fig. 1 is a plot of bubble (air) residence time per centimetre of non-aerated liquid (water) depth above the gas entrance versus superficial gas velocity (cm^3/min per cm^2 of absorber cross-sectional area) with absorber diameter as a parameter. The curve for 80 mm diameter is from the data of Houghton on gas hold-up and that for 22 mm is from the author's data on hold-up in a midget impinger.

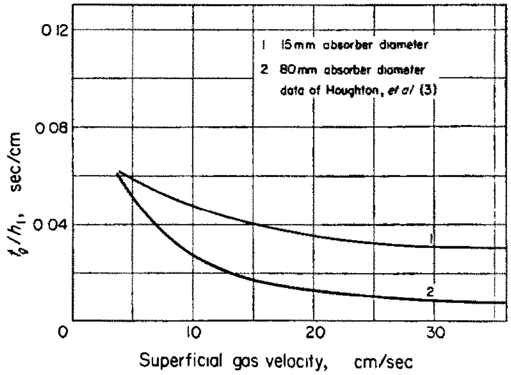

FIG. 1.

The residence time is practically independent of the method of gas dispersion so long as the superficial gas velocity is high enough to provide many bubbles. This would not be true for bubbles rising singly with a large distance between bubbles. It can be seen that so far as residence time and bubble diameter are concerned, there appears to be no value in using a fine fritted disc as compared with a coarse one. Although there is no information on the point, it would probably be unwise to use extremely large nozzles for dispersion. The midget impinger nozzle, for example, was about 1 mm, which would provide a gas jet velocity of 6,000 cm/sec at the point of maximum absorption efficiency.

The velocity of rise of single bubbles[4] is approximately constant at 24 cm/sec for diameters greater than 0.2 cm. While the average velocity relative to the absorber walls is lower than this where bubble population is high, we will approximate the velocity relative to the liquid as being equal to the velocity of rise of a single bubble.

DEFINITIONS OF SYMBOLS

A = Designation of transferring component.
a = Bubble radius, *cm*.
B = Designation of reactant in liquid.
C = Concentration of A in liquid, *mol/cm*^{3}.
C_a = Average concentration of A in liquid at any instant, *mol/cm*^{3}.
C_0 = Initial average concentration of A in liquid, *mol/cm*^{3}.
C_{Ai} = Concentration of A in the liquid interface, *mol/cm*^{3}.
D = Diffusivity coefficient for A, *cm*^{2}*/sec*.
D_g = Gas phase diffusivity, *cm*^{2}*/sec*.
D_f = Fictitious gas phase diffusivity for cases of mixed resistance.
D_{T_1} = Diffusivity of A in water at T_1.
D_{T_2} = Diffusivity of A in water at T_2.
F = Overall instantaneous collection efficiency $= f\left(\frac{p_1 - HC_a}{p_1}\right) = f\left(\frac{p_1 - p_e}{p_1}\right)$.

f = Fractional instantaneous approach to equilibrium = $\frac{p_1 - p_2}{p_1 - HC_a}$ = equilibrium collection efficiency.

f_g = Equilibrium collection efficiency for gas phase controlling.

f_L = Equilibrium collection efficiency for liquid phase controlling.

f_L' = Equilibrium collection efficiency during period of movement of one bubble diameter relative to liquid.

G = Gas flow rate, *cm³/sec.*

H = Henry's Law Constant, $\frac{atm}{mol/cm^3}$.

k_g = Mass transfer coefficient for gas phase, *mols/cm²-sec-atm.*

k_{OG} = Overall gas-phase mass transfer coefficient based on driving force equal to average partial pressure of A in the gas minus the partial pressure in equilibrium with average liquid concentration, C_a.

k_L = Liquid-phase mass transfer coefficient, *mols/cm²-sec-mol/cm³* based on driving force = $C_{A_i} - C_a$.

N = Diffusion rate, *mol/sec-cm².*

n = Total number of bubble diameters of relative motion during bubble residence time.

P = Total pressure, *atm.*

p_1 = Partial pressure of A in inlet gas, *atm.*

p_2 = Partial pressure of A in outlet gas, *atm.*

p_e = Partial pressure of A in equilibrium with liquid concentration, C_a, *atm.*

q = Concentration (average) of B in liquid for one mole of B reacting with one mole of A, *mol/cm³.*

R = Gas law constant = 82.057, $\frac{atm\text{-}cm^3.}{mol\text{-}°K.}$

T = Absolute temperature, °K.

t_a = Total time of absorption, *sec.*

t_g = Residence time of a gas bubble, *sec.*

t_L = Time of exposure of fresh liquid surface to gas bubble.

u_b = Bubble velocity relative to liquid, *cm/sec.*

u_g = Superficial gas velocity, *cm³/min-cm².*

V_L = Volume of liquid in absorber, *cm³.*

x = Distance in direction of diffusion, *cm.*

π = 3.1416.

ρ_g' = Molar density of gas, *mol/cm³.*

μ_{T_1} = Viscosity of water at T_1, *centipoises.*

μ_{T_2} = Viscosity of water at T_2.

Mass transfer

The fundamental process in an absorber involves the tendency toward equilibrium between the gas and the liquid in contact with it. This may involve the transfer of several components between the phases, but it will be assumed here that the liquid is non-volatile and that if there is more than one component in the gas phase, they may be considered independently. Thus we are concerned with the transfer of one component, A, from the gas to the liquid.

Because each bubble is in contact with the liquid for a limited time, equilibrium will not be attained and the degree of approach to equilibrium will be determined by the rate of transfer of A. Mass transfer rate in a bubbler can best be considered quantitatively in terms of unsteady-state diffusion rather than the "two-film" theory because of the generally small effects of turbulence in either fluid phase. However, a simpler qualitative description can be given in terms of steady-state diffusion, where for a one-dimensional case:

$$N = -D\frac{\partial c}{\partial x}\frac{(\text{mols})}{(\text{sec–cm}^2)} \tag{1}$$

Equation (1) states that the rate of diffusion depends on the diffusivity and the concentration gradient, $\partial c/\partial x$.

Although, in general, the rate of mass transfer is determined by the concentration gradients and diffusivities of both phases, there are two limiting cases in which the rate is controlled by either the liquid or the gas phase. To illustrate, consider the purely physical absorption (*i.e.*, a reversible equilibrium process such as the solution of oxygen in water) of A from a bubble rising through a liquid. If A is extremely soluble in the liquid just at the interface, a low gas-phase concentration would be in equilibrium with a high liquid-phase concentration. Consequently, a high concentration gradient would exist between the liquid at the interface and the bulk of the liquid. Because the rate of diffusion from the gas must equal the rate of diffusion into the liquid, there must be a fixed ratio of gas concentration gradient to liquid concentration gradient. In order to maintain this ratio the interfacial gas concentration must be quite small and indeed, it approaches the concentration in equilibrium with the bulk of the liquid. In this limiting case the concentration gradient in the gas phase becomes practically identical with that which would exist if there were no liquid phase concentration gradient.

The other limiting case, liquid phase controlling, occurs when a gas of very low solubility is being absorbed. The maximum possible liquid-phase concentration gradient will be so small that the gas-phase concentration gradient must be small if the transfer rates in the two phases are to be equal. Here the liquid-phase concentration gradient may be approximated as that which would exist if there were no concentration gradient in the gas.

Gas phase controlling

The rate of mass transfer from a bubble, if gas-phase resistance controls, is represented in Fig. 2, a graph of fractional approach to equilibrium, f_g, versus a

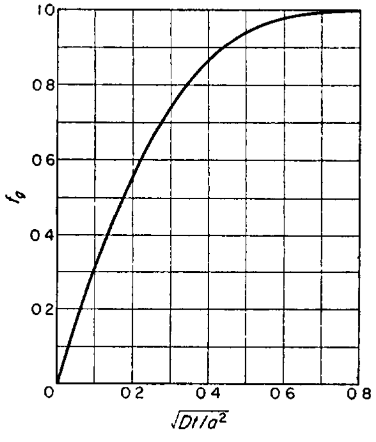

FIG. 2.

dimensionless time group, $\sqrt{Dt_g/a^2}$. This figure represents the solution of the equations for unsteady-state diffusion from a sphere which is initially at a uniform concentration and which is in contact with liquid of constant, uniform composition as given by Crank[5]. Physically, this corresponds to a bubble contacting liquid whose composition does not change appreciably during the period of contact (for this bubble) and under conditions such that gas-phase resistance is controlling.

One must distinguish between overall collection efficiency, F, which represents simply the fraction of A absorbed, and equilibrium collection efficiency, f, which represents the fractional absorption of that portion of A which would be absorbed if equilibrium were attained. It will be recognised that if the reaction products are such that there is an appreciable equilibrium vapour pressure above the liquid, the amount of A which can be removed from the gas will decrease as the concentration of the liquid increases. Thus, while the first bubbles of gas might transfer 99% of their A-content to fresh liquid (barren of A-reaction products), later bubbles might contact liquid so concentrated that they could not possibly transfer more than, say, 50% of the A-content even though they would still attain 99% of this equilibrium limit.

Liquid phase controlling

If liquid-phase resistance is controlling, the fractional approach to equilibrium is given by:

$$f_L' = \left(\frac{2D}{\pi a u_b}\right)^{1/2}\left(\frac{6\mathrm{RT}}{H}\right) \tag{2}$$

and

$$(1 - f_L) = (1 - f_L')^n \tag{3}$$

These relationships were derived on the basis of Higbie's Penetration Theory, which states that the rate of diffusion from a sphere is given by the rate of diffusion into a semi-infinite medium which is originally at a uniform concentration, C_0, over a period of time, t_L, which may be approximated as the time required for the bubble to rise one diameter, $2a/u_b$. The fraction f_L' is equal to the change in concentration of the gas divided by the maximum change possible (for gas in equilibrium with liquid at C_0) which occurs during the time the bubble rises one diameter. The total fractional approach to equilibrium, f_L, is given for a bubble rising through n diameters, where n equals the number of diameters of relative movement per second, $u_b/2a$ times the residence time. The velocity relative to the liquid, u_b, may be taken as 24 cm/sec for this purpose and for bubble diameters of 3.5–4.5 mm.

Although the distinction between gas phase controlling and liquid phase controlling has been given above in comparative qualitative terms, it can now be given quantitatively. The basic relationship is based on the two-film concept of mass transfer, which is discussed in any text-book of chemical engineering, and describes the relationship between a mass transfer coefficient, k_g, based on the actual gradient in the gas phase (which requires that interfacial concentrations be known), and an overall coefficient, k_{OG}, based on the gradient for the assumption of gas-phase controlling (which requires knowledge of bulk concentrations only):

$$\frac{k_g}{k_{OG}} = 1 + H\frac{k_g}{k_L} \tag{4}$$

If the ratio, k_g/k_{OG}, is unity, then the gas phase controls. Liquid-phase resistance is important if the ratio is significantly greater than one and may be said to control if the ratio is greater than 10. We may evaluate the ratio by using the following expressions for gas-phase coefficient, k_g, and liquid-phase coefficient, k_L. The expression for k_g is an approximate representation of the relationship given in Fig. 2 and the expression for k_L results from penetration theory.

$$k_g = \frac{7.6(D_g)^{0.7}}{3RT(t_g)^{0.3}(a)^{0.4}} \tag{5}$$

$$k_L = 2\sqrt{\frac{D_L u_b}{2\pi a}} \tag{6}$$

We can estimate the ratio k_g/k_L for average conditions where a gas is being absorbed from air into an aqueous solution at room temperature. The bubble radius, a, is taken as 0.2 cm and the velocity of rise, u_b, as 24 cm/sec. Representative diffusivities are gas diffusivity, $D_g = 0.1$ cm²/sec and liquid diffusivity $= 1.5 \times 10^{-5}$ cm²/sec. Upon making the substitutions it is seen that $k_g/k_L = 1.87 \times 10^{-3}$ for "average" conditions. Thus we may say that gas-phase resistance controls [*i.e.* $-(k_g/k_{OG}) < 1.1$] if H is less than 54 $\frac{(\text{atm})}{(\text{mol/cm}^3)}$ and that liquid phase controls $[(k_g/k_{OG}) > 10]$ if H is greater than 4,800 $\frac{(\text{atm})}{(\text{mol/cc})}$.

Intermediate cases may be approximated by considering the absorption to be gas-phase controlled and by using a fictitious diffusivity, D_f, such that:

$$\frac{k_g}{k_{OG}} = \left(\frac{D_g}{D_f}\right)^{0.7} \tag{7}$$

or

$$D_f = D_g\left(\frac{k_{OG}}{k_g}\right)^{1.43}$$

Chemically reactive solutions

Examples of the prediction of absorption efficiencies for each of the three cases discussed above are given later in this paper. Before turning to them we must consider two more matters of general importance. The first of these is the consideration of absorption by a chemically reactive solution, which probably includes the majority of applications in gas analysis. In the ideal situation one might picture the liquid-phase reaction as being extremely rapid and the reaction products such that the vapour pressure of A in equilibrium with the liquid interface is negligible. Where this is approximately true, the absorption is gas-phase controlled, and the absorption will be substantially complete in the contact time attained in most laboratory absorbers.

Even though the reaction products might be non-volatile, however, there is still no assurance that liquid-phase resistance will be negligible. It is necessary that the reacting substance, B, diffuses through the liquid towards the interface and reacts at a high enough rate to match the rate of diffusion of A into the liquid. If B diffuses too slowly or if the reaction is too slow, the reaction zone may be displaced a considerable distance into the liquid with the result that the equilibrium pressure of A above the liquid interface will rise.

The magnitude of the effect of reactant diffusion rate is illustrated mathematically in the solution[6] for the case wherein the second order reaction between A and B, yielding a non-volatile product, is infinitely rapid and the diffusivities of A and B are equal:

$$k_L = \left(1 + \frac{q}{C_{Ai}}\right) 2\sqrt{\frac{D_L u_b}{2\pi a}} \tag{8}$$

It can be seen that if the ratio of the average concentration of B to the concentration of A at the liquid interface, q/C_{Ai} is small, the liquid-phase transfer coefficient, k_L, is the same as that for physical absorption. This bears out the qualitative observation that the concentration of B must be high relative to the concentration of A in order for liquid-phase resistance to be substantially eliminated. If the absorption can be described as liquid-phase controlled at zero concentration of B, then the effect of B on the fractional approach to equilibrium per bubble diameter of rise is given by:

$$f_L' = \left(1 + \frac{q}{C_{Ai}}\right)\left(\frac{2D}{\pi a u_b}\right)^{1/2}\left(\frac{6\mathrm{RT}}{H}\right) \tag{9}$$

If the absorption is to be considered as overall gas-phase controlled, then the ratio k_g/k_L in equation (4) should be divided by $[1 + (q/C_{Ai})]$.

Liquid flow pattern

The final matter of general importance is the effect of liquid flow pattern in the absorber. In the previous discussion it has been assumed that the liquid is completely mixed so that the liquid composition encountered by any one bubble at the bottom of the absorber is the same as that encountered at the top by the same bubble. In other words, the rate of change of liquid-phase composition was assumed small with respect to the residence time of any one bubble because the amount of liquid associated with the bubble is large.

It is possible to have a definite circulatory liquid flow pattern set up so that some small fraction of the liquid travels up with a bubble and experiences little mixing with the bulk of the liquid during its upward travel. The result will be that the liquid contacting the bubble at the top of the absorber is more concentrated in A than the bulk of the liquid. Where the absorption process is purely physical, the minimum concentration of A in the gas leaving the absorber will be limited to that in equilibrium with the liquid last contacting the bubble. In the case of absorption with a reactive solution there may be no adverse effect if the concentration of the reactant is not appreciably depleted.

While it is not now possible to quantitatively characterise the co-current movement of liquid with the gas, evidence of its existence has been observed. The discussion of the absorption of ammonia in water, given later, points out the probable effect of co-current flow at low gas flow rates. Study of the absorption of carbon dioxide in water in an absorber in which the bubbles travel up in a helical path formed in a glass liner is at present being conducted by the authors and has shown that there is pronounced co-current flow in this apparatus.

Where co-current flow does exist in physical absorption, it can be shown mathematically that, for the same residence time, the approach to equilibrium, *f*, will be greater than for the case of complete mixing of the liquid phase. However, the shifting of the equilibrium limit will more than compensate for the increase of *f* in causing overall collection efficiency, *F*, to decrease.

EXAMPLES

Some examples of gas absorption in bubblers for which experimental data are available will now be considered in order to illustrate both the application of the design principles and the order of accuracy which can be attained. It must be emphasised that the predicted efficiencies can only be interpreted as approximations and that for precise work the efficiency must be determined for the particular system.

Liquid phase controlling

The absorption of carbon dioxide by aqueous solutions of sodium hydroxide, sodium carbonate and ammonia in nozzle-type bubblers has been reported by Mochalova and Kishinevskii[7]. Their data for absorption in pure water (extrapolated to 0% Na_2CO_3) will be compared with predictions based on liquid-phase resistance controlling. The apparatus used consisted of a 0.5-cm diameter tube pointed downward with the end of the tube submerged 1.7 cm below the liquid level in a 5-cm diameter cylinder. Measured absorption efficiencies were 7.61% at 5°C and 7.39% at 45°C. The total gas rate was cited as 0.6 litres per minute (we assume this to be at standard conditions), which corresponds to a superficial gas velocity of 0.51 (cm/sec).

Solubility data[8] were converted to values of H equal to $1.57 \times 10^4 \left(\frac{\text{atm}}{\text{mol/cm}^3}\right)$ at 5° and $4.57 \times 10^4 \left(\frac{\text{atm}}{\text{mol/cm}^3}\right)$ at 45°. Applying the criterion of equation (4) indicates that liquid phase controls, since H is greater than 4.8×10^3. Thus the absorption efficiency should be predicted with equations (2) and (3). Diffusivities for carbon dioxide in water of 1.14×10^{-5} (cm^2/sec) at 5°C and 3.19×10^{-5} (cm^2/sec) at 45°C were estimated from the International Critical Tables value of 1.8×10^{-5} (cm^2/sec) at 20°C by means of the following relationship[9] for dilute aqueous solutions:

$$D_{T_1} = D_{T_2}\left(\frac{\mu_{T_2}}{\mu_{T_1}}\right) \tag{10}$$

The viscosities μ_{T_2} and μ_{T_1} are those of water at the temperatures T_2 and T_1. If the liquid viscosity is much different from that of water, equation (10) will not apply and another relationship[9] must be used.

Because the orifice size is relatively large (5 mm) and the gas rate is low, we would expect that the bubbles would emerge singly as reported. Thus, the velocity of rise, u_b would be about 24 (cm/sec) for an assumed bubble radius, *a*, of 0.2 cm. Substitution of these values into equation (2) leads to values for f_L' of 0.0107 at 5° and 0.007 at 45°. At the low superficial gas velocity used there is no significant difference between aerated and non-aerated liquid heights, so the value of *n* is 4.25 bubble diameters for a submergence of 1.7 cm.

The efficiencies, f_L, are then computed to be 4.5% at 5°C and 3.0% at 45°C. If we take into account the fact that, because the orifice is pointed downward the bubble path will be a curve rather than a straight line, we might reasonably expect (as confirmed by observation) the path to be a few bubble diameters longer. If n is taken as 7.0, the values of f_L will be 7.3% at 5°C and 4.8% at 45°C. This approximation to the experimental values of 7.61% and 7.39% is about as good as can be expected considering all of the estimations involved in the calculations and the extremely small contact time.

Chemical reaction and gas phase controlling

Air contaminant absorption efficiencies for several models of bubblers have been determined by Roberts and McKee[10]. Collection of sulphur dioxide in disodium tetrachloromercurate and of chlorine in 0.1N sodium hydroxide were reported as "... substantially complete regardless of the type of sampler or the flow rate used ...". For the absorption of 1 ppm (by volume) of ammonia from air in distilled water the efficiencies were lower and were dependent on air flow rate (see Fig. 3).

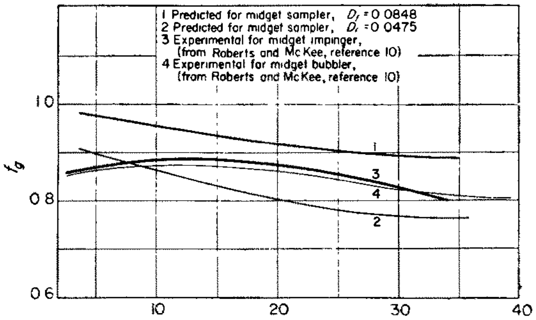

FIG. 3.

If we assume that the concentrations of sulphur dioxide and chlorine (data were not given) were of the same order as that of ammonia,* we may consider these two cases as being gas-phase controlled because the ratio (q/C_{Ai}) would be very high. Considering the case of chlorine absorption, for example, we find a value of $H = 1.33 \times 10^4 \left(\frac{\text{atm}}{\text{mols/cm}^3}\right)$ for un-ionised chlorine solubility[6] and approximately half that for total chlorine solubility. Employing the criterion of equation (4), this value of H indicates liquid-phase controlling if there is no chemical reaction. The effect of chemical reaction (assuming a second order, rapid reaction) can be estimated by means of equation (8) if we assume that C_{Ai} is in equilibrium with a gas-phase interface with chlorine concentration of 1 ppm ($p_1 = 1 \times 10^{-6}$ atm). Computation yields $C_{Ai} = 0.75 \times 10^{-10}$ mols/cm³ and we have $q = 1 \times 10^{-4}$ equiv./cm³. Putting C_{Ai} in terms of equivalents, since one mole of chlorine reacts with two equivalents of sodium hydroxide, we compute $q/C_{Ai} = 0.67 \times 10^6$.

For purposes of estimation we take $k_g/k_L = 1.65 \times 10^{-3}$ for the case of no reaction and obtain $k_g/k_L = 2.46 \times 10^{-9}$ for this case of chemical reaction. The group $H(k_g/k_L)$ can now be computed to be 3.3×10^{-5} and substitution in equation (8)

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* Communication with Dr. McKee verified this assumption.

indicates that this is a case of gas-phase resistance controlling. One notes that, since gas phase is controlling, the concentration gradient in the gas would cause the partial pressure of chlorine at the interface, and consequently C_{Ai}, to be lower than that assumed (the average partial pressure, p_1), and thus the ratio, q/C_{Ai}, would be larger. It can be seen, then, that to base the computation on C_{Ai}, as given by the maximum gas-phase composition, will yield a conservative result.

The next step is to compute fractional approach to equilibrium based on gas-phase controlling. Diffusivities in air at 20°C were computed from values at 0°C by the method recommended in Reid and Sherwood[9] as 0.14 cm^2/sec for sulphur dioxide, 0.143 cm^2/sec for chlorine and 0.228 cm^2/sec for ammonia. Assuming a bubble radius of 0.2 cm, a liquid volume of 10 cm^3,* and a bubbler cross-sectional area of 3.6 cm^2 (for a standard Midget Impinger), we compute the un-aerated liquid height to be 2.78 cm and can proceed to find residence time and f_g. At a superficial gas velocity of 15 cm/sec, Fig. 1 indicates a residence time of 0.04 seconds per centimetre of un-aerated height or 0.11 sec for 2.78 cm of liquid. By use of Fig. 2 the efficiencies are computed to be 0.984 for sulphur dioxide and chlorine, and 0.998 for ammonia.

Resistance in both phases

These predictions of f_g may be assumed to be equivalent to F if the testing time was so short that the liquid concentration did not rise appreciably. The predictions for sulphur dioxide and chlorine bear out the statement[10] that absorption was substantially complete. The prediction for ammonia is far from agreement with the experimental results shown in Fig. 3, in spite of the fact that $H = 13.5 \frac{\text{atm}}{\text{mol/cm}^3}$ (for dilute solutions[6]), and one would expect gas phase to be controlling from the criterion of equation (4).

We find that this same characteristic of ammonia absorption in water has been observed in large, industrial equipment[6] and that ratios of k_g/k_{OG} ranging from 2 to 3 have been determined experimentally. The existence of this additional resistance has been attributed to the possibility of a slow reaction between dissolved ammonia and ionised ammonia. There is also the possibility that the rate of accommodation at the interface is low. If we employ the extremes of the ratio, as given above, the corresponding values for D_f are 2.69 and 4.8 (see equation (7)). The predicted curves of efficiency versus flow rate are shown in Fig. 3.

While it is clear that the prediction covers too large a range of efficiencies to be useful in precise work, the "bracketing" of the experimental values at higher velocities is good confirmation of the mechanistic approach. The deviation of the slopes at low gas velocities is believed, by us, to be largely due to co-current flow, and to some extent to inaccuracy of bubble residence times as computed from gas hold-up. A definite circulatory liquid flow pattern can be observed at low gas flow rates and we believe that this results in a significant increase of ammonia concentration in the small volume of liquid which accompanies the bubbles.

CONCLUSIONS

The design methods presented above may be used to predict an estimate of absorption efficiency for a bubbler-type absorber and to point out which factors have the

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* Communication with Dr. McKee verified this assumption.

most important effect on efficiency. A recommended procedure for predicting efficiency is given below. It should be emphasised that this procedure is based on conservative approximations. High values for both bubble diameter and bubble velocity are used and the beneficial effect of circulation within bubbles is neglected. The approximate method for treating cases of mixed resistance is presented because of its simplicity although a rigorous solution for this case is given by Crank[5]. In any case, the prediction cannot be relied on for precise results and the specific system must be calibrated experimentally.

Recommended procedure

I. Determine whether the system is gas- or liquid-phase controlled or intermediate by means of the criterion of equation (4). For high concentration, either an average value of H may have to be estimated or the absorption process may have to be considered over incremental ranges of concentration in which H is approximately constant.

II. If the system involves purely physical absorption, evaluate the fractional approach to equilibrium by means of Fig. 2 for gas-phase controlling and equations (2) and (3) for liquid-phase controlling. For intermediate resistance use the relationship of Fig. 2 with a fictitious diffusivity given by equations (4) and (7). The ratio of k_g/k_L may be either estimated as the "average" value of 1.86×10^{-3} or it may be computed by means of equations (5) and (6).

If the absorption is to be carried on for a long time so that the liquid concentration builds up enough to impose an equilibrium limit on efficiency, the total amount of collection can be determined by integrating the relationship between the instantaneous rate of increase of liquid concentration and the liquid concentration. For an initial liquid phase concentration of zero and constant inlet gas concentration, the result is:

$$\ln\left(1 - \frac{HC_o}{p_1}\right) = -f\left(\frac{HG\,\rho_g'}{V_L P}\right) t_a \tag{11}$$

III. If the system involves chemical reaction in the liquid phase and there is negligible equilibrium pressure of the transferring component above the reaction products, the maximum collection efficiency corresponds to the case of gas-phase controlling. The effect of reactant concentration for a second order reaction may be estimated by dividing k_g/k_L in equation (4) by $(1 + (q/C_{Ai}))$. Other reaction mechanisms are discussed by Crank.[5]

In cases where an appreciable equilibrium pressure results from the reaction, the overall collection efficiency must be computed from the fractional approach to equilibrium as in the case of physical absorption.

IV. Having used the methods described above to design an appropriate absorption system, the performance of the system should be determined experimentally. The preferable method is to sample a gas mixture of known composition. If this is not possible, use two or more absorbers in series.

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Zusammenfassung—Die Eigenschaften von Absorber des Gasblasentyps werden diskutiert. Es wird versucht auf Grund der Eigenschaften vorauszusagen wie gross die Absorptionsfähigkeit solcher Absorber ist und die Faktoren herauszuarbeiten, die den grössten Einfluss auf die Leistungsfähigkeit haben.

Résumé—Les auteurs discutent le comportement d'absorbeurs du type barboteur et utilisent les résultats obtenus pour prévoir une estimation du pouvoir d'absorption de tels absorbeurs et pour indiquer les facteurs qui influent le plus sur ce pouvoir d'absorption.

REFERENCES

[1] M. B. Jacobs, *The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents*, Interscience Publishers, Inc., New York, 2nd Ed., 1949.

[2] *American Public Health Association Yearbook*, 1939–40.

[3] G. Houghton, A. M. McLean and P. D. Ritchie, *Chem. Eng. Sci.*, 1957, **7**, 44.
[4] F. H. Garner, and D. Hammerton, *Chem. Eng. Sci.*, 1954, **3**, 1.
[5] J. Crank, *The Mathematics of Diffusion*, Oxford Univ. Press, London, 1st Ed., 1956.
[6] T. K. Sherwood and R. L. Pigford, *Absorption and Extraction*, McGraw-Hill Book Co., New York, 2nd Ed., 1952.
[7] L. A. Mochalova and M. Kishinevskii, *J. Appl. Chem.*, 1958, **31**, 525.
[8] *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Co., 39th Ed., 1957.
[9] R. C. Reid, and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill Book Co., New York, 1st Ed. 1958.
[10] L. R. Roberts and H. C. McKee, *J. Air Pollution Control Assn.*, 1959, **9**, 51.

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THE ANALYSIS OF BERYLLIUM AND BERYLLIUM OXIDE—II

THE DETERMINATION OF COPPER

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Summary—A method is described for the determination of copper in beryllium or beryllium oxide by extraction of the neocuproïne complex with methyl *iso*butyl ketone. The method is accurate to ±5% or ±2.5 micrograms of copper, whichever is greater. The accuracy and sensitivity could be improved by appropriate choice of sample size, volume of extract and/or cell length. Of the 68 elements investigated, only gold interferes in 10 mg amounts; in this case a slight loss of copper is caused by occlusion or co-precipitation.

INTRODUCTION

In a previous paper,[1] the authors discussed the necessity of obtaining accurate chemical methods for the analysis of beryllium and beryllium oxide. Certain desirable features of such methods were also discussed. In the present paper a method is presented which is, assuming no synergistic effects, specific for copper. No interference was caused by 10 mg amounts of 67 elements. The presence of 5 or 10 mg of gold resulted in an 8% loss of copper by occlusion or co-precipitation. The method is accurate to ±5% relative or ±2.5 micrograms of copper, whichever is greater. The accuracy and sensitivity could be improved by appropriate choice of sample size, volume of extract and/or cell length.

The method adopted is a modification of that presented by Gahler.[2] The sample is dissolved as previously described,[1] and citric acid is added to prevent precipitation of beryllium. The copper is reduced with hydroxylamine hydrochloride, and the pH is adjusted to 5.0 ± 0.1. Neocuproïne is added and the complex is extracted with methyl *iso*butyl ketone (4-methyl-2-pentanone). The absorbance of the organic extract, measured at 457 millimicrons, is a linear function of concentration, at least from 0 to 5 ppm, and is stable for at least 24 hours.

EXPERIMENTAL

Apparatus

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

Reagents

Standard copper solution: Remove the oxide film from high-purity copper metal shot by treating it with $3M$ nitric acid. Rinse and dry. Dissolve approximately 0.1 g in 12 ml of $4M$ nitric acid. Add 10 ml of perchloric acid and evaporate to fumes to expel nitric acid. Cool and dilute to 1 litre. Dilute this solution to obtain a solution containing 10 μg of copper per ml.

Hydroxylamine hydrochloride, 10% (w/v): Store in refrigerator.

Neocuproïne, (2:9-dimethyl-1:10-phenanthroline): 0.1% (w/v), in absolute ethanol. Store in refrigerator.

Citric acid, 50% (w/v).

Methyl iso*butyl ketone,* (4-methyl-2-pentanone): B.P. 114–116°.

Hydrochloric acid, (Sp. gr. 1.19).

Sulphuric acid, (Sp. gr. 1.84).

Sodium hydroxide, 50% (w/v).

Procedure

Dissolve a sample, containing about 50 μg of copper, according to the directions previously given[1] and transfer to a 400-ml beaker. Add sufficient acid to have present 5 ml of hydrochloric acid and 10 ml of sulphuric acid. Add 10 ml of 50% citric acid, 5 ml of 10% hydroxylamine hydrochloride, dilute to about 100 ml with water and cool in an ice-bath. Adjust the pH to 5.0 ± 0.1 with 50% sodium hydroxide, keeping the solution at room temperature with an ice-bath. Transfer to a 250-ml separatory funnel. Add 10 ml of 0.1% neocuproïne solution and allow to stand for 2 hours. Add exactly 10 ml of methyl *iso*butyl ketone. Stopper tightly and shake for 1 minute. Allow the layers to separate, and discard the aqueous phase. Centrifuge the organic layer and measure its absorbance in 1-cm cells at 457 millimicrons versus methyl *iso*butyl ketone in the reference cell. Determine the copper concentration by reference to a standard curve obtained by carrying known amounts of copper through the above procedure. A blank and standard should be carried through the entire procedure.

Extraction of the copper-neocuproïne complex

In attempting to apply Gahler's method[2] to the determination of copper in beryllium or beryllium oxide, it was found that chloroform was unsatisfactory as an extractant because of a tendency for emulsion formation. Also, in many cases a precipitate formed at the phase interface. Methyl *iso*butyl ketone was found to be a satisfactory extractant under these conditions. It has been reported[3] that methyl *iso*butyl ketone is soluble to the extent of 2% in water. However, its solubility is negligible in this medium of high salt content. Copper is quantitatively extracted according to the procedure described.

Measurement of the copper-neocuproïne complex

The absorption spectrum and molar absorptivity (8400) of the copper-neocuproïne complex are essentially the same as those observed when chloroform is used as the extractant. The absorbance is stable for at least 24 hours and is a linear function of concentration, at least from 0–5 ppm. In the presence of large amounts of beryllium, the copper-neocuproïne complex does not attain full colour development for 15 or 20 minutes. Chromium and hafnium are the only elements of the 68 tested which retard complete colour development. A minimum of 2 hours is required for complete colour development when 10-mg amounts of these elements are present. The addition of neocuproïne, up to three times the amount usually added, did not hasten colour development; it was hastened to some extent by the addition of five times the amount of hydroxylamine normally added.

The concentration of neocuproïne has little effect on the molar absorptivity, at least between 0.05 and 1.00 weight per cent.

Effect of other elements

In testing the effect of other elements on the determination of copper using the procedure described, a solution containing the appropriate amount of sodium sulphate and sodium chloride was added.

Luke and Campbell[4] reported that Gahler's method yielded satisfactory results in the presence of 50-μg quantities of 56 metal ions. It was thought that the effects of larger amounts of impurities needed investigation. No interference was observed by 10 mg of Al, Sb^{III}, As^{III}, Ba, Be, Bi, B, Br, Cd, Ca, Ce^{IV}, Cs, Cr^{III}, Cr^{VI}, Co, Dy, Er, Eu, F, Gd, Ga, Ge, Hf, Ho, In, I, Ir, Fe^{III}, La, Pb, Li, Lu, Mg, Mn^{II}, Mn^{VII}, Hg^{II}, Mo, Nd, Ni, Nb, Pd, P, Pt, K, Pr, Re, Rh, Rb, Sm, Sc, Se, Si, Na, Sr, Ta, Te, Tb, Tl^{I}, Th, Tm, Sn^{II}, Ti^{III}, W, U^{VI}, V^{V}, Yb, Y, Zn, or Zr. The presence of 5–10 mg of gold caused a loss of copper by occlusion or co-precipitation amounting to about 8% of the amount of copper present (in this case 53.7 μg). Citric acid prevented lead sulphate from precipitating, and reduced the amount of precipitation of barium sulphate considerably. Slight precipitation occurred during the test with mercury.

Application of the method

A sample of beryllium oxide analysed using this procedure was found to contain 6.1 and 6.6 ppm copper. When 1 g of this oxide was "spiked" with 53.7 μg of copper, recoveries of 104% and 99% were obtained, indicating the applicability of the procedure to large amounts of beryllium.

Blank values corresponding to 5.0, 5.6, and 5.5 μg of copper were obtained with the amounts of reagents used during the analysis. Demineralised water was used throughout the procedure.

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

TABLE I.—ANALYSIS OF NEW BRUNSWICK STANDARDS[a]

Sample No.	Cu found, *ppm*	Average	Nominal value
Be 85	23.2, 25.2	24.2	30
86	264, 264	264	300
87	207, 200	204	210
88	237, 241	239	250
BeO 72-1	35.9, 34.4	35.2	36.0
72-2	18.3, 20.1	19.2	18.0
72-3	7.0, 7.0	7.0	7·21
72-4	5.9, 3.9	4.9	3.60
72-5	1.8, 1.8	1.8	—

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

Zusammenfassung—Eine Methode zur Bestimmung von Kupfer in Beryllium oder Berylliumoxyd wird beschrieben, die auf der Extraktion des Kupfer-Neocuproinkomplexes mit Methyl-Isobutylketon beruht. Die Methode ist auf ±5% oder 2.5 ppm (Mikrogramm per Gramm) genau, abhängig davon welches der grössere Wert ist.

Résumé—Les auteurs décrivent une méthode de dosage du cuivre dans le béryllium ou l'oxyde de béryllium par extraction du complexe néocuproïne dans la méthylisobutylcétone. La méthode est précise à ±5% près (limite de sensibilité: 2,5 ppm). On pourrait augmenter la précision et la sensibilité par un choix approprié de la taille de l'échantillon, du volume du corps extrait, et/ou de la longueur de la cellule. Parmi les 68 éléments étudiés, seul l'or gêne pour une quantité de 10 mg; dans ce cas il y a une légère perte de cuivre causée par occlusion ou coprécipitation.

REFERENCES

[1] J. O. Hibbits, W. F. Davis, and M. R. Menke, *Talanta*, 1960, **4**, 61
[2] A. R. Gahler, *Analyt. Chem.*, 1954, **26**, 577.
[3] Report 5006/23, 1959, United Kingdom Atomic Energy Authority, Industrial Group Headquarters, Lancashire.
[4] C. L. Luke and M. E. Campbell, *Analyt. Chem.*, 1953, **25**, 1958.

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THE ANALYSIS OF BERYLLIUM AND BERYLLIUM OXIDE—III·

THE DETERMINATION OF MOLYBDENUM

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Summary—A method is described for the determination of molybdenum by extraction of its thiocyanate complex with methyl *iso*butyl ketone. The method is accurate to ±4% or ±3 micrograms of molybdenum, whichever is greater. The accuracy and sensitivity can be improved by appropriate choice of sample size, volume of extract and/or cell length. Of 68 elements investigated, only rhenium, platinum, palladium, rhodium, vanadium, and tellurium interfere in 10-mg amounts. Of these, only rhenium interferes seriously.

INTRODUCTION

PREVIOUS papers[1,2] have discussed the determination of iron and copper in beryllium and beryllium oxide and the requirements for methods used for the analysis of these materials. In the present paper a method is presented which is almost specific for the determination of molybdenum. Of the 68 elements investigated, only rhenium, platinum, palladium, rhodium, vanadium, and tellurium interfere in 10-mg amounts. Of these, only rhenium interferes seriously.

The determination of molybdenum as the thiocyanate is treated extensively in the literature. The method which we have found most satisfactory is based on information supplied by Tombu[3]. Molybdenum thiocyanate, in a sulphuric-hydrochloric acid medium, is reduced with stannous chloride and extracted with methyl *iso*butyl ketone. The extraction is performed in the presence of iron in order to obtain maximum colour intensity. The extract is washed with a solution of oxalic acid in dilute hydrochloric acid; this removes cobalt and any zirconium which may have been extracted. A final wash with dilute hydrochloric acid eliminates any turbidity which may exist in the organic phase. After 2 hours, the absorbance of the extract is measured at 500 mμ. The method is accurate to ±4% or ±3 micrograms of molybdenum, whichever is greater. The accuracy and sensitivity can be improved by appropriate choice of sample size, volume of extract and/or cell length.

EXPERIMENTAL

Apparatus

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

Reagents

Standard molybdenum solution. Dissolve 3 g of molybdenum trioxide in 200 ml of 10% sodium hydroxide and dilute to 2 litres with water. Store in a polyethylene container. Standardise this solution and dilute an aliquot to obtain a solution containing 25 μg of molybdenum per ml.

Citric acid, crystals.

Bromine water, saturated solution.

Sulphuric acid, sp. gr. 1.84 and $6M$.

Potassium thiocyanate, 25% (w/v).

Stannous chloride, 25% (w/v), in $12M$ hydrochloric acid.

Oxalic acid, 2% (w/v), in $1.2M$ hydrochloric acid.

Hydrochloric acid, sp. gr. 1.19, $6M$ and $2.4M$.

Iron solution. Dissolve 0.48 g ferric chloride hexahydrate in 33 ml of hydrochloric acid (sp. gr. 1.19) and dilute to 100 ml with distilled water.

Methyl iso*butyl ketone* (4-methyl-2-pentanone), B.P. 114–116°.

Procedure

Dissolve a sample of beryllium metal or beryllium oxide, containing up to 75 μg of molybdenum, according to the procedure described previously.[1] Transfer to a 250-ml separatory funnel and add 1 g of citric acid (to prevent possible precipitation of tungsten, which might occlude molybdenum). Add 1 ml of a solution containing 1 mg of iron per ml. Add water and hydrochloric or sulphuric acids until 5 ml of hydrochloric acid and 10 ml of sulphuric acid are contained in a final volume of 70 ml. Cool to room temperature. Add 2 ml of bromine water, 10 ml of 25% potassium thiocyanate solution and 5 ml of 25% stannous chloride solution. Mix and allow the solutions to stand at least 10 minutes. Add exactly 25 ml of methyl *iso*butyl ketone and shake for 1½ minutes. Allow the layers to separate and discard the aqueous phase. Add 35 ml of 2% oxalic acid solution and shake for 1 minute. Discard the acid wash. Add 35 ml of $2.4M$ hydrochloric acid, shake for 1 minute and discard the acid wash. Allow the organic phase to stand at least 2 hours in the tightly stoppered separatory funnel. Transfer to a centrifuge tube and centrifuge for 1 minute. Measure the absorbance of the extract in 2-cm cells at 500 mμ using methyl *iso*butyl ketone in the reference cell. Determine the molybdenum concentration by reference to a standard curve obtained by carrying known amounts of molybdenum through the above procedure. A blank and standard should be carried through the entire procedure.

Extraction of the molybdenum-thiocyanate complex

Molybdenum is quantitatively extracted using the procedure described. Minor variations in the amounts of hydrochloric or sulphuric acids have no significant effect.

Measurement of the molybdenum-thiocyanate complex

A comprehensive discussion of the molybdenum thiocyanate complexes and the difficulties in attaining maximum colour development has been given by Crouthamel and Johnson.[4] A number of workers have observed that the presence of small amounts of iron (or copper) increases the colour intensity. In this study, 1 mg of iron was added in order to obtain maximum colour formation.

The maximum absorbance of the molybdenum-thiocyanate complex occurs at 470 mμ. Interference from tungsten is minimised by measuring the absorbance at 500 mμ. Eighteen hours are required for maximum colour development. The colour increases by approximately 10% over that obtained in 2 hours. Solutions can be measured at any time after 2 hours provided the same time interval is used for establishment of the standard curve. The complex obeys Beer's law and has a molar absorptivity of approximately 10,000 at 500 mμ when extracted in the manner described.

Effect of other elements

No interference was obtained from 10 mg of Al, $\mathrm{Sb^{III}}$, $\mathrm{As^{III}}$, Ba, Be, Bi, B, Cd, Ca, $\mathrm{Ce^{III}}$, $\mathrm{Ce^{IV}}$, Cs, $\mathrm{Cr^{III}}$, $\mathrm{Cr^{VI}}$, Co, Cu, Dy, Er, Eu, Gd, Ga, Ge, Au, Hf, Ho, In, Ir, $\mathrm{Fe^{II}}$, $\mathrm{Fe^{III}}$, La, Pb, Li, Lu, Mg, $\mathrm{Mn^{II}}$, $\mathrm{Mn^{VII}}$, $\mathrm{Hg^{II}}$, Nd, Ni, Nb, P (as phosphate), K, Pr, Rb, Sm, Sc, Se, Si, Na, Sr, Ta, Tb, $\mathrm{Tl^{I}}$, Th, Tm, $\mathrm{Sn^{II}}$ $\mathrm{Sn^{IV}}$, $\mathrm{Ti^{III}}$, $\mathrm{Ti^{IV}}$, W, $\mathrm{U^{VI}}$, Yb, Y, Zn, or Zr, or 100 mg of F or Br. The effects of the few elements which did interfere at the 10-mg level are shown in Table I.

APPLICATION OF THE METHOD

When 1 g of beryllium oxide containing no detectable amount of molybdenum was "spiked" with 75 μg of this element, complete recovery (within ±4%) of the

Table I.—Effect of interfering elements on the determination of 75 μg of molybdenum

Element added	Amount	% Error
I (as iodide)	1 mg	<4
	10 mg	−12.5
	100 mg	−21.7
	100 mg	<4[a]
Te	5 mg	−50
	5 mg	<4[b]
	10 mg	−8[b]
V^{V}	5 mg	<4
	10 mg	−8
Re^{VII}	100 μg	+82[c]
Pt^{IV}	100 μg	+5
	1 mg	+50
Pd^{II}	100 μg	<4
	1 mg	+24
Rh^{III}	100 μg	<4
	1 mg	+30

[a] Iodide was removed by the addition of 0.4 g of ferric ammonium sulphate, 2 ml of 9*M* sulphuric acid, a few drops of nitric acid, and boiling.

[b] Solution filtered before extraction.

[c] $\lambda_{max} = 433$ mμ.

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

Table II.—Analysis of new Brunswick standards[a]

Sample No.	Mo found[b], ppm	Average	Nominal value[c]
Be 85	4.6, 5.1	4.8	5
86	25.8, 25.6	25.7	25
87	32.4, 32.4, 32.4	32.4	32
88	52.5, 50.4	51.5	51
BeO 72–1	18.8, 18.7, 18.8, 19.5	18.9	18.0
72–2	7.5, 7.5, 7.9, 7.9	7.7	6.5
72–3	3.9, 3.8, 4.2, 4.2	4.0	2.9
72–4	2.1, 1.9, 2.6, 2.6	2.3	1.8
72–5	0.1, 0.9, 0.9, 0.7	0.7	—

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

[b] Results should be accurate to within 1 ppm. Five-cm cells were used.

[c] Private communication with NBL.[6] Certificate values to be regarded as only tentative.

If there are no synergistic effects, high results are obtained with this procedure only when significant amounts of platinum, palladium, or rhodium, or small amounts of rhenium are present. Spectrographic analysis of all of the New Brunswick standards indicated less than 10 ppm of rhodium or palladium, and less than 20 ppm of platinum. Rhenium was not detected in the beryllium metal samples when these were analysed by the method of Hoffman and Lundell.[5] The rhenium content in each case was estimated to be less than 2 ppm. It was also found that rhenium is volatilised during the dissolution of beryllium oxide with sulphuric acid. The rhenium content of the beryllium oxide samples is also estimated to be less than 2 ppm.

The method has also been applied to yttrium oxide with the results shown in Table III.

TABLE III.—APPLICATION OF THE METHOD TO YTTRIUM OXIDE

Sample	Mo added, μg	Mo found, μg
1.3 g Y_2O_3	75	75
1.3 g 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, Cr^{VI}, W, Nb, 200 μg Cu, 400 μg Ta, 1 mg Fe^{III}, 5 mg F, 4 mg Ti^{III}, 10 mg Zr	75	79

Zusammenfassung—Eine Methode zur Bestimmung von Molybdän wird beschrieben, basierend auf der Extraktion des Thiocyanat Komplexes mit Methyl-Isobutylketon. Die Methode ist auf ±4% oder 3 Mikrogramm per Gramm genau, abhängig davon was der grössere Wert ist. Genauigkeit und Empfindlichkeit der Methode können gesteigert werden durch geeignete Auswahl von Probenmenge, Extraktionvolum und/oder Zellänge. Von 68 untersuchten Elementen stören nur Rhenium, Platin, Palladium, Rhodium Vanadin und Tellur in Mengen bis zu 10 Milligrammen. Lediglich die durch Rhenium bewirkte Störung ist schwer.

Résumé—Les auteurs décrivent une méthode de dosage du molybdène par extraction du complexe thiocyanate dans la méthylisobutylcétone. La méthode est précise à ±4% près (limite de sensibilité: 3 p.p.m.). On peut augmenter la précision et la sensibilité par un choix approprié de la taille de l'échantillon, du volume du corps extrait, et/ou la longueur de la callule. Parmi les 68 éléments étudiés, seuls le rhénium, le platine, le palladium, le rhodium, le vanadium et le tellure gênent pour des quantités de 10 mg. Parmi ceux-ci, seul le rhénium gêne sérieusement.

REFERENCES

[1] J. O. Hibbits, W. F. Davis, and M. R. Menke, *Talanta* 1960, **4**, 61.
[2] *Ibid.*, 101.
[3] C. Tombu, Société Générale Metallurgique de Hoboken. Private Communication.
[4] C. E. Crouthamel and C. E. Johnson, *Analyt. Chem.* 1954, **26**, 1284.
[5] J. I. Hoffman and G. E. F. Lundell, *J. Res. Nat. Bur. Stand.* 1939, **23**, 497.
[6] C. J. Rodden, Atomic Energy Commission Laboratory, New Brunswick, New Jersey, U.S.A.

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SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM IN URANIUM ALLOYS OF THE FISSION ELEMENTS*

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Summary—Alizarin-Red S has been used to determine zirconium spectrophotometrically in uranium alloys of the fission elements. Separation from interferences is effected by co-precipitating the zirconium with barium fluosilicate. Colour stability and improved precision have been realised through changes in the colour development procedure. Alloys containing from 1 to 0·01 % zirconium can be analysed by this method with coefficients of variation from 1.5 to 20.

INTRODUCTION

To re-establish the integrity of the fuel and remove certain undesirable fission elements, portions of the uranium core of the Experimental Breeder Reactor-II will be routinely melted down in oxide crucibles and recast. The process affords little or no separation of the fission elements zirconium to tellurium, and after a number of processing cycles an equilibrium alloy evolves which contains 1% or more of zirconium, molybdenum, and ruthenium, and lesser amounts of niobium, rhodium, and palladium. Since zirconium may impart certain undesirable metallurgical properties to these alloys, it has been necessary to seek process modifications which will afford significant zirconium removal in each process cycle. To make these studies, inactive uranium alloys containing from 0.01% to 1% zirconium, and the amounts of the other fission elements indicated, were used. Zirconium analyses were required which were precise enough to reveal small process-induced concentration changes at the higher level and sensitive enough to indicate within a factor of two or better the concentration at the lower level.

The success which other authors[1–3] had reported with Alizarin-Red S as a colorimetric reagent for zirconium led to its use in this work. The reported precision of replicate determinations was such that small changes in the higher zirconium alloys would be revealed and the sensitivity of the reagent such that sample sizes could be kept within reasonable limits, 0.1 g, even if the zirconium content were 0.01%. Alizarin-Red S (sodium alizarin sulphonate), like most other colorimetric reagents for zirconium, is rather unspecific, and separation from a number of the other alloying constituents had to be made.

Moore's solvent-extraction with TTA (thenoyltrifluoroacetone),[4] a cupferron extraction, an ion-exchange system developed by Krause and Nelson[5] and an extension of Hume's[6] barium fluozirconate precipitation of fission product zirconium were considered as possible separation methods. The TTA extraction was considered to be prohibitively slow for large numbers of samples. The cupferron extraction is not

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† Operated by The University of Chicago under Contract No. W-31-109-eng-38.

particularly selective and additional separations from one or more of the other fission elements would probably have been needed. Furthermore, both TTA and cupferron must be destroyed by wet ashing before the colour development can be carried out. The ion-exchange separation in hydrochloric-hydrofluoric acid mixtures is very straightforward, but reducing the large volume of eluant and freeing it of its fluoride content is not easily effected. Platinum, in the presence of even small amounts of hydrochloric acid, is attacked by perchloric acid, Pyrex and Vycor both contain prohibitive amounts of leachable zirconium. Even commercial quartz-ware contains 2 to 3 ppm zirconium and significant errors are introduced in low-level analyses when the large volumes of $0.5M$ hydrofluoric acid eluant are evaporated.

The precipitation of barium fluozirconate as a means of separating zirconium from other cations has been used by several workers. Hume[6] used it in the determination of fission-product zirconium as a method of purification but made no attempt to make the precipitation quantitative. Telford[7] showed that the precipitation is quantitative at the 100-mg level in separating zirconium from niobium before gravimetric determination. Milner and Barnett[8] found it to be quantitative at the milligram level providing the acidity is $3N$ or less. They also showed that the separation from niobium, tantalum, tungsten, uranium, molybdenum, lead, iron, copper, and tin was adequate for the titrimetric determination of zirconium with EDTA. In eliminating the yield determination in Hume's fission-product method the authors of this paper[9] had also shown that the precipitation was quantitative at the milligram level.

By co-precipitating barium fluozirconate with barium fluosilicate, satisfactory separation is made from the other fission elements and from the bulk of the uranium. The fluoride in the precipitate is removed by perchloric acid fuming; colour development can be carried out on an aqueous dilution without further manipulation.

A marked improvement in colour stability has been realised through changes in the method of acidity adjustment before colour development.

EXPERIMENTAL

Separations

Zirconium which had been tagged with ^{95}zirconium (65 d) was used to monitor the separation studies reported in this work. The daughter activity, ^{95}niobium, (35 d), was removed by extracting it into methyl *iso*butyl ketone from $8M$ hydrochloric acid. After three equal-volume extractions, less than 0.1% of the niobium remains in the aqueous phase while the zirconium loss is less than 20%. A well-type scintillation counter was used to assay the zirconium activity. Both precipitates and supernates were counted.

For uranium alloys of the fission elements which contain 0.5% or more zirconium, the precipitation of barium fluozirconate affords a satisfactory separation from interferences. In the absence of uranium and the other fission elements as little as 70 μg of zirconium can be quantitatively precipitated from 5 ml of solution. High fluoride and barium concentrations, $5M$ and $0.1M$, and low nitric acid concentration, $0.5N$ are essential for minimising the solubility of the salt. The effect of acidity on the precipitation of barium fluozirconate is shown in Table I. The nitric acid concentration selected for use is $0.5N$; this is low enough to insure the quantitative precipitation of the zirconium but high enough to prevent the precipitation of barium fluoride.

Unfortunately, uranium has a solubilising effect on the fluozirconate precipitate and complete zirconium recovery cannot be obtained when the uranium to zirconium weight-ratio is greater than 200. However, by co-precipitating barium fluozirconate with barium fluosilicate, zirconium can be quantitatively precipitated from solution even at the tracer level (Table II). Barium fluosilicate is not a particularly insoluble salt (the handbook value is 26 mg per 100 ml of water), but quantitative precipitation is apparently not a requisite for quantitative carrying of the zirconium. When separating the zirconium from larger volumes of solution, the standard addition of 6 mg of fluosilicic acid

TABLE I.—EFFECT OF NITRIC ACID CONCENTRATION ON THE PRECIPITATION OF FLUOZIRCONATE

Monitored with ^{95}Zr Activity

Vol = 3 ml $\quad$ $Ba(NO_3)_2 = 0.1N$

$^{95}Zr = 10^4$ cpm $\quad$ $HF = 5N$

Zirconium taken, μg	Nitric acid, N	Zirconium recovered, %
70	0.5	101
140		100
70	1.0	100
140		99
70	2.0	94
140		100
70	3.0	53
140		89

often does not initiate precipitation, and a further addition of fluosilicic acid produces only a relatively small amount. To repress the solubility the same conditions which minimise the solubility of barium fluozirconate, high fluoride and barium concentrations and low acidity are used. The precipitation is not easily initiated, particularly at room temperature, but vigorous stirring and heating will usually overcome this difficulty.

That zirconium in the amounts given in Table II is determinable with Alizarin-Red S after co-precipitation with barium fluosilicate is demonstrated by the results in Table III.

TABLE II.—CO-PRECIPITATION OF BARIUM FLUOZIRCONATE WITH BARIUM FLUOSILICATE

Monitored with ^{95}Zr Activity

Vol = 3 ml $\quad$ $H_2SiF_6 = 4$ mg

$^{95}Zr = 10^4$ cpm $\quad$ $Ba(NO_3)_2 = 0.1M$

$HF = 5M$ $\quad$ $HNO_3 = 0.5M$

Zirconium taken, μg	^{95}Zr recovered, %
Tracer	98
1	99
10	101
20	99
30	99
50	101
75	102
100	98

The effectiveness of the barium fluozirconate fluosilicate precipitation in separating zirconium from each of the other fission elements and uranium in the alloys is shown in Table IV. At the highest uranium : zirconium ratios, 10^4 : 1, the amount of uranium must be limited to about 150 mg to secure quantitative precipitation of the zirconium. Although the co-precipitation of uranyl fluoride is considerable at the 100-mg level, it does not constitute an interference since it neither reacts with the Alizarin-Red S nor absorbs at the zirconium-Alizarin-Red S wave length.

At ruthenium : zirconium and rhodium : zirconium ratios of 50 and more, some co-precipitation of these elements with barium fluorosilicate may also occur. For a particular sample this behaviour is reproducible, but for other samples, although very similar, the amount of co-precipitation may

TABLE III. DETERMINATION OF ZIRCONIUM WITH ALIZARIN-RED S AFTER CO-PRECIPITATION WITH BARIUM FLUOSILICATE

Vol = 3 ml, HF = $5M$, H_2SiF_6 = 4 mg, $Ba(NO_3)_2$ = $0.1M$, HNO_3 = $0.5M$

Zirconium taken, μg	Absorbance*	
	Direct	After pptn.
9.1	0.036	0.038
23.0	0.105	0.110
29.4	0.144	0.146
45 2	0 220	0.226

* 2-cm cells.

vary considerably. When it does occur it is always indicated by coloration, usually rose, of the precipitate. The ruthenium offers no problem as it is fumed off as the tetroxide in the subsequent perchloric acid fuming, but the rhodium interferes by absorbing at the wave length used for zirconium.

Colour development and stability

The perchloric acid fuming which is used to convert from the fluoride medium used for precipitation to one which is anionically satisfactory for colour development results in a 70% perchloric acid solution of unknown volume. Since the acidity at which the absorbance measurement is made must be controlled to ±5% and be in the range of $0.5N$ to $1.0N$, practice has been to make the acidity adjustment by either fuming the sample to incipient dryness or by neutralising the diluted acid with alkali. The latter has been done by either adding alkali until the pH to be used in the colour development has been reached or by a complete neutralisation and then adding a fixed amount of standard acid.

Each of these methods of acidity adjustment can easily result in irreversible zirconium hydrolysis. In fuming zirconium to incipient dryness, there is always grave danger that localised overheating will prevent some of the zirconium from redissolving in dilute acid. Zirconium which has been

TABLE IV. SEPARATION OF ZIRCONIUM FROM OTHER FISSION ELEMENTS AND URANIUM BY THE BARIUM FLUOZIRCONATE-FLUOSILICATE PRECIPITATION

2-cm cells

Interference	Foreign ion to zirconium weight ratio	Zirconium, μg	
		Taken	Found
None	—	61	61
Mo^{VI}	300	61	61
Ru^{III-IV} [a]	260	61	60
Rh^{III}	10	61	61
Pd^{II}	35	61	62
Nb^{V}	10	61	61
Ce^{III}	150	61	62
U^{VI}	1×10^3	61	61
	1×10^4 (600 mg)	61	15[b]
	1×10^4 (150 mg)	15	15[b]

[a] Removed in part by the $HClO_4$ fuming step.

[b] At uranium : zirconium weight ratios of 10^4, complete zirconium recovery can be realised only at the 150-milligram uranium level.

fumed to complete dryness cannot be resolubilised without treating the samples with fluoride and re-fuming. Partial neutralisation of the acid with alkali will result in some zirconium hydrolysis because of localised alkaline conditions no matter how carefully it is done, and complete neutralisation and re-acidification will result in even more extensive hydrolysis.

By fuming the sample to about 1 ml of perchloric acid in a tared crucible and adding 70% acid until there is a standard weight of acid in the crucible, the subsequent dilution to volume can be made without danger of hydrolysis. (In this work, 2.30 g of perchloric acid were used. Diluted to 25 ml this gives an acidity of 0.60*N*.) That there is far less hydrolysis of zirconium when the acid adjustment is made in this manner is shown by the colour stability of the Alizarin-Red S complex. In contrast to colour stabilities of a few hours to a day reported by other authors[1-3] no decrease in colour intensity was noted in a group of samples measured every day for more than a week. In the routine application of the method several days often elapse between the final dilution to volume and the absorbance measurement with no effect on the colour. Since colour development is rather slow, the samples are allowed to stand over-night before the absorbances are measured.

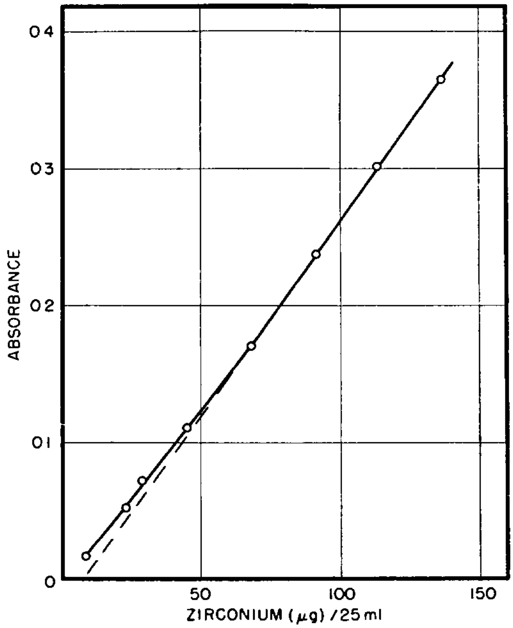

Fig. 1. The absorbance of zirconium alizarin sulphonate vs micrograms of zirconium.

Deviations from Beer's law

A plot of absorbance vs. concentration in the concentration range 0 to 150 μg/25 ml is shown in Fig. 1. The dashed line, an extension of the linear portion of the curve above 75 μg, has been drawn to help to emphasise the negative deviation from Beer's Law below 75 μg.

Reagents

Standard zirconium solution: dissolve 18 g of hafnium-free zirconium tetrachloride in 1 litre of 3*M* hydrochloric acid. Standardise by precipitation with cupferron and ignition to the oxide. Working dilutions, containing about 0.5 mg/ml, are prepared by making dilutions in 1*M* perchloric acid.

Alizarin-Red S: 0.2%, in 0.1*M* perchloric acid
Perchloric acid: 70%
Fluosilicic acid: 0.2*M*
Ammonium hydroxide: 15*M*
Nitric acid: 16*M*
Barium nitrate: saturated

Equipment

Quartz crucibles must be used for fuming samples which contain fluoride as both Pyrex and Vycor contain appreciable amounts of zirconium. The quartz used in this work was found to contain 2 to 3 ppm zirconium. However, the fluoride content of the fluozirconate-fluosilicate precipitate is relatively low and detectable amounts of zirconium are not solubilised.

A Beckman Model B spectrophotometer was used for this work. The sensitivity was "3", and the shutter was in the open position.

Standard curve

Pipette duplicate aliquots of the working standard containing 25, 50, 75, 100, 150, 200, and 300 μg of zirconium into 25-ml volumetric flasks. Add 15 ml of water and 1.30 ml of 70% perchloric acid. Add 1.0 ml of the Alizarin-Red S reagent and dilute to volume with water. Measure the absorbance after 18 hours against a reagent blank at 520 mμ. Use 2-cm cells for those samples containing 75 μg or less.

Procedure for alloys

Dissolve the sample in a quartz flask using the special hydrochloric-nitric-hydrofluoric acid mixture and procedure described by Larsen[10]. Dilute to a known volume and pipette an aliquot of the sample containing 70–300 μg of zirconium into a 10-ml Lusteroid centrifuge tube. Dilute to 3 ml with water. Neutralise by the dropwise addition of 15*N* ammonium hydroxide until ammonium diuranate precipitates (yellow). Dissolve the precipitate by the dropwise addition of 16*N* nitric acid. Add 0.5 ml of 16*N* nitric acid, 1.0 ml of 27*N* hydrofluoric acid, (polyethylene pipettes), and four drops of 0.2*M* fluosilicic acid. Stir. Heat in a water bath (90° to 100°) for 1 minute. Add 1.5 ml of saturated barium nitrate solution and stir (the stirring rod must be platinum, quartz or polyethylene) until the barium fluosilicate precipitate begins to form (avoid excessive stirring). Continue heating for 1 minute. Centrifuge for 3 minutes. Remove the supernate by suction. Slurry the precipitate in 2 ml of water and transfer with two 1-ml water washes to a quartz crucible. Add 1 ml of 70% perchloric acid and evaporate to dryness. Tare the crucible to the nearest 0.01 g. Add 3 drops of 3*N* hydrofluoric acid, 1 ml of water and 2ml of 70% perchloric acid, and heat to fumes of perchloric acid. Re-fume twice after cooling and adding 1 ml of water. (The removal of fluoride by repeated water addition and fuming is superior to a single prolonged fuming.) When there is less than 2.3 g of perchloric acid in the crucible, cool, tare, and add 70% perchloric acid until the crucible contains 2.30 g of acid. Add 5 ml of water and warm gently on a hot plate. Transfer the solution with 10 to 15 ml of water to a 25-ml volumetric flask. Add 1.0 ml of the Alizarin-Red S reagent and dilute to volume with water. After 18 hours measure the absorbance of the sample against a reagent blank in 1-cm cells at 520 mμ.

RESULTS AND DISCUSSION

The reliability of the method was ascertained through the analysis of synthetic uranium solutions which contain percentage amounts of molybdenum, ruthenium, rhodium, and palladium and varying amounts of zirconium. The results are shown in Table V. In the range 0.3–1% the 2% coefficient of variation demonstrates that

TABLE V. ZIRCONIUM DETERMINATION IN SIMULATED ALLOY SOLUTIONS

Nominal alloy composition, % U, 95: Mo, 2.5: Ru, 1.5: Rh, 0.5: Pd, 0.3

Zirconium, %	Coeff. of variation.	Bias	Recovered activity, %	Number of Determinations
1.0	1.5	0	100	20
0.3	2	0	100	20
0.1	5	−1	99	5
0.03	11	+8	96	7
0.01	20	+10	94	6

the method will adequately reveal small changes in alloy composition; at 0.01% zirconium the accuracy and precision will adequately reveal changes in alloy composition within a factor of 2. The positive bias in the results at the lower zirconium concentrations is undoubtedly due to rhodium which is not completely separated.

Zusammenfassung—Alizarin S wurde zur spektrophotometrischen Bestimmung von Zirkonium in Uranlegierungen der Kernspaltelemente verwendet. Abtrennung von Störelementen wurde durch Mitfällung des Zirkonium mit Bariumfluosilikat erreicht. Verbesserung des Farbstabilität sowie der Reproduzierbarkeit der Methode wurden durch Änderungen in der Farbentwicklung erzielt. Legierungen mit 1–0.01% Zirkonium wurden analysiert.

Résumé—On a utilisé le rouge d'alizarine S pour doser par spectrophotométrie le zirconium dans les alliages d'uranium avec les éléments de fission. Le zirconium est séparé par coprécipitation avec le fluosilicate de barium. Une coloration stable et une meilleure précision ont été obtenues en modifiant le procédé de développement de la couleur. Des alliages contenant de 1 à 0,01 pour cent de zirconium peuvent etre analysés par cette méthode avec des coefficients de variation de 1,5 à 20.

REFERENCES

[1] H. G. King and W. H. Owens, U.S. Atomic Energy Comm. Report Y-917, October 1952.
[2] D. L. Manning and J. C. White, *Analyt. Chem.*, 1955, **27**, 1389.
[3] L. Silverman and D. W. Hawley, *ibid.*, 1956, **28**, 806.
[4] F. L. Moore, *ibid.*, 997.
[5] K. A. Krause and F. Nelson, Symposium on *Ion Exchange and Chromatography in Analytical Chemistry* ASTM Spec. Pub. No. 195 (1956).
[6] D. Hume, U.S. Atomic Energy Comm. Report CN-1312, 1945: see C. D. Coryell and N. Sugarman, *Radiochemical Studies of the Fission Products*, McGraw-Hill, New York, 1951, p. 1499.
[7] R. E. Telford, U.S. Atomic Energy Comm. Report MUC-J. W-686, 1945: see C. J. Rodden *Analytical Chemistry of the Manhattan Project*, McGraw-Hill, New York, 1950, p. 477.
[8] G. W. C. Milner and G. A. Barnett, *Analyt. Chim. Acta*, 1956, **14**, 414.
[9] R. P. Larsen and L. E. Ross, U.S. Atomic Energy Comm. Report ANL-5388, October, 1954, p. 84.
[10] R. P. Larsen, *Analyt. Chem.*, 1959, **31**, 545.

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THE MINIMUM IGNITION TEMPERATURE OF ALUMINIUM OXIDE PRECIPITATES

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Summary—Although other workers have shown by thermogravimetric analysis of aluminium oxide precipitates that constant weight can sometimes be reached at temperatures below 700°, the results of the present investigation indicate that, at least where conventional ignition and weighing techniques are used, the safe minimum temperature for the ignition of aluminium oxide to constant weight is 1200°.

IT is common practice among analytical chemists to use a temperature of about 1200° for the ignition of either hydrated aluminium oxide or basic aluminium salts to aluminium oxide[1]. Willard and Tang[2] also recommend this temperature for the ignition of basic aluminium sulphate or basic aluminium succinate precipitates obtained by the urea method. Duval[3] states that 611° is the minimum temperature required in the thermogravimetric ignition of basic aluminium succinate obtained by urea hydrolysis. Although Duval also states that 672° is the minimum temperature for aluminium precipitated with urea, it is not clear if it is basic aluminium sulphate which was ignited; Duval refers to the "urea/succinate" method in the one case but only to the "urea", *i.e.* not the "urea/sulphate", method in the other case. For aluminium precipitated with ammonium hydroxide in the presence of ammonium chloride, he recommends a minimum thermogravimetric temperature of 1031°. Duval quite correctly indicates that higher temperatures are often necessitated by ordinary ignition methods because crucibles must be cooled before weighing and this can expose the precipitate to atmospheric water vapour or other substances which may be absorbed by it.

This investigation was undertaken to determine whether ignition temperatures lower than those usually recommended can be used in the conventional ignition of aluminium oxide precipitates.

EXPERIMENTAL RESULTS

(a) *Conventional ignition*

Four solutions of aluminium chloride, each containing the equivalent of 0.2 g of Al_2O_3, were diluted to 400 ml; these solutions were at pH 2 to 3. A few drops of methyl red indicator and 5 g of ammonium chloride were added to each solution. The subsequent treatment of each solution was as follows:

Method A: Two g of potassium sulphate and 5 g of urea were added. The solution was heated to boiling. After precipitation began, in about 30 minutes, boiling was continued for about 1½ hours more.

Method B: Five g of succinic acid and 5 g of urea were added and precipitation carried out as with solution *A*.

Method C: Five g of urea were added and precipitation carried out as in the previous cases. Though this is not a procedure recommended by Willard and Tang, because it precipitates aluminium in a gelatinous form, hydrous aluminium oxide was thus precipitated and ignited because of the uncertainty, previously stated, as to whether Duval used sulphate in his "urea" method.

Method D: Ammonium hydroxide (1 : 1) was added dropwise to the boiling solution until the indicator changed colour. Then, one additional drop of the hydroxide was added and the solution boiled for 1 minute more.

In all four cases, the precipitates were filtered on paper and washed with 1% ammonium nitrate solution. The filter papers and precipitates were charred and allowed to ignite at 500° for 8 hours. The resulting residues were then further ignited in tared platinum crucibles for 1-hour periods at 650°, 800°, 950°, 1100°, and 1200°. After each ignition period, before being ignited at the next higher temperature, the covered crucibles were cooled in air for a minute, transferred to a desiccator containing phosphorus pentoxide, and weighed rapidly after 10 minutes. The final ignition at 1200° was repeated for a second hour. The results of this series of experiments are shown in Table I.

TABLE I.—EFFECT OF IGNITION TEMPERATURE ON THE WEIGHTS OF ALUMINIUM OXIDE PRECIPITATES OBTAINED BY DIFFERENT METHODS

Temperature[a]	Per cent excess weight over final reference value			
	Method *A* (urea-basic sulphate method)	Method *B* (urea-basic succinate method)	Method *C* (urea method)[b]	Method *D* (ammonium hydroxide method)
°C	%	%	%	%
650	19.2	3.9	3.1	4.5
800	9.8	2.3	1.7	2.4
950	3.4	1.0	1.0	1.2
1100	0.6	0.0	0.0	0.2
1200	0.2	0.0	0.0	0.1
1200 (2nd hour)	Ref. value	Ref. value	Ref. value	Ref. value

[a] After charring of the filter paper, the precipitates were ignited at 500° for 8 hours before being ignited for 1 hour at each of the stated temperatures.

[b] Chloride, but not sulphate or succinate, was present.

Each of the four experiments described above was performed in duplicate on two separate occasions so that four values were obtained for each. These results were averaged to obtain the values reported in the table. Agreement between the replicates was quite good, thus indicating the negligible effects of weighing errors and possible variations of muffle temperatures.

In order to reduce exposure of the precipitates to the atmosphere to a minimum, and thus approximate more closely the conditions encountered in a thermogravimetric ignition, the experiments described for Method *B* and Method *C* were repeated (each in duplicate) with slight modification. After the filter papers were burned off, overnight at 525° this time, ignitions were carried out as before. However, after each incremental ignition, one set of precipitates from *B* and *C* was transferred, red-hot and covered, to a desiccator containing phosphorus pentoxide and allowed to cool before weighing. Because the weight was known to within a few milligrams, the time of weighing and hence exposure to the atmosphere was very short. The other set of precipitates from *B* and *C* was allowed to cool for 3 minutes in the atmosphere before being placed in the desiccator. The results of these experiments are shown in Table II.

(b) *Ignition in a thermobalance*

Precipitates were prepared by Methods *A*, *B*, and *C* as previously described. Filter papers and precipitates were charred and ignited overnight at 525°. Then the precipitates were placed in a quartz-fibre thermobalance and heated from room temperature to about 600° in 45 minutes, while a stream of dry air was passed over the sample. The weight and temperature at this point were taken as base values; the temperature was then raised by nominal 50-degree increments every 50 minutes, the exact temperature being measured with a thermocouple. Because constant temperature was reached in every case in about 10 minutes, the alumina was thus held at each temperature value for 40 minutes before being heated to a higher value. The percentage cumulative weight loss at each temperature level was calculated using as a base value the weight at the initial temperature, nominally 600°. The results for the three precipitates are plotted in Figure 1. All weights are uncorrected for buoyancy in air.

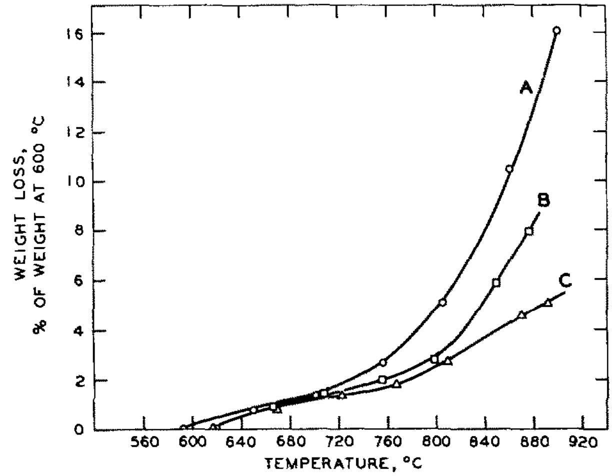

FIG. 1.—Ignition of aluminas after preliminary charring.

TABLE II.—EFFECT OF ATMOSPHERIC EXPOSURE ON WEIGHT OF IGNITED ALUMINIUM OXIDE PRECIPITATES

Temperature	Per cent excess weight over final reference value			
	Precipitate placed in desiccator immediately upon removal from furnace		Precipitate placed in desiccator after 3-minute cooling in atmosphere	
	Method *B* (urea-basic succinate method)	Method *C* (urea method)[a]	Method *B* (urea-basic succinate method)	Method *C* (urea method)[a]
°C	%	%	%	%
650	2.4	2.5	3.1	2.8
800	1.8	1.9	2.4	2.6
950	1.6	1.6	1.9	2.2
1100	0.3	0.4	0.4	0.5
1200	Ref. value	Ref. value	Ref. value	Ref. value

[a] Chloride, but not sulphate or succinate, was present.

In a final experiment, a precipitate obtained by Method *A* was thoroughly air-dried, transferred to the thermobalance, heated rapidly to about 600°, and then heated in 50-degree increments as before. Percentage weight losses were calculated using the initial, *i.e.* the air-dried, value as a base. The results are plotted in Figure 2.

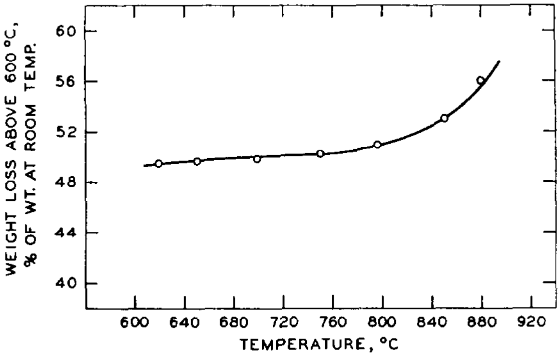

FIG. 2.—Ignition of basic aluminium sulphate.

DISCUSSION

The results in both Table I and Table II show quite clearly that the minimum *conventional* ignition requirement for several of the aluminium oxide precipitates is 1 hour at 1100° (following charring of the paper). Where sulphate is present, as in the basic sulphate method, an even higher temperature is indicated.

Although some of the results in Table II were obtained in a way tending to minimise the effect of atmospheric contamination upon the precipitates, they do not afford unequivocal proof that higher ignition temperatures are mandatory, in contrast to Duval's recommendation of lower values. This proof is given finally by the results obtained with the thermobalance as is shown by the plots of Fig. 1 and 2. The figures show a continuing weight loss up to 900° (the limit of the thermobalance). It is interesting to note in Fig. 2 that the weight of the precipitate is relatively constant between 620° and 760° and upon further heating begins to lose weight again. Although the discontinuously rising temperature did not duplicate exactly the dynamic conditions used by Duval, it is nevertheless concluded that Duval's recommendations for minimum ignition temperatures below 700° must be used with great caution. This conclusion is supported by the work of Erdey and Paulik[4], who repeated Duval's dynamic thermogravimetry on aluminas precipitated by various reagents. Their thermograms differed from those obtained by Duval. From their experiments they concluded that only precipitates that are formed with the hydrargillite crystal structure can be converted to water-free alumina at relatively low temperature. The internal structure of the precipitate, in turn, is primarily determined by the conditions of precipitation (such as rate, temperature, concentration), and influenced to only a small extent by the nature of the precipitating agent.

They attribute the lower ignition temperatures reported by Duval not to the reagents used but to differences in the physical conditions of precipitation, which produced, for Duval, precipitates with an internal structure similar to that of hydrargillite. They imply that such conditions might be difficult to reproduce, because they had noted in their work that the compositions and structures were not exactly the same even for preparations precipitated in parallel with each other under ostensibly the same conditions. Even small variations have a marked effect upon the structure and hence upon the ignition temperature.

Other workers[5,6] have also shown the importance of precipitation conditions in determining the thermal stability of precipitated aluminas. Imelik and co-workers[5] showed, for example, that it is possible to obtain constant weight at a low temperature without completely eliminating water. Wiele[7] has found that with aluminas precipitated by ammonia or thiosulphate ignition at 1200° it is necessary to remove water completely, and that even after ignition at this temperature, the precipitate is still hygroscopic and should be weighed rapidly.

In view of the authors' results and evidence presented by other investigators, it is recommended that a minimum ignition temperature of 1200° should be used for aluminium oxide precipitates which are to be ignited and weighed by conventional techniques, and that such precipitates be weighed as rapidly as possible.

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Zusammenfassung—Wenngleich andere Autoren auf Grund thermogravimetrischer Untersuchungen gezeigt haben, dass es möglich ist für Aluminiumoxyd-Niederschläge konstantes Gewicht bei Temperaturen unter 700°C zu erreichen, muss auf Grund der vorliegenden Untersuchungen gefolgert werden, dass zumindest bei Anwendung konventioneller Glüh- und Wägeverfahren die sichere Mindesttemperatur zum Konstantglühen von Aluminiumoxyd 1200°C ist.

Résumé—Bien que d'autres auteurs aient montré par analyse thermogravimétrique de précipités d'oxyde d'aluminium, que l'on peut parfois atteindre un poids constant à des températures inférieures à 700°, les résultats de la présente étude indiquent que, tout au moins pour les techniques courantes de calcination et de pesée, une température minimum de 1200° est nécessaire pour la calcination à poids constant de l'oxyde d'aluminium.

REFERENCES

[1] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, *Applied Inorganic Analysis*, 2nd edition, New York, John Wiley and Sons, Inc., 1953, pp. 500–505.
[2] H. H. Willard and N. K. Tang, *Ind. Eng. Chem. Analyt.*, 1937, **9**, 357.
[3] C. Duval, *Inorganic Thermogravimetric Analysis*, Amsterdam, Elsevier Publishing Company, 1953, pp. 105–116.
[4] L. Erdey and F. Paulik, *Acta Chim. Acad. Sci. Hung.*, 1955, **7**, 45.
[5] B. Imelik, M. V. Mathieu, M. Prettre, and S. Teichner, *J. Chim. Phys.*, 1954, **51**, 651.
[6] J. H. Lewis and C. A. Taylor, *J. Appl. Chem.*, 1958, **8**, 223.
[7] H. Wiele, *Analyt. Chim. Acta.* 1956, **15**, 326.

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DETERMINATION OF THE ACTUAL CONTENT OF ACID CHLORIDE IN THE CHLORIDES OF CARBOXYLIC ACIDS

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Summary—A new method has been evolved for the determination of the actual contents of acid chloride, and of the amounts of free hydrochloric acid and free carboxylic acid resulting from decomposition, in carboxylic acid chlorides. The sample to be analysed is treated with anhydrous ethanol. The acid chloride reacts with ethanol to form an ester. The volume of standard alkali consumed in saponifying this ester indicates the actual content of acid chloride in the sample.

THE chlorides of carboxylic acids are materials of great fundamental importance in preparative organic chemistry, in analytical chemistry and in industrial organic chemistry.

Most of them are extremely labile, due to their strong acylating activity. They decompose partially by the action of atmospheric moisture, yielding the corresponding carboxylic acid and hydrochloric acid. Therefore samples of carboxylic acid chlorides almost always contain some free carboxylic acid and hydrochloric acid, in addition to their actual content of carboxylic acid chloride. Few authors[6,7] have dealt with the analysis of these compounds. One of the most used methods for the evaluation of carboxylic acid chlorides, that suggested by Siggia and Stahl[4], is rather cumbersome and often difficult to apply.

In certain work we required to evaluate palmityl chloride, a substance used in the pharmaceutical industry. As no suitable method was found in the literature available to us, a new procedure had to be worked out.

In essence, the method may be summarised as follows. Palmityl chloride was treated with anhydrous ethanol, producing ethyl palmitate and hydrochloric acid through the acylating action of palmityl chloride. Free palmitic acid present in the sample as a product of previous decomposition did not react with ethanol. The total content of hydrochloric acid in the ethanolic solution (hydrochloric acid formed during ester formation plus hydrochloric acid formed as a result of earlier decomposition) can be titrated with a standard solution of alkali using methyl red as indicator. (The pH of an ethanolic solution of palmitic acid is the same as for the colour change of methyl red.) Subsequently, titration with alkali is continued in the presence of phenolphthalein as indicator. This latter procedure indicates the free palmitic acid content of the sample. Under the experimental conditions chosen, the ester does not react with alkali. The ethanolic solution contains ester in an amount equivalent to the acid chloride content of the sample, and this ester can be hydrolysed in hot solution by treatment with excess alkali. The acid chloride content of the sample can then be calculated from the quantity of alkali required for saponifying the ester.

Carboxylic acids with fewer carbon atoms than palmitic acid are stronger acids, and their ethanolic solution shows an acid reaction with respect to methyl red. The content of free carboxylic acid and hydrochloric acid formed during decomposition in samples of the chlorides of these acids cannot be determined by this acidimetric method using two indicators. On titrating with alkali in the presence of methyl red, a portion of free organic acid will be neutralised in addition to hydrochloric acid. The complete analysis of acid chlorides of this type is carried out by titrating the hydrochloric acid liberated during formation of ester, together with the hydrochloric acid and organic acid ultimately present due to decomposition, with standard alkali hydroxide solution using phenolphthalein as indicator. Then the titrated solution is treated with excess alkali and the quantity of alkali required for the saponification of ester equivalent to the actual content of acid chloride is determined, by titration with standard sulphuric acid solution. Finally the amount of hydrochloric acid liberated during ester formation and that of hydrochloric acid due to decomposition are determined by a Volhard argentometric titration. From the results (content of total acid, actual content of acid chloride and content of chloride) not only the actual acid chloride content but also the quantity of free carboxylic acid and hydrochloric acid due to decomposition can be calculated.

In some exceptional cases, acid chlorides may contain impurities, resulting from improper storage, which can be acylated (*e.g.* phenols, alcohols etc.). These contaminants will obviously be present in the acid chloride in the form of esters. In the present method, esters will raise the apparent content of acid chloride. However, as these esters produce no acid on reaction of the acid chloride with ethanol, their presence is evident on taking into account the quantity of free hydrochloric acid developed during ester formation and that of alkali required for the saponification of the ester. In the presence of contaminating esters, more alkali is consumed in the saponification than corresponds to the quantity of hydrochloric acid liberated during the reaction of acid chloride with ethanol. In the case of samples of undecomposed chlorides of carboxylic acids, both these values are obviously identical. However, in practice the chlorides of carboxylic acids always contain some free hydrochloric acid and carboxylic acid, due to decomposition. Thus, in general, more alkali is needed to neutralise the hydrochloric acid content of the reaction mixture of acid chloride and ethanol, than is required for the saponification of the ester.

In the course of evolving this method, the conditions for ester formation in the reaction of palmityl chloride (and other carboxylic chlorides) with ethanol were investigated. It was found that on dissolving palmityl chloride and acetyl chloride in anhydrous ethanol (0·05–0·20 g chloride in 20 ml of ethanol), conversion to ester was complete in 10 minutes at room temperature. With benzoyl chloride or chloroacetyl chloride, ethanol was more slowly acylated. To facilitate ester formation, the ethanolic solution was heated with the latter acid chlorides for 5 min in a hot-water bath. Contrary to reports in the literature, no special acid-binding substance (such as *e.g.* pyridine) is needed in an ethanolic solution to ensure quantitative ester formation. Acid (protons) liberated during ester formation is bound by the solvent molecule and alcoholium ion is formed.

In addition the conditions of hydrolysis of ethyl palmitate, acetate, chloroacetate and benzoate were investigated. It was found that a 0·1*N* solution of alkali does not react with these esters when the free acid developed during ester formation (plus the original acid content of the sample) are titrated in the presence of phenolphthalein as indicator at 0° (in melting ice). The colour of a solution overtitrated with one drop of 0·1N alkali does not change for some minutes. (The only exception is with ethyl chloroacetate, which decomposes somewhat more readily. On determining this compound, the colour of a solution titrated to pink in the presence of phenolphthalein faded in about a minute.) Further, it was found that the esters mentioned above can be saponified quantitatively in an hour when treated on a hot-water bath with at least 40–50% excess of alkali. In the case of palmityl chloride care must be taken to maintain in the reaction mixture during hydrolysis an ethanol content sufficient to keep the undecomposed ester in solution.

EXPERIMENTAL

Reagents (analytical grade)

Anhydrous ethanol: 100·0%, dehydrated by metallic calcium according to Winkler.[5]
Sodium hydroxide: 0·1N solution.
Hydrochloric acid: 0·1N (or sulphuric acid) solution.
Silver nitrate: 0.1N solution.
Ammonium thiocyanate: 0·1N solution.
Methyl red indicator.
Phenolphthalein indicator.
Ferric nitrate indicator: 10% solution of ferric nitrate in 10% nitric acid.

Determination of the content of hydrochloric acid and of free carboxylic acid

About 20 ml of anhydrous ethanol are poured into a 100-ml Erlenmyer flask with a ground-glass stopper, which has been carefully dried or repeatedly rinsed with anhydrous ethanol. After drying the ground joint thoroughly, the flask is weighed on an analytical balance, and a sample of carboxylic acid chloride equivalent to about 6–12 ml of 0·1N sodium hydroxide solution is weighed into the flask with analytical accuracy. A glass funnel, with a small piece of cotton wool, to serve as a reflux condenser, is then placed in the mouth of the flask. The reaction mixture is heated for 5 min on a hot-water bath, and is then cooled in melting ice. In the case of acetyl chloride and palmityl chloride, ester formation is completed even at room temperature in 10 min.

In the case of palmityl or stearyl chloride, the quantity of hydrochloric acid liberated during ester formation, together with the final free hydrochloric acid content of the sample, are established by titration with 0·1N sodium hydroxide in the presence of two drops of methyl red as indicator. Then 5 drops of phenolphthalein indicator are added and the free carboxylic acid content of the sample is measured by further titration with the standard solution of sodium hydroxide. When analysing acid chlorides of strong acids, the hydrochloric acid liberated during ester formation together with the content of initial free hydrochloric acid and free carboxylic acid after the reaction with anhydrous ethanol, are titrated with 0·1N sodium hydroxide in the presence of 5 drops of phenolphthalein indicator. When not only the determination of the actual content of acid chloride but a complete analysis is needed, the excess of alkali is back-titrated with standard sulphuric acid solution. Then chloride is precipitated with an excess of 0·1N silver nitrate solution, about 1 g of potassium nitrate is added to the reaction mixture, which is boiled to complete coagulation and excess silver nitrate is titrated with 0·1N ammonium or potassium thiocyanate, using 1 ml of ferric nitrate solution as indicator.

Determination of the actual content of acid chloride in the sample

About 1·5–2·0 times as much 0·1N sodium hydroxide as was used in the previous titration is added with analytical accuracy to the solution which has already been titrated with sodium hydroxide using phenolphthalein as indicator. If the reaction mixture becomes turbid on adding alkali, 96% ethanol is added until the liquid clears. The flask is then heated on the hot-water bath for about an hour and excess alkali is back-titrated with 0·1N hydrochloric or sulphuric acid until the pink colour of phenolphthalein completely disappears. The quantity of 0·1N sodium hydroxide required for saponifying the ester is a measure of the actual content of acid chloride.

CALCULATION OF THE RESULTS

The actual composition of the sample is expressed by the formulae

$$\text{Percentage of acid chloride} = \frac{100[\{C - (B + D)\}M]}{A}$$

$$\text{Content of free HCl of sample, } \% = \frac{100[E - \{C - (B + D)\}\ 3{\cdot}646]}{A}$$

$$\text{Content of free carboxylic acid of sample, } \% = \frac{100\{(B - E)Mc\}}{A}$$

where A is the weight of sample, B the volume of 0·1N alkali consumed in the presence of phenolphthalein, C the total volume of 0·1N alkali consumed, D the volume of 0·1N acid consumed when back-titrating the excess alkali, E the volume of 0·1N silver nitrate consumed when titrating the chloride content in A mg of sample (in the case of palmityl chloride E refers to 0·1N alkali), and M is 1/10 of the milligram-molecular weight of the acid chloride analysed (*i.e.* 27·487 for palmityl chloride, 7·850 for acetyl chloride, 11·295 for chloroacetyl chloride, and 14·057 for benzoyl chloride), Mc is 1/10 of the milligram-molecular weight of the carboxylic acid analysed (*i.e.* 25·64 for palmitic acid, 6·005 for acetic acid, 9·45 for chloroacetic acid and 12·213 for benzoic acid). Of these values, A is expressed in milligrams whilst B-E are expressed in ml. When $E < C - (B + D)$, the sample contains ester contaminants.

Control tests

In our control tests, the following samples were used.

1. Palmityl chloride, analytical grade, refined by distillation,
2. Palmityl chloride, analytical grade,
3. Palmityl chloride, technical grade,
4. Acetyl chloride, analytical grade,
5. Acetyl chloride, technical grade,
6. Chloroacetyl chloride, analytical grade,
7. Benzoyl chloride, analytical grade.

The content of total carboxylic acid and hydrochloric acid (*i.e.* of acid chloride plus hydrochloric acid and carboxylic acid produced during decomposition) was measured in the analytical grade samples by the method prescribed in *Ph. Hung. V* for the determination of the saponification number. On hydrolysis by alkali, the content of chloride was measured in the samples, by argentimetry. In the case of palmityl chloride and benzoyl chloride, the content of total carboxylic acid (*i.e.* that of acid chloride plus that of free carboxylic acid produced during decomposition) was isolated and determined by an appropriate method, after hydrolysis by alkali. The results of measurements were in fair accordance with the results obtained by the newly evolved method.

With this new method, the contents of acid chloride, free hydrochloric acid and free carboxylic acid were determined in the listed samples. The combined values of the results were compared with the weighed amounts (*cf.* Table I).

The relative error of the method lies within ±1.0%. Some results are summarised in Tables I and II.

TABLE I.—RESULTS OF THE COMPLETE ANALYSIS

Nature of sample	Sample weighed, *mg*	Actual content of acid chloride		Decomposition products				Total	
				HCl		Carboxylic acid			
		mg	%	*mg*	%	*mg*	%	*mg*	%
Acetyl chloride, technical	104·0	83·5	80·31	1·31	1·26	19·20	18·46	104·0	100·0
	118·0	94·4	80·03	0·73	0·62	21·80	18·47	116·9	99·1
Benzoyl chloride, analytical grade	95·8	94·6	98·75	0·80	0·83	0·0	0·0	94·5	99·58
	211·4	210·4	99·53	1·2	0·57	0·0	0·0	211·6	100·1
Palmityl chloride, analytical grade refined by distillation	127·4	121·7	95·5	0·25	0·2	4·59	3·6	126·5	99·3
	207·9	200·2	96·3	0·31	0·15	7·07	3·4	207·6	99·85
Palmityl chloride, analytical grade	139·5	132·9	95·3	0·0	0·0	5·58	4·0	138·5	99·3
	123·2	117·0	95·0	0·0	0·0	5·05	4·1	122·1	99·1
Palmityl chloride, technical grade	143·5	130·6	91·0	0·86	0·6	8·18	5·7	139·6	97·3
	208·7	189·1	90·6	1·25	0·6	12·10	5·8	202·5	97·0

TABLE II.—ACTUAL CONTENT OF ACID CHLORIDE IN VARIOUS CARBOXYLIC ACID CHLORIDES

Nature of sample	Amount weighed, *mg*	Actual content of acid chloride	
		mg	%
Acetyl chloride, analytical grade	43·5	43·1	99·1
	66·9	65·7	98·2
	106·6	105·0	98·5
Acetyl chloride technical grade	104·0	83·5	80·3
	118·0	94·4	80·0
Chloroacetyl chloride, analytical grade	79·6	77·7	97·6
	117·4	114·2	97·3
Benzoyl chloride, analytical grade	95·8	94·6	98·8
	211·4	210·4	99·5
Palmityl chloride, analytical grade, refined by distillation	127·4	121·7	95·5
	207·9	200·2	96·3
Palmityl chloride, analytical grade	139·5	132·9	95·3
	123·2	117·0	95·0
Palmityl chloride, technical grade	143·5	130·6	91·0
	208·7	189·1	90·6

Zusammenfassung—Verfasser geben einen Arbeitsgang zur Untersuchung verschiedener Carbonsäurechloride zwecks Bestimmung ihrer effektiven Säurechloridgehalte sowie ihrer eventuellen infolge Hydrolyse entstandenen Salzsäure, sowie Carbonsäuregehalte an. Die Carbonsäurechloride reagieren mit absolutem Äthanol unter Bildung von Estern. Aus der Esterzahl dieser Lösung lässt sich der Carbonsäurechloridgehalt berechnen.

Wird das Reaktionsgemenge im Falle von Palmityl- bzw. Stearylsäurechloride nach der Esterifizierung und vor der Esterzahlbestimmung zuerst gegen Methylrot, dann gegen Phenolphthalein genau neutralisiert, so kann auch die eventuelle freie Salzsäure, bzw. Carbonsäure berechnet werden. Bei der Untersuchung von Acetylchlorid neutralisiert man gegen Phenolphthalein und bedient sich bei der Esterzahlbestimmung einer volumetrischen Schwefelsäure. Nach Durchführung einer Gesamtchlorbestimmung kann der Gehalt an freier Salzsäure bzw. Carbonsäure ebenfalls berechnet werden.

Résumé—On développe une nouvelle méthode pour la détermination de la teneur en chlorure d'acide présent et de la quantité d'acide chlorhydrique et carboxylique libre formés après décomposition, dans des échantillons de différents chlorures d'acides carboxyliques. L'échantillon à analyser est traité par de l'éthanol anhydride. Le chlorure d'acide réagit avec l'éthanol pour former un ester. Le volume de base alcaline titrée consommé dans la saponification de l'ester correspond à la teneur en chlorure d'acide présent.

REFERENCES

[1] D. M. Smith and W. M. Bryant, *J. Amer. Chem. Soc.*, 1935, **57**, 61.
[2] *Idem*, *ibid.*, 841.
[3] J. Mitchell and C. E. Askby, *ibid.*, 1945, **67**, 161.
[4] S. Siggia, *Quantitative Organic Analysis via Functional Groups*, John Wiley, New York, 1954, p. 55.
[5] L. Winkler, *Ber.*, 1915, **38**, 3612; *Z. angew. Chem.*, 1916, **29**, I, 18.
[6] J. Mitchell and D. M. Smith. *Aquametry*, Interscience Publ., New York, 1948, p. 369.
[7] B. Saville, *Analyst.*, 1957, **82**, 269.

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SPECTROPHOTOMETRIC DETERMINATION OF FLUORIDE USING LANTHANUM CHLORANILATE

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Summary—Spectrophotometric determination of fluoride has been investigated using lanthanum chloranilate. It has been found possible to determine 2–200 ppm of fluoride with an accuracy of ±2%, if the proper reaction conditions are chosen. Sulphate, chloride and nitrate ions do not interfere up to 200 ppm. Application of this procedure to fluoride determination in organic fluorocompounds is described.

INTRODUCTION

THE use of chloranilic acid (2:5-dichloro-3:6-dihydroxy-*p*-benzoquinone) as an analytical reagent for various cations has been known for many years. However, since Bertolacini and Barney[1,3] proposed the photometric determination of sulphate by utilising the metathesis reaction between barium chloranilate and sulphate ion, the application of polyvalent metal chloranilates to the photometric determination of various anions has received considerable attention. Thus, mercuric chloranilate has been used for the determination of chloride ion[2,3] and strontium chloranilate has been proposed for the determination of fluoride ion.[3]

The photometric determination of anions using metal chloranilate depends on the reaction

$$\text{anion}^{n-} + \underset{\substack{\text{finely}\\\text{powdered}\\\text{crystals}}}{\text{M-}Ch} + \text{H}^+ \rightarrow \underset{\substack{\text{purple}\\\text{solution}}}{\text{H}Ch} + \underset{\substack{\text{insoluble}\\\text{precipitate}}}{\text{M-anion}}$$

On addition of a finely powdered metal chloranilate to the sample solution containing a suitable anion, the metal salt of the anion is precipitated, with the liberation of purple acid chloranilate ion (H*Ch*). After the reaction, excess metal chloranilate and insoluble metal salt are filtered off, and acid chloranilate ion is determined photometrically in the filtrate; this corresponds to the amount of fluoride in the sample. The sensitivity of the determination is, therefore, dependent mainly upon the insolubility of the metal salt formed by the metathesis. The sensitivity of the fluoride determination with strontium chloranilate will not be very high, since the solubility product of strontium fluoride is not small enough.

On the other hand, the solubility of lanthanum fluoride is very low, and therefore lanthanum chloranilate has been tried for fluoride determination in an analogous manner.† This reagent has been found to give much more satisfactory results than strontium chloranilate.

The procedure with the lanthanum reagent is rapid and simple, and 2 to 200 ppm of fluoride can be determined with an accuracy of ±2%.

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† During the course of this investigation, Fisher Scientific Co. (U.S.A.) announced the availability of lanthanum chloranilate as an analytical reagent for fluoride determination, but no detailed account has been available to the present authors.

EXPERIMENTAL

Reagents

Lanthanum chloranilate was prepared by mixing a hot solution of 20 g of chloranilic acid in 4.6 litres of distilled water with a solution of 17 g of lanthanum oxide (99·9%) in 27 ml of nitric acid (sp. gr. 1·42) and 200 ml of distilled water. After standing overnight, the fine dense precipitate of lanthanum chloranilate was collected by filtration and washed with distilled water until the filtrate was free from nitrate. The dark grey product was dried under a heating lamp, and was kept in an amber bottle. The yield was almost quantitative, and the reagent can be kept for an indefinite period without appreciable deterioration.

Standard fluoride solution (approximately 4000 ppm of F^-) was prepared by dissolving 7·8 g of ammonium fluoride in 1 litre of distilled water, and the fluoride ion concentration was determined by indirect EDTA titration via calcium fluoride.[4]

Buffer solutions employed in this investigation, ranged from pH 2 to 7, and were prepared according to the standard recipes as follows: Acetate buffer, pH 2 (sodium acetate and hydrochloric acid); acetate buffers, pH 4, 5 and 7 (sodium acetate and acetic acid); phthalate buffer, pH 6 (potassium acid phthalate and potassium hydroxide); succinate buffer, pH 7 (sodium succinate).

Methylcellosolve, ethanol (95%) and all other reagents were reagent grade.

Apparatus

Spectrophotometric determinations were carried out by a Beckman Model DU spectrophotometer equipped with a tungsten lamp and 1-cm Corex cells. A glass-electrode pH meter was used for all pH measurements, and a mechanical shaking apparatus with a time switch was employed to ensure constant reaction conditions.

General procedure

The following general procedure was employed to investigate the effects of reaction conditions and of various interfering ions: Pipette the standard fluoride solution containing 0·2–10 mg of fluoride into a 100-ml volumetric flask. To this, add 10 ml of buffer solution, 50 ml of water-miscible organic solvent and 0·2 g of lanthanum chloranilate (crystalline powder), and dilute the mixture to volume with distilled water. After shaking the flask on a shaking machine for a given period, filter the solution through a filter paper. Discard the first portion of filtrate, then collect the middle portion in a Corex cell. Determine the optical density of this solution at 530 mμ against a reagent blank.

RESULTS AND DISCUSSION

Selection of absorption peak

The absorption spectrum of acid chloranilate ion in aqueous solution has two maxima, one in the visible region (520–550 mμ) and the other in the ultraviolet region (280–350 mμ); the intensity of the ultraviolet peak is 20–30 times greater than that of the visible one. Either maximum can be used for the photometric determination of chloranilic acid up to a concentration as high as 100 mg per 100 ml.

With the absorption peak in the ultraviolet region a higher sensitivity is possible than in the case of visible spectrophotometry; but ultraviolet spectrophotometry suffers from more interference, especially in the analysis of actual samples. It was therefore decided to utilise the absorption peak in the visible region so that the procedure would be less influenced by foreign material, although there would be some sacrifice of sensitivity; and so that a visible spectrophotometer or a filter photometer could be used instead of the more expensive ultraviolet spectrophotometer.

Effect of organic solvent

As in the case of sulphate determination using barium chloranilate,[1,3] and of chloride determination using mercuric chloranilate,[2,3] addition of a water-miscible organic solvent increased the sensitivity of the colour reaction. Presumably the addition of organic solvent reduces the solubility or dissociation of the insoluble salt. Of the organic solvents investigated, only methylcellosolve and ethanol were found to be useful, and this is shown in Fig. 1. At any given pH (*i.e.* with a given buffer solution) methylcellosolve gave better sensitivity than ethanol.

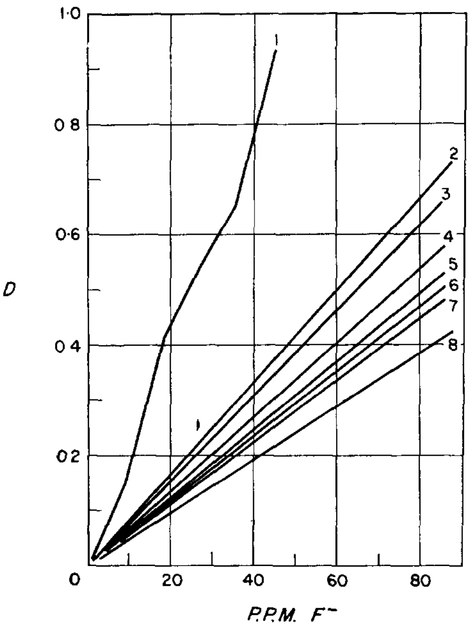

FIG. 1.—Effect of buffer solution and solvent on calibration curves

1. Acetate buffer pH 2, 1:1 ethanol:water
2. Acetate buffer pH 4, 1:1 methylcellosolve:water
3. Acetate buffer pH 4, 1:1 ethanol:water
4. Succinate buffer pH 7, 1:1 methylcellosolve:water
5. Acetate buffer pH 7, 1:1 methylcellosolve:water
6. Succinate buffer pH 7, 1:1:2 ethanol:methylcellosolve:water
7. Succinate buffer pH 7, 1:1 ethanol:water
8. Acetate buffer pH 7, 1:1 ethanol:water

(shaking time, 20 minutes)

Effect of pH and the buffer composition

As the absorption spectrum of acid chloranilate ion is markedly influenced by the pH of solution, the sensitivity and the reproducibility of the colour reaction are also dependent on pH. The intensity of the absorption maximum decreases with increasing pH of the solution, and the influence of pH is more marked in the lower pH range (pH 1–2). Therefore, if the colour reaction is carried out at pH 2, the sensitivity becomes higher, but reproducible results are very difficult to obtain. When the pH of the reaction medium is increased to 7, the reproducibility is improved, but the sensitivity decreases. At intermediate pH values (pH about 4), the sensitivity is sufficiently high without too great a sacrifice of reproducibility. The reaction was therefore carried out at pH 4, if no interfering ion was present in the sample. However, if anions such as sulphate, nitrate or chloride were present, the reaction was carried out at pH 7 where the photometric determination of chloranilate ion was less influenced by those anions.

While the absorbance of the reagent blank is generally low and is almost constant in the range pH 4–6, the composition of the buffer solution and the nature of the organic solvent may affect the absorbance of the reagent blank markedly, as shown in Table I. Of the buffer solutions, phthalate buffer (pH 6) gave an abnormally high blank value and was therefore unsatisfactory. Regarding the reagent blank, a lower value for the reagent blank was found for ethanol than for methylcellosolve.

TABLE I.—INFLUENCE OF BUFFER SOLUTIONS AND ORGANIC SOLVENTS UPON THE REAGENT BLANK ABSORBANCE AT 530 mμ.

Buffer and pH		Absorbance in	
		50% ethanol	50% methylcellosolve
Succinate	7	0·019	0·047
Acetate	7	0·018	0·070
Phthalate	6	0·125	0·360
Acetate	5	0·013	0·044
Acetate	4	0·010	0·038

Reaction time

The method of shaking is fairly important in this reaction, since the metathesis reaction occurs on the surface of the crystalline particle of lanthanum chloranilate. Although the results obtained using manual shaking are fairly reproducible, it is better to employ a mechanical shaker to ensure constant conditions. A suitable rate of shaking is 350 strokes per minute. As the reaction is heterogeneous, colour development depends on time of shaking as shown in Fig. 2. The absorbancy increases with increasing duration of shaking, but the value becomes nearly constant after 15 minutes, and reproducible results are obtained when the spectrophotometric determinations are carried out after 20 minutes shaking in these conditions.

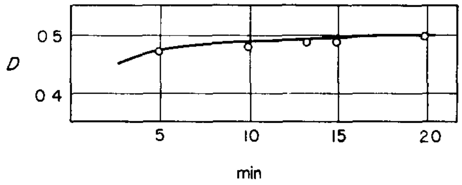

FIG. 2.—Effect of shaking time on colour development
86 ppm of F$^-$
Succinate buffer pH 7; 1:1 ethanol:water

Interfering ions

Almost all cations interfere in the determination, since the absorption spectrum of acid chloranilate is more or less influenced by the cations. Even sodium and potassium ions, if present in large amounts, influence the absorbancy. Although it has been reported that the interference of these two cations can be cancelled by adding large amount of sodium or potassium ion to the reagent blank,[5] it was found desirable to remove all cations in the sample solution by ion-exchange before the determination.

TABLE II.—INTERFERENCES OF SULPHATE, CHLORIDE AND NITRATE

Buffer, pH	Solvent	Absorbance[a]												
		With no interfering ion	With sulphate				With chloride				With nitrate			
			400 ppm	% error	200 ppm	% error	400 ppm	% error	200 ppm	% error	400 ppm	% error	200 ppm	% error
Succinate, 7	Methylcellosolve	0·458	0·501	+9·4	0·493	+7·6	0·467	+2·0	0·467	+2·0	0·457	−0·2	0·473	+3·3
	Methylcellosolve and ethanol (1 : 1)	0·411	0·435	+5·8	0·425	+3·4	0·414	+0·7	0·412	+0·2	0·401	−2·4	0·407	−1·0
	Ethanol	0·388	0·397	+2·3	0·392	+1·0	0·384	−1·0	0·384	−1·0	0·386	−0·5	0·390	+0·5
Acetate, 7	Methylcellosolve	0·428	0·465	+8·6	0·450	+5·1	0·410	−4·3	0·409	−4·4	0·425	−0·7	0·426	−0·5
	Ethanol	0·321	0·374	+16·5	0·374	+16·5	0·324	+0·9	0·326	+1·6	0·324	+0·9	0·330	+2·8
Acetate, 4	Methylcellosolve	0·564	0·647	+14·7	0·623	+10·5	0·548	−2·8	0·559	−0·9	0·558	−1·1	0·578	+2·5
	Ethanol	0·562	0·612	+8·9	0·597	+6·2	0·526	−6·4	0·542	−3·6	0·550	−2·1	0·570	+1·4

[a] Absorbance was measured after treating the sample, containing 70 ppm of F^-, according to the standard procedure. Values shown in the table are the average of five determinations.

Efforts to find a suitable masking agent for certain cations were unsuccessful. The only exception in respect of interference is ammonium ion which does not interfere even in large amounts.

The interferences of anions were investigated using ammonium salts of various anions, and the results are shown in Table II, which shows that chloride, nitrate and sulphate do not interfere appreciably up to the 200 ppm-level if the proper pH and buffer solution are chosen. However, in the presence of larger amounts of anions, the interferences cannot be overlooked, and calibration curves have to be prepared using standard solutions containing the same amount of interfering anions.

Recommended procedure

On the basis of these results, the following procedure is recommended for the determination of fluoride: Place the sample solution, containing 0·2–10 mg of fluoride ion, in a 100-ml volumetric flask. To this, add 10 ml of 0·03*M* sodium succinate (pH 7), 50 ml of 95% ethanol and 0·2 g of lanthanum chloranilate (crystalline powder*), and make the solution to 100 ml with distilled water. Shake the flask for 20 minutes, and filter the solution through a filter paper. Discard the first portion of the filtrate, and collect the middle portion in a cell for spectrophotometric measurement. Read the light absorbancy at 530 mμ against a reagent blank.

FLUORINE DETERMINATION IN ORGANIC FLUORINE COMPOUNDS

Since the lanthanum chloranilate method is very convenient for determination of fluorine in samples free from cations, determination of fluorine in organic fluorocompounds, after a suitable decomposition, is one of the promising applications of the method. For example, if the flask combustion method[6] is combined with this chloranilate procedure, it is possible to carry out a single determination in 50 minutes with satisfactory accuracy.

Determination of fluorine in 2-thenoyltrifluoroacetone

A weighed amount of 2-thenoyltrifluoroacetone (about 50 mg) was decomposed in a Schöniger flask containing 30 ml of distilled water. After combustion, the flask was shaken for 10 minutes to ensure complete absorption of the decomposition products. The contents of the flask were quantitatively transferred to a 100-ml volumetric flask and diluted to volume with distilled water. The chloranilate procedure was carried out on 15–30 ml aliquots of this solution. The results of the determinations are shown in Table III.

TABLE III.—DETERMINATION OF FLUORINE IN 2-THENOYLTRIFLUOROACETONE

Amount of sample, *mg*	Absorbancy	Fluorine, *mg*		
		Observed	Theoretical	Error %
48	0·200	12·13	12·32	−1·5
48·5	0·203	12·33	12·45	−1·0

Zusammenfassung—Die spektrophotometrische Bestimmung von Fluorid unter Verwendung eines neuen Reagenses (Lanthanchloranilat) wurde studiert. Es wurde gezeigt, dass es möglich ist 2–200 ppm Fluorid mit einer Genauigkeit von ±2% zu bestimmen, wenn geeignete Reaktionsbedingungen eingehalten werden. Sulfate, Chlorid und Nitrationen stören nicht in Mengen bis zu 200 ppm. Die Anwendung der neuen Methode auf die Fluorbestimmung in organischen Fluorverbindungen wird beschrieben.

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* The amount of lanthanum chloranilate need not be accurately measured and can be weighed on an ordinary laboratory balance.

Résumé—Le dosage spectrophotométrique du fluorure a été étudié en utilisant un nouveau réactif, le chloranilate de lanthane. On montre qu'il est possible de doser 2 à 200 p.p.m. de fluorure avec une précision de ±2% si l'on choisit des conditions de réaction appropriées. Les ions sulfate, chlorure et nitrate ne gênent pas jusqu'à une teneur de 200 p.p.m. Les auteurs décrivent une application de ce procédé au dosage du fluor dans les composés organiques fluorés.

REFERENCES

[1] R. J. Bertolacini and J. E. Barney, *Analyt. Chem.*, 1957, **29**, 281.
[2] J. E. Berney and R. J. Bertolacini, *ibid.*, 1187.
[3] R. J. Bertolacini and J. E. Berney, *ibid.*, 1958, **30**, 202.
[4] K. Sato and Y. Osumi, *Osaka Kōgyō Gijutsu Shikenjo Kihō*, 1956, **7**, 232.
[5] R. E. U. Frost-Jones and J. T. Yardley, *Analyst*, 1952, **77**, 468.
[6] W. Schöniger, *Mikrochim. Acta*, 1955, 123; 1956, 869.

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COMPLEXOMETRIC DETERMINATION OF MERCURY^{II} AND ALUMINIUM IONS

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Summary—Mercury^{II} ions can be titrated directly in slightly acid medium by Na_2-EDTA using a diphenylcarbazide + *o*-phenanthroline indicator system. This indicator system is suitable, with a little modification, for detecting the end-point in the back-titration of aluminium ions by mercury^{II} nitrate. Xylenol Orange indicator is also suitable for this purpose. Moderate amounts of alkaline earth metals or magnesium, or large amounts of alkali metal salts, do not interfere with the method.

DIRECT complexometric determination of mercury^{II} ions, using metal indicators, is only possible if acid is also added; without a suitable complexing agent mercury^{II} ions cannot persist in solution in alkaline media. In the literature, Xylenol Orange,[1] Methyl Thymol Blue[2] and the Cu-PAN indicator system[3] are recommended for end-point detection. There is a brief note on the use of PAR.[4] Recently, easily dissociated mercury^{II} salts have been used for back-titration with potentiometric end-point detection.[5–8] Because of the small number of indicators suitable for an acid medium (pH 4-6) it seemed advisable to examine the possibility of using for this purpose colorimetric reagents which give a strong colour reaction with mercury^{II} ion. Diphenylcarbazide, diphenylcarbazone and *p*-dimethylaminobenzylidinerhodanine have been examined as metal indicators.

Reagents

0·05M *Disodium ethylenediaminetetra-acetate* (*Na_2-EDTA*) *solution*: dissolve 18·605 g of Na_2-EDTA in distilled water and make up to 1 litre. Determine the factor of the solution against pure zinc using Eriochrome Black T indicator.

0·01M *Na_2-EDTA solution*: obtained by diluting the 0·05*M* solution.

0·05M (*slightly acid*) *mercury^{II} nitrate solution*: dissolve 11 g of mercury^{II} oxide in 20 ml of 1 : 1 nitric acid with constant shaking. Filter the cloudy solution and bring its volume with water to about 950 ml. One ml of this solution contains 10·03 mg mercury ion. Determine the factor against potassium thiocyanate, and also against sodium chloride, using sodium nitroprusside and potassium iodate indicator.[9] Titration with Na_2-EDTA using Xylenol Orange agrees closely with the values thus obtained.

0·01M *and* 0·001M (*slightly acid*) *mercury^{II} nitrate*: made from the 0·05*M* solution suitably diluted with water.

0.05M (*slightly acid*) *aluminium nitrate solution*: dissolve 1·35 g of metallic aluminium (99·99%) in 40 ml of conc. nitric acid, and make with water to 1 litre.

Other solutions. 20% hexamethylenetetramine buffer, 0·2% ethanolic *o*-phenanthroline, 0·04*M*, 0·02*M*, 0·01*M* and 0·005*M* ethanolic diphenylcarbazide; 0·01*M* ethanolic diphenylcarbazone.

Determination of mercury^{II} ions (*end-point detection by diphenylcarbazide*)

Examination of the indicator system. Diphenylcarbazide was first recommended by Cazeneuve[10] for the detection of mercury ions, giving in moderately acid medium (pH 3·6–7·0) a bright violet-blue precipitate, or, in more dilute solution, a colour. The structure of the complex is uncertain; it may be the chelate complex of mercury^{II} ions with either diphenylcarbazide or with diphenylcarbazone (the oxidation product of diphenylcarbazide).[11–13] Diphenylcarbazone is produced by air-oxidation of diphenylcarbazide.

Job's curve, determined with equimolar solutions (Fig. 1), and the extinction-concentration relation of mercury^{II} and diphenylcarbazide solutions of different ratio (Fig. 2) both indicate that the composition of the complex is 1:2 Hg:organic complex (the latter being referred to as DC.)

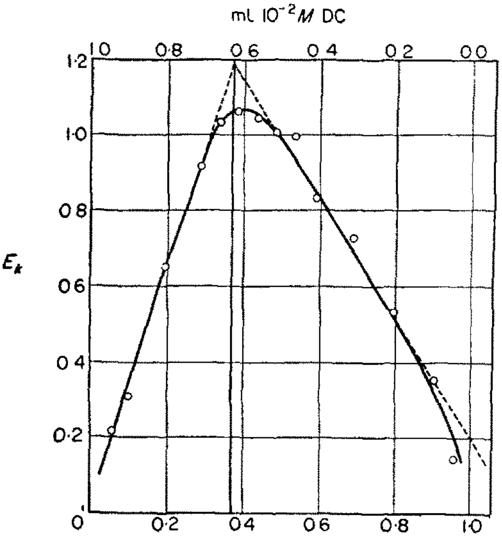

FIG. 1.

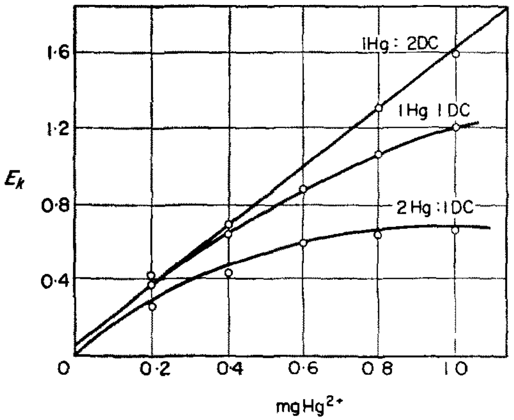

FIG. 2.

The photometric measurements were made by pipetting a convenient amount of mercury solution and 5 ml of 20% buffer solution into a flask, adding the required amounts of water and diphenylcarbazide solution, making to the mark, shaking, and measuring the violet solution at the maximum of the absorption curve in a long cuvette with an S53 filter after 20 min.

The apparent stability constant was determined by Job's method from the position of the extinction maximum of the non-equimolar solutions.[13] From the experimental results (summarised in Table I) the apparent stability constant can be calculated from the following equation:*

$$K'_{Hg(DC)_2} = \frac{(p-1)^2.(2\text{–}3x)}{\Gamma^2[p(p+2)x-2]^3}.$$

Mercury^{II} ions react with Na_2-EDTA in moderately acid solution forming HgY^{2-} (Y^{4-} = ethylene-diaminetetra-acetate ion).

The stability constant[14] of this reaction,

$$K_{HgY} = 10^{21\cdot8},$$

and the apparent stability constant[14] at pH = 5,

$$K'_{HgY} = 10^{15\cdot3}.$$

The relation of the K'_{HgY} and $K'_{Hg(DC)_2}$ values indicates that the end-point of the complexometric titration of mercury^{II} should readily be detected with diphenylcarbazide indicator. In spite of this, we found that the violet colour of the indicator complex does not disappear at the end-point, and only does so after over-titration by 2–3 ml. On reverse titration a pale rose colour appears well before the equivalence-point, and gradually becomes stronger on further titration. Acting on the information that sometimes a good result can be obtained in such cases by using additives that simulate catalysis of the indicator reaction[15] we found, in fact, that with a small amount of *o*-phenanthroline present, end-points of both forward and reverse titrations can be detected precisely with diphenylcarbazide. The diphenylcarbazide + *o*-phenanthroline indicator system works reversibly and acts quickly; and, being a uni-coloured indicator system, is very sensitive to change in the mercury concentration.

TABLE I.—DETERMINATION OF THE STABILITY CONSTANT OF THE $Hg(DC)_2$ COMPLEX

$[Hg^2]^+$, *mole/litre*	[DC], *mole/litre*	$[DC]/[Hg^{2+}]$	x	$K'_{Hg(DC)_2}$* pH 6·5
10^{-3}	5×10^{-3}	5	0·40	$10^{6\cdot7}$
10^{-3}	1×10^{-2}	10	0·26	$10^{6\cdot8}$
10^{-3}	2×10^{-2}	20	0·20	$10^{6\cdot3}$

The behaviour of the diphenylcarbazide indicator can be explained by the assumption that it does not form a genuine solution with the mercury^{II} ions, but a colloidal one, which does not react with the necessary velocity. We are as yet unable to propose any explanation of the increase in reaction velocity caused by *o*-phenanthroline. According to the work of Anderegg[16] it forms with mercury^{II} a very stable complex with an $Hg(Ph)_3$ structure. It does not seem likely that its role can be explained as a redox effect, because its presence is also necessary for reversible working of diphenylcarbazone indicator, and the redox potentials are almost the same, whether *o*-phenanthroline is present in the solution or not. Investigations are under way to determine if a "phenanthroline-mercury-diphenylcarbazide" complex forms; this could provide an explanation. We have, however, attained no result with "alcoholic dosing", which often helps an indicator system to act reversibly.

Determination of experimental conditions

The stability constant of the *o*-phenanthroline-mercury^{II} complex is 10^{19}, so that Na_2-EDTA cannot decompose this complex. Therefore in titrating mercury^{II} ions a negative error occurs (positive in the reverse titration) which depends on the amount of *o*-phenanthroline. In 0·05*M* titrations the diphenylcarbazide indicator works properly in the presence of 1·5 ml of 0·2 per cent *o*-phenanthroline; the corresponding value for an 0·01*M* titration is half this amount. This amount of *o*-phenanthroline consumes 0·03 ml of 0·05*M* titrating solution, which is negligible in practice.

In a uni-coloured indicator system the transition depends on the indicator concentration. In this case, observation of the end-point is best in $10^{-4}M$ indicator solution—0·2 ml of 0·04*M* diphenylcarbazide per 100 ml. The mercury^{II} concentration at the equivalence-point is so low that at this

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* $\Gamma = [Hg^{2+}]$ Mole/l, $r' = [DC]$ Mole/l, $p = \Gamma'/\Gamma$. x = volume of complex-forming solution giving maximum extinction, $K'_{Hg(DC)_2}$ = apparent stability constant.

indicator concentration the coloured $Hg(DC)_2$ complex does not pass the visibility limit (about $2 \times 10^{-6}M$ by photometric measurements). Therefore the solution is without colour at the equivalence-point.

The titration is only slightly pH sensitive, but, depending on the acidity of the solution, may be carried out after adding 5–10 ml of 20% hexamethylenetetramine to the solution buffered thus to pH 5-6.

Taking all these factors into account, the following procedure is recommended for the determination of mercury^{II} ions.

TABLE II.—TITRATION OF Hg^{2+} IONS

with 0·05*M* Na_2-EDTA			with 0·01*M* Na_2-EDTA		
Hg^{2+} ion added, *mg*	Hg^{2+} ion found, *mg*	Deviation, *mg*	Hg^{2+} ion added, *mg*	Hg^{2+} ion found, *mg*	Deviation, *mg*
50·15	50·26	+0·11	10·03	10·12	+0·09
100·30	100·70	+0·40	20·06	20·17	+0·11
150·45	151·25	+0·80	30·09	30·07	−0·02
201·60	202·10	+0·50	40·12	39·98	−0·14
250·75	252·65	+1·90	50·15	50·04	−0·11

Procedure

To the solution, containing 50–250mg of mercury^{II}, add 5–10ml of 20% hexamethylenetetramine, 1·5 ml of 0·2% ethanolic *o*-phenanthroline, and 5–6 drops of 1% freshly prepared ethanolic diphenylcarbazide, and make up with water to a volume of about 100 ml. Titrate this solution with 0·05*M* Na_2-EDTA, constantly shaking, and making additions drop by drop near the end of the titration, to the disappearance of the violet colour. If the mercury content of the solution is only 10–15 mg, add only half the amount of *o*-phenanthroline, and titrate with 0·01*M* Na_2-EDTA.

Table II summarises results obtained by this method. The standard deviation of the system is ±0·05 ml at 20 ml of 0·05*M* titrating solution. The percentage standard deviation is ±0·24.

Alkali metal sulphates and nitrates (up to 5 g) do not cause trouble, nor does fluoride ion, halides forming a stable complex with mercury^{II} ions, but cyanide, thiocyanate, manganese^{II} and mercury^{I} interfere. With mercury^{I} ions present, disproportioning causes metallic mercury to separate at the pH employed.

By this method the mercury content of a mercury^{II} nitrate preparation was found to be 60·9%; by a Volhard determination it was 61·0%; the corresponding values for a mercury^{II} sulphate preparation were 66·3% and 66·8%.

Diphenylcarbazone is less suitable for the end-point detection in this titration. In the foam on the surface of the solution violet granules can be seen—it is probable that some solid mercury complex is precipitated—and there is 1% over-consumption. With *p*-dimethylaminobenzylidenerhodanine the end-point of the titration cannot be determined.

Back-titration of aluminium ions with mercury^{II} nitrate solution

The direct complexometric titration of aluminium ions is rather difficult, although the stability constant of the aluminium-EDTA complex[14] is relatively high ($K_{AlY} = 10^{16 \cdot 1}$). This is because, in the first place, the formation of aluminium ethylenediaminetetra-acetate is not momentary; and, in addition, the determination is pH-sensitive because of hydrolytic phenomena and the formation of hydroxyl complexes. The number of aluminium reagents that can be used for end-point detection is small.

Theis[18] proposed a direct titration in hot solution at pH 4 with Chrome-azurol S as indicator, but preferred a back-titration method. Taylor[19] titrated Na_2-EDTA solution with aluminium solution using haematoxylin indicator. The method of Flaschka and Abdine,[20] who titrate the aluminium in hot solution at pH 3 with

PAN indicator, with a small quantity of Cu^{II} complexonate present, is also essentially a back-titration method.

At present, exact results can be obtained only with back-titration methods. Among them the titrations carried out in moderately acid medium (in the range pH 3-6) are more interesting because of the absence of the interference of alkaline earth metals, manganese and magnesium. Aluminium can therefore be determined in glass, silicates, rocks, in the presence of calcium and magnesium, without prior separation.

Wänninen and Ringbom[17,21] dealt in detail with theoretical aspects of the back-titration method, with the titration error and with the effects of the Na_2-EDTA excess and of the pH of the solution on the end-point. Their investigations elucidated the background of the different empirical procedures.

$Iron^{III}$ chloride was first used as back-titrant, with potentiometric,[22] and, later, with a salicyclic acid[23] indication. The most frequently proposed titrating solution is probably a zinc solution. For end-point detection either a reagent sensitive to zinc ions, such as dithizone,[21] Xylenol Orange,[24] or a reagent indicating aluminium ions, such as Eriochrome Cyanine R,[25,26] ferri-ferrocyanide + benzidine, or dimethylnaphthidine[26,27] may be used. $Cadmium^{II}$ back-titrant has been used with Eriochrome Cyanine R indicator;[25] in more acid medium $thorium^{IV}$ nitrate with Alizarin-S indicator[28,29]; $copper^{II}$ salt with Pyrocatechol Violet,[30] PAN[31] or Calcein W fluorescent indicator;[32] copper-$zinc^{II}$ mixed titrating solution with the Variamine Blue-thiocyanate redox indicator system.[33] Přibil and his co-workers examined the possibility of employing Xylenol Orange indicator, which is very useful in acid medium, for back-titration with lead nitrate, zinc sulphate and thorium nitrate solutions.[24]

Experimental conditions for formation of aluminium^{III} ethylenediaminetetra-acetate

Because of the different procedures given in the literature, we first examined conditions for quantitative formation of aluminium ethylenediaminetetra-acetate, then the effect of pH, of excess of Na_2-EDTA, and of several extraneous salts on the end-point. The results are summarised in Table III. The velocity of formation of the aluminium complex is increased by 2–3 min heating, since it was found that the excess of Na_2-EDTA used did not bind the aluminium quantitatively in the cold. For the back-titration, $mercury^{II}$ nitrate solution and the diphenylcarbazone-*o*-phenanthroline indicator system were used. Diphenylcarbazide cannot be used in this case, since in the presence of aluminium ethylenediaminetetra-acetate the colour development of the indicator complex is so slow that the violet colour produced by excess of $mercury^{II}$ cannot be seen even after considerable over-titration. The reversibility of the diphenylcarbazone indicator is assured by addition of 0.5 ml of 0.2% *o*-phenanthroline, so that once more an indicator correction need not be taken into account, especially since the factor of the Na_2-EDTA solution was determined against $mercury^{II}$ solution.

Determination of aluminium by back-titration with mercury^{II}

Add 20–200 per cent excess of Na_2-EDTA to a nitric acid or sulphuric acid solution containing 1–20 mg of aluminium ion, and adjust the volume to about 100 ml with distilled water. Neutralise the solution with sodium hydroxide to the slight rose colour of phenolphthalein, and re-acidify with 1 ml of 1*N* nitric acid. Heat for 2–3 minutes, cool, and add 10 ml of 20% hexamethylenetetramine.

TABLE III.—THE EFFECT OF EXPERIMENTAL CONDITIONS ON THE DETERMINATION OF Al^{3+}

Al^{3+} added, *mg*	0·05*M* Na_2-EDTA *ml*	Condition of solution	Al^{3+} found, *mg*	Deviation, *mg*
10·12	25	Neutralisation + 1 ml *N* HNO_3	10·12	—
10·12	15	Neutralisation + 2 ml *N* HNO_3	10·11	−0·01
10·12	15	Neutralisation + 5 ml *N* HNO_3	9·91	−0·21
10·12	25	Neutralisation + 10 ml *N* HNO_3	9·81	−0·31
10·12	10	Neutralisation + 1 ml *N* HNO_3	10·16	+0·04
10·12	12		10·18	+0·06
10·12	15		10·12	—
10·12	20		10·21	+0·09
20·24	20		20·31	+0·07
20·24	25		20·26	+0·02
20·24	25	Acid Al^{3+} solution without previous neutralisation	19·95	−0·29
20·24	50		20·20	−0·04
10·12	25	10 g KNO_3	10·15	+0·03
10·12	25	10 g K_2SO_4	10·27	+0·15
10·12	25	1 mg Ca^{2+}	10·11	−0·01
10·12	25	10 mg Ca^{2+}	10·12	—
10·12	25	100 mg Ca^{2+}	10·19	+0·07
6·72	25	1 mg Mg^{2+}	6·74	+0·02
6·72	25	10 mg Mg^{2+}	6·74	+0·02
6·72	25	100 mg Mg^{2+}	6·75	+0·03

TABLE IV.—DETERMINATION OF Al^{3+} ION

Al^{3+} added, *mg*	Diphenylcarbazone indicator		Xylenol Orange indicator	
	Al^{3+} found, *mg*	Deviation, *mg*	Al^{3+} found, *mg*	Deviation, *mg*
1·350	1·323	−0·027	1·336	−0·014
2·70	2·70	—	2·71	+0·01
6·75	6·72	−0·03	6·75	—
13·50	13·57	−0·03	13·47	−0·03
20·25	20·21	−0·04	20·27	+0·02

Titrate with mercury^{II} nitrate solution, with 0·2 ml of 0·01*M* diphenylcarbazone and 0·5 ml of 0·2% *o*-phenanthroline present, constantly shaking, until the appearance of the violet colour. The end-point is very sharp. Or use 10 drops of 0·1% aqueous Xylenol Orange in 100 ml end volume: the transition is then from yellow to violet-red. The results obtained with the two-indicator system are summarised in Table IV.

DISCUSSION

Mercury^{II} nitrate solution can be usefully employed for back-titration of aluminium ions in slightly acid medium. Excess is clearly indicated by the diphenylcarbazone-*o*-phenanthroline indicator system, or by Xylenol Orange.

The more acid the solution, the greater excess of Na_2-EDTA is needed to bind the aluminium ions quantitatively, *i.e.*, to move the equilibrium

$$Al^{3+} + H_2Y^{2-} \rightleftharpoons AlY^- + 2H^+$$

to the right. The pH setting after heating and cooling only influences the formation of the AlY^- complex slightly.

In back-titration, although the complex of mercury^{II} with ethylenediaminetetra-acetate is much more stable than that of aluminium, no exchange reaction between aluminium ethylenediaminetetra-acetate and mercury^{II} of the titrating solution was found. According to the literature, no exchange reaction is found with iron^{III}, thorium^{IV} or lead^{II} solutions; this may be explained to some extent by the assumption that the velocity of the displacement reaction

$$AlY^- + C^+ \rightarrow CY^{3-} + Al^{3+}$$

(where C^+ represents the cation of the back-titration solution)

is very small in the cold as compared with the velocity of the development of the coloured indicator complex.

The determination of excess Na_2-EDTA by mercury^{II} nitrate is only slightly sensitive to hexamethylenetetramine concentration. It is immediately apparent whether the buffering is sufficient. In too acid a solution a white cloudiness and a slight water-blue colour can be seen at the point where the titrant is being added. In such a case more buffer can be added in the course of the titration.

Large amounts of alkali metal salts, or alkaline earth metal or magnesium salts, as well as fluoride ion, do not interfere with the determination of aluminium. With larger amounts of calcium (value marked * in Table IV) the end-point is somewhat uncertain. Chloride ion causes some trouble, and the determination is therefore only possible in nitric acid or sulphuric acid medium. With manganese^{II} salts present, the end-point is so uncertain that an exact titration cannot be carried out.

Zusammenfassung—Zweiwertiges Quecksilber kann mit ÄDTA in leicht saurem Medium unter Verwendung des Diphenylcarbazid-o-phenanthrolin-Systems als Indicator direkt titriert werden. Mit geringen Abänderungen kann die Methode zur Bestimmung von Aluminium durch Rücktitration mit Quecksilbersalzlösung verwendet werden. Auch Xylenolorange ist ein geeigneter Indicator. Grosse Mengen Alkalisalze und und mittelere Konzentrationen von alkalischen Erden und Magnesium stören nicht.

Résumé—On peut titrer immédiatement les ions mercuriques en solution faiblement acide par Na_2-EDTA en utilisant le système diphénylcarbazide-o.phénanthroline comme indicateur. On peut utiliser le système indicateur avec une petite modification pour déceler le point équivalent du titrage en retour des ions aluminium par le nitrate mercurique. Le xylénol orange est aussi un indicateur convenable. Une quantité modérée d'ions alcalino-terreux ou d'ions magnésium ou une grande quantité de sels alcalins ne gêne pas dans cette méthode.

REFERENCES

[1] R. Přibil and E. Körös, *Acta Pharm. Hung.*, 1957, **27**, 1.
[2] J. Körbl and R. Přibil, *Coll. Czech. Chem. Comm.*, 1958, **23**, 873.
[3] H. Flaschka, A. J. Barnard and W. C. Broad, *Chem.-Analyst*, 1958, **47**, 52.
[4] P. Wehber, *Z. analyt. Chem.*, 1959, **166**, 186.
[5] J. Polcin, *Coll. Czech. Chem. Comm.*, 1957, **22**, 1057.
[6] H. Khalifa, *Z. analyt. Chem.*, 1958, **159**, 410.
[7] H. Khalifa, R. Patzak and G. Doppler, *ibid.*, **161**, 264.

[8] H. Khalifa, *Analyt. Chim. Acta*, 1958, **18,** 310.

[9] L. Erdey, *Volumetric Analysis*, 2nd. edition, Budapest 1956, p. 288.

[10] M. P. Cazeneuve, *Bull. Soc. Chim.*, 1900, **23,** 592.

[11] F. J. Welcher, *Organic Analytical Reagents*, Princeton Vol. III, pp. 430, 456.

[12] I. M. Korenmann and A. S. Ojahovszkaja, *Zsurn. Him.*, No. 44655, 1954.

[13] P. Job, *Ann. Chim.*, 1928, 10, **9,** 113.

[14] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, 1954, **37,** 937.

[15] R. Přibil and co-workers, private communication.

[16] G. Anderegg, *Helv. Chim. Acta*, 1959, **42,** 344.

[17] A. Ringbom and E. Wänninen, *Analyt. Chim. Acta*, 1954, **11,** 153.

[18] M. Theis, *Z. analyt. Chem.*, 1955, **144,** 106.

[19] M. P. Taylor, *Analyst*, 1955, **80,** 153.

[20] H. Flaschka and H. Abdine, *Z. analyt. Chem.*, 1956, **152,** 77.

[21] E. Wänninen and A. Ringbom, *Analyt. Chim. Acta*, 1955, **12,** 308.

[22] R. Přibil, Z. Koudela and B. Matyska, *Coll. Czech. Chem. Comm.*, 1951, **16,** 80.

[23] G. W. C. Milner and J. L. Woodhead, *Analyst*, 1954, **79,** 363.

[24] M. Houda, J. Körbl, V. Bažant and R. Přibil, *Coll. Czech. Chem. Comm.*, 1959, **24,** 700.

[25] I. Sajó, Magy. Kém. Folyóirat, 1953, **59,** 319.

[26] *Idem, ibid.*, 1954, 60, 268.

[27] H. Flaschka and H. Abdine, *Mikrochim. Acta*, 1955, 37.

[28] H. Flaschka, K. Ter Haar and J. Bazen, *ibid.*, 1953, 345.

[29] K. Ter Haar and J. Bazen, *Analyt. Chim. Acta*, 1954, **10,** 23.

[30] V. Patrovský and M. Huka, *Coll. Czech. Chem. Comm.*, 1957, **22,** 37.

[31] D. H. Wilkins and L. E. Hibbs, *Analyt. Chim. Acta*, 1958, **18,** 372.

[32] L. E. Hibbs and D. H. Wilkins, *Talanta*, 1959, **2,** 16.

[33] P. Wehber, *Metall.*, 1956, **10,** 211.

Talanta, 1960, Vol. 4, pp. 141 to 146. Pergamon Press Ltd. Printed in Northern Ireland

THE INDIRECT COMPLEXOMETRIC TITRATION OF ALUMINIUM

A STUDY OF THE WÄNNINEN-RINGBOM METHOD

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Summary—In the indirect complexometric titration of aluminium according to the procedure of Wänninen and Ringbom, the AlY^- complex behaves as an indifferent substance, thus considerably reducing the calculated titration error. Actual titrations of 2–0·02 millimoles of aluminium, with varying excesses of EDTA, and with zinc as standard substance, gave mean yields of 99·93% (0·1*M* titrant) and 100·04% (0·01*M* titrant) with standard deviations of 0·072 and 0·063, respectively. Some features of the method are discussed.

IN 1955 Wänninen and Ringbom[1] published a method for the indirect complexometric titration of aluminium. In this method an excess of EDTA is added to the aluminium solution, the pH is adjusted to 4·5 with an acetate buffer, ethanol is added to a concentration of 40–50% by volume and the excess of EDTA is titrated with zinc sulphate solution using dithizone as indicator for zinc ions. The addition of ethanol serves to keep the dithizone in solution. The colour change from greenish-violet to red is marked and very sharp.

The method proposed by the above authors was based on calculations of the titration error; these showed that the error would be rather dependent on variations of such factors as the excess of EDTA and the concentration of the aluminium complex. The EDTA complexes of aluminium and zinc have about the same value for their stability constants (p*K* = 16·1 and 16·5, respectively). The titration error should be at a minimum if the final concentrations of the two metal complexes are about the same and the pZn chosen for the end-point is equal to the pAl at the equivalence point. When one or both of these conditions are not fulfilled, the titration error may rise to considerable values (Table II). Wänninen and Ringbom propose, therefore, the use of 0·2–0·5 millimoles of aluminium and 0·3–0·7 millimoles of EDTA in a volume which probably may have been about 100 ml. The seven titrations carried out in the above experimental conditions show deviations from −0·66% to +0·8%, but mostly smaller than 0·1%. No experiments were published, however, verifying the calculated errors outside the standard conditions.

Naturally, a pre-requisite for the validity of the calculated titration errors is that the solution equilibrium should adjust itself. Observations on another complexometric titration method for aluminium made this assumption seem rather dubious. The year before Wänninen and Ringbom's publication, Milner and Woodhead[2] published a similar method in which the excess of EDTA was titrated with ferric chloride and the end-point detected with salicyclic acid. The results obtained were fairly good; this has been confirmed in the present laboratory. The large stability constant of the iron-EDTA-complex seems to make this method theoretically dubious. This contradiction of the results actually obtained may be explained by inertness of reaction of the aluminium-EDTA-complex which, then, is assumed to behave more or less as an indifferent substance. This might also occur in Wänninen and Ringbom's method, thus giving it a far wider range than its originators anticipated. As the method is outstanding in regard to colour contrast and sharpness of the end-point, it is to be preferred to other methods whenever possible; it is, therefore, further investigated in this paper.

EXPERIMENTAL

Reagents

Only reagent grade chemicals were used. Water and hydrochloric acid were quartz-distilled, acetic acid and ethanol Pyrex-distilled. Ammonia was prepared from tank-ammonia.

Standard solutions were prepared on a weight basis because the use of weight burettes was intended.

Aluminium standard solution: $0{\cdot}1M$ by weight, prepared by dissolving 2·7 g of aluminium ribbon (Merck, 99·99%) in 100 ml of $6{\cdot}4M$ hydrochloric acid in a Pyrex flask, fitted with a splash trap, and diluting to 1000 g. To facilitate the dissolution, 1 micromole of copper sulphate was added.

Zinc standard solution: $0{\cdot}1M$ by weight, prepared in the same apparatus from 6·5 g of zinc rod (Johnson, Matthey & Co, "Specpure") and 200 ml of $1{\cdot}5M$ hydrochloric acid; the zinc rod was wrapped in platinum gauze to facilitate dissolution.

EDTA standard solutions: It was found that certain preparations of the disodium salt of EDTA differed in sharpness of end-point in the titration. Re-precipitation of EDTA or recrystallisation of its disodium salt from ethanol-water mixtures improved the end-point sharpness. The latter procedure was used for preparing $0{\cdot}1M$ by weight EDTA solution which was standardised against the zinc solution according to the method given below. $0{\cdot}01M$ standard solutions were prepared from those above through dilution by weight.

Dithizone solution: $0{\cdot}0004M$, prepared by dissolving 25·6 mg of dithizone in 250 ml of 95% ethanol.

Buffer solution: 1 mole ammonium acetate, 1 mole acetic acid per litre.

Thymol blue solution: 0·1%.

Procedure

Appropriate amounts of aluminium and EDTA standard solutions were weighed out from weight burettes into a 250-ml Vycor beaker. Water was added to about 40 ml, followed by 2 drops of thymol blue and, if necessary, dilute ammonia to about pH 2. The solution was heated and maintained near boiling during the dropwise addition of 10 ml of buffer, then left to stand for a couple of minutes before cooling to room temperature. After addition of an equal volume of 95% ethanol and 2·5 ml dithizone solution, the solution was titrated with zinc standard solution from a weight burette to a distinctly red colour. A drop in the pH, which occurred when the consumption of zinc was large, was compensated for by adding dilute ammonia during the titration, the dithizone also serving as a pH indicator. An indicator correction of −0·00012 millimoles was applied to the zinc consumed.

The EDTA solution was standardised against the zinc solution in the same way, omitting the heating.

RESULTS

Titration of EDTA with zinc in the absence of the aluminium complex

Starting from the data and equations given by Wänninen and Ringbom, the error in the titration of EDTA with zinc is calculated from the equation

$$\Delta_{\mathrm{EDTA}},\ \% = \frac{[\mathrm{Zn}^{2+}] - \sum_{i=0}^{4} [\mathrm{H_iY}]}{[\mathrm{ZnY}^{2-}]} \cdot 100$$

where EDTA = H_4Y. Table I shows the error calculated in this way for pH = 4·5 and pZn = 6 at the colour transition point as assumed by Wänninen and Ringbom for the aluminium titration. The titration error does not exceed ±0·06% in the concentration range 0·05–0·001M.

Titration of excess EDTA in the presence of the aluminium complex

If an excess of EDTA is added to an aluminium solution and the pH is adjusted to the appropriate value, the complex AlY^- is formed quantitatively. Titrating the excess of EDTA with zinc in order to determine the amount of EDTA consumed by the aluminium will, according to Wänninen and Ringbom, give an error of

TABLE I.—ERROR CALCULATED ON TITRATION OF EDTA WITH ZINC SOLUTION

$pZnY^{2-}$ at equiv. point	Δ_{EDTA}, %
1·3	−0·03
1·6	−0·03
2·0	−0·02
2·3	−0·01
2·7	+0·03
3·0	+0·06
3·3	+0·2
3·7	+0·5
4·0	+1·0
5·0	+10

$$\Delta_{Al}, \% = \frac{\sum_{i=0}^{4} [H_iY] - [Al^{3+}] - [Zn^{2+}]}{[AlY^-]} \cdot 100$$

which can be calculated from the equations and data given by these authors. Results for some extreme cases of such a calculation are given in Table II; the conditions at the colour transition point are assumed to be pH = 4·5 and pZn = 6. The calculated titration error is considerable with a small excess of EDTA *i.e.* low concentration of ZnY^{2-}, at the equivalence point.

The above calculation involves the pre-requisite that the solution equilibrium really adjusts itself. However, as there is reason to assume that AlY^- reacts very slowly it may, as a second hypotheses, be proposed that AlY^- is completely indifferent. In the equation for the titration error $[Al^{3+}]$ will, then, not represent the concentration at the end-point, but the concentration in equilibrium with the added excess of EDTA on formation of AlY^-. This concentration, however, is, under the experimental conditions of Table II, sufficiently small to be neglected and the equation for the titration error will be

$$\Delta_{Al}, \% (AlY^- \text{ indiff.}) = \frac{\sum_{i=0}^{4} [H_iY] - [Zn^{2+}]}{[AlY^-]} \cdot 100$$

i.e. the titration error with changed sign will be the same as for titration of EDTA with zinc, calculated on the amount of aluminium. Some calculated results, for extreme cases, are given in Table II.

To decide which of these two hypotheses comes nearest to the truth, the titrations presented in Table II were carried out. The results show that the aluminium complex behaves as an indifferent substance within the limits of experimental error.

TABLE II.—TITRATION OF ALUMINIUM AT VARIOUS EXCESSES OF EDTA

excess EDTA added		Zn consumed, *mmoles*	Al		Error, %		
%	*mmoles*		found, *mmoles*	added, *mmoles*	found	calcd. accd. to W. and R.	calcd. with Al-complex indifferent
			Titrations performed with $0{\cdot}1M$ solutions				
1	1·0127	0·0121	1·0008	1·0015	−0·07	−2·5	−0·01
1	1·0104	0·0093	1·0011	1·0021	−0·10	−2·5	−0·01
20	1·2037	0·1986	1·0051	1·0055	−0·04	−0·007	+0·006
20	1·1975	0·1944	1·0031	1·0042	−0·11	−0·007	+0·006
20	1·2027	0·1997	1·0030	1·0035	−0·05	−0·007	+0·006
28	1·1320	0·2458	0·8862	0·8866	−0·05		
40	2·5121	0·7255	1·7866	1·7867	−0·01		
49	2·0015	0·6609	1·3406	1·3409	−0·02		
68	1·4990	0·6033	0·8957	0·8956	+0·01		
73	0·3074	0·1297	0·1777	0·1779	−0·11		
100	1·9970	0·9941	1·0029	1·0048	−0·19	+0·04	+0·007
100	2·0053	1·0058	0·9995	1·0011	−0·16	+0·04	+0·007
100	2·0116	1·0067	1·0049	1·0062	−0·13	+0·04	+0·007
134	1·0509	0·6018	0·4491	0·4494	−0·07		
159	0·5041	0·3093	0·1948	0·1946	+0·10		
			Titrations performed with $0{\cdot}01M$ solutions				
1	0·10086	0·00084	0·10002	0·09995	+0·07	−25	−0·1
1	0·10073	0·00086	0·09987	0·09979	+0·08	−25	−0·1
11	0·11126	0·01072	0·10054	0·10049	+0·06		
20	0·12003	0·01973	0·10030	0·10027	+0·03	−1·1	−0·08
20	0·11979	0·01923	0·10056	0·10050	+0·06	−1·1	−0·08
21	0·06068	0·01052	0·05016	0·05013	+0·06		
44	0·03041	0·00921	0·02120	0·02117	+0·15		
51	0·15031	0·05040	0·09991	0·09985	+0·06		
100	0·19993	0·09992	0·10001	0·10009	−0·08	−0·3	−0·02
101	0·10056	0·05054	0·05002	0·05001	+0·02		
145	0·05062	0·02999	0·02063	0·02064	−0·05		

The accuracy and precision obtained were as follows: For the titration of 2–0·2 millimoles of aluminium by $0{\cdot}1M$ solutions, the mean yield is 99·93% with a standard deviation of 0·072; for the titration of 0·1–0·02 millimoles of aluminium, the mean yield is 100·04% with a standard deviation of 0·063.

The deviation of the mean yield from 100% may be due to an error in the standardisation of EDTA against zinc; also, a difference in purity of the zinc and aluminium preparations used may add to the errors. In practice it is better to standardise the EDTA solution against high purity aluminium and use a zinc sulphate solution, standardised against the EDTA solution, for back titration. The bias of the yield will then disappear.

DISCUSSION

EDTA reacts very slowly with the hydroxo complexes of aluminium. Hence, it is essential, as Wänninen and Ringbom found, to add the EDTA before the buffer; the opposite causes low results. Milner and Woodhead boil the solution to speed up the formation of AlY^-. Observations in this laboratory have shown, moreover, that care must be exercised when any excess of acid is neutralised with ammonia; local excesses of ammonia obviously form slowly reacting hydroxo complexes. A reliable method is to add ammonia to about pH 2 (thymol blue), then boil, add the buffer dropwise and keep the solution hot for 2 minutes before cooling it. The faint yellow colour of thymol blue does not interfere with the titration.

TABLE III.—10 ML 0·1*M* Al-EDTA COMPLEX WITH ABOUT 10% EXCESS OF EDTA TITRATED WITH 0·1*M* ZINC AT VARIOUS pH-VALUES.

pH before addn. of ethanol	Zinc soln. consumed, *ml*	Colour of indicator before colour change
4·4	1·044	Greyish-violet
4·7	1·046	
5·0	1·057	Brownish-yellow
5·5	1·078	
6·0	1·100	Intensely yellow
6·7	1·105	

Variations of pH within the range 4·4–5·0 in the titration, do not cause any serious error, as will be seen from Table III. The colour change is not quite as sharp at higher pH values as in the range mentioned. The small additional consumption of zinc at higher pH may be due to the formation of aluminium hydroxo complexes combined with liberation of EDTA. Wänninen and Ringbom, on account of this assumption, are of the opinion that the titration will give poor results at higher pH values. However, in this case also, the inertness of the AlY^- is advantageous.

A saturated solution of dithizone in 95% ethanol was found to be about 0·0005*M*; hence, a concentration of 0·0004*M* for the indicator solution was considered appropriate. Of this solution 2·5 ml (0·001 millimole of dithizone) were used per 100 ml, a larger amount giving too strongly coloured a solution. Titration of this amount of dithizone with 0·001*M* zinc solution indicated that the colour change most obvious to the eye occurs at a zinc consumption of about 0·12 ml, *i.e.* $\frac{1}{4}$ of the indicator has been consumed for the formation of $ZnDz_2$. Thus, this amount, 0·00012 millimole, has been subtracted from zinc consumed in the titrations as indicator correction.

The above circumstances lead to a pZn at the end-point deviating somewhat from that calculated according to Wänninen and Ringbom. It seems, however, to be of little value to recalculate the errors, as the equilibrium constants in the water-ethanol mixture are not known with sufficient accuracy.

Zusammenfassung—Bei der indirekten komplexometrischen Titration von Aluminium nach der Methode von Wänninen und Ringbom verhält sich der AlY^--Komplex als indifferente Substanz, wodurch der berechnete Titrationsfehler wesentlich herabgesetzt wird. Titrationen von 0.02-2 Millimolen Aluminium unter Verwendung wechselnden Mengen überschüssiger ÄDTA und mit Zink als Urtitersubstanz ergaben Genauigkeiten von 99.93 % (Titrator 0.1 m) und 100.04 % (Titrator 0.01 m). Die entsprechenden Standardabweichungen waren 0.072 bzw. 0.063. Einige die Methode betreffende Gesichtpunkte werden diskutiert.

Résumé—Dans le titrage en retour de l'aluminium par le complexon selon le procédé de Wänningen et Ringbom, le complexe AlY^- se comporte comme une substance indifférente, réduisant considérablement l'erreur de titrage calculée. Actuellement, les titrages de 2 à 0,02 millimoles d'aluminium, avec des excès variables d'EDTA et avec le zinc comme substance étalon fournissent un rendement moyen de 99,93 pour cent (réactif titrant 0,1 M) et 100,04 pour cent (réactif titrant 0,01 M) avec un écart-type de 0,072 et 0,063 respectivement. On discute quelques caractéristiques de la méthode.

REFERENCES

[1] E. Wänninen and A. Ringbom, *Analyt. Chim. Acta*, 1955, **12**, 308.
[2] G. W. C. Milner and J. L. Woodhead, *Analyst*, 1954, **79**, 363.

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LETTER TO THE EDITOR

SIR,

IN his letter headed "An Appeal" which appeared in the February edition of *Talanta* A. A. Moss makes a specific if incomplete reference to a paper which appeared in *The Analyst*. Despite the incompleteness of the reference I, and I presume others, must conclude that the paper is mine.[1]

I question his good taste in illustrating a general point by a specific reference, since the incompleteness does little to mask the identity of the author. Of more importance however, this isolated and selected reference leaves the reader with the impression, intended or otherwise, that my method is one of the inferior and suspect ones to which he refers.

A. A. Moss has presumably found that sodium peroxide gains in weight due to the absorption of water and carbon dioxide. This rate of increase is small, approximately 0·0002 g in 20 secs, but the purpose in quoting the weight of peroxide to four places of decimals was to emphasise the importance of weighing the amount as accurately as the material and balance would allow since the acidity of the final solution is important. The whole of my instructions were aimed at maintaining as tight a control over the operations as possible and a note to this effect was added. Surely nothing slipshod here!

I am willing to demonstrate in my own laboratory, where this method is in routine use, that even in inexpert hands it will give the results claimed for it providing the instructions are closely followed.

I am in sympathy with some of the aims of the appeal but I would suggest humility as the correct approach to the testing of other people's work; it does not follow that a method should be rejected or criticised if one person cannot obtain reliable results, as anyone who has served on an Analysis Committee will know.

Finally, I think it will be unfortunate if papers are to be delayed or rejected on grounds of style or presentation as original ideas however badly expressed are still useful.

Yours faithfully,

S. GREENFIELD.

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REFERENCES

[1] S. Greenfield, *Analyst*, 1959, **84**, 380.

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BOOK REVIEWS

The Analysis of Titanium and Its Alloys. Third edition. Imperial Chemical Industries Limited, London, S.W.1. 1959. Pp. 119. 21s.

THE appearance of a third edition of this useful work is evidence of the popularity of the first two editions and of the steadily increasing interest in the metallurgy of titanium.

This latest edition retains the same clear format as previously, but there are significant changes in the contents which reflect the considerable amount of research work which has obviously preceded publication. This is also shown in the wealth of detail and ancillary data included.

The inclusion of a figure for the standard deviation of each method is a praiseworthy feature, which is regrettably absent in many works of this type.

Prominent amongst the many additional and alternative methods are the replacement of the turbidimetric method for chloride determination by a much more elegant amperometric method, and the inclusion of a method for determination of boron. Another welcome addition is the colorimetric determination of small amounts of nitrogen, which is of particular importance in view of the influence exerted by small traces of this element on the metallurgical properties of titanium.

Refinements of methods previously described include a gas pressure method for routine carbon determination; a differential absorptiometric procedure for large amounts of molybdenum in presence of tungsten; an additional colorimetric method for copper, using the well tried diethyl dithiocarbamate; and a technique for phosphorus determination at low levels.

As in previous editions, there is a section covering sampling of the various forms of titanium metal, while an additional most useful chapter is devoted to the identification of titanium alloys by means of simple and rapid spot tests, employing a virtually non-destructive technique on the metal surface.

This third edition forms an essential part of the literature on the analysis of titanium and its alloys. It is strongly recommended to all workers in this field.

J. BURGESS

Chemical Analysis, Volume 9: Analytical Chemistry of Titanium Metals and Compounds. MAURICE CODELL. Pp. 378. Interscience Publishers, New York, 1959. $12.00.

THE rapid growth of the titanium industry has made it necessary to analyse a great many titanium-containing materials. Performance of such analyses has been hampered by the scattered sources for such information throughout the scientific literature. This book is designed to overcome this difficulty by providing a compact source for this wide spread information.

Unpublished laboratory reports as well as scientific journals have been used to compile this authoritative summary. Doubtful procedures have been tested to insure reliability. By intelligent modification of the principles presented in this book, analytical chemists should be able to analyse any titanium-containing sample.

The first 101 pages deal with the fundamental chemistry of titanium, the sampling and separation problems encountered with titanium-containing materials, emission spectrographic and vacuum-line methods for analysing various substances in titanium-rich materials, and procedures for determining titanium.

The remainder of the book is devoted to the analysis of metals and non-metals in titanium and titanium alloys, and to the analysis of titanium-base materials. Detailed information concerning

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The remainder of the book is devoted to the analysis of metals and non-metals in titanium and titanium alloys, and to the analysis of titanium-base materials. Detailed information concerning the various procedures for determining a specific element are presented and thoroughly discussed. An evaluation of alternative methods is given, along with statements about the suitable range and interferences of each method. This will simplify the selection of suitable methods for a particular sample.

There is a bibliography of 233 references. However, the more recent literature, including 1958, is not satisfactorily covered.

The writing throughout the book is simple and direct, making many of the highly technical sections relatively easy to understand. This book is essential reading for the chemist with analytical problems involving titanium, and adequately fills a void that had existed in this field.

F. H. FIRSCHING

Optics and Spectroscopy, Vol. VI, No. 1. The Optical Society of America, National Bureau of Standards, Washington, 25, D.C., U.S.A. Jan. 1959. Pp. 84. Single copy price $3.00.

THIS is the first issue of the translated version of the Russian journal *Optika i Spektroskopiia* which is published monthly in two volumes a year. This journal is being translated on the initiative of the Optical Society of America and the translation, together with the Journal of the Optical Society of America, will be received by all members and subscribers of the Society.

Articles in this issue, the translation of the first number of the sixth volume of the Russian journal, cover a variety of subjects including theoretical and experimental studies of the optical properties of crystals, experimental studies of the temperature of sparks, studies of fluorescence—*e.g.* of polystyrene excited by electron bombardment, and several studies of the electronic and vibrational spectra of fairly complicated compounds of mainly chemical interest.

In this issue there were no articles on spectroscopic or other optical instruments and most of the articles would normally be classified as physical chemistry or chemical physics. This may, however, be an accidental characteristic of this particular issue.

The translation seems well done and few errors were noticed. The type size used in the theoretical papers is at times uncomfortably small.

DAVID PULLIN

Reactor Technology, Report No. 10. Chemistry. A.E.C. Research and Development Report KAPL-2000-7. Office of Technical Services, Department of Commerce, Washington 25, D.C., U.S.A. *September* 1959. Pp. x + 62. $2.00.

THIS document is one of a series of progress reports, the stated aim of which is to keep industry informed of unclassified developments in the various fields of reactor technology. The subject matter is discussed under five headings, analytical chemistry, spectroscopy, radiochemistry, physical chemistry and corrosion and coolant chemistry. The material presented will be of general interest to analysts associated with atomic energy work, but to analysts in other fields the usefulness is mainly restricted to the sections on analytical chemistry (analysis of zirconium and niobium-based materials) and spectroscopy (isotopic analysis of uranium and boron by mass spectrometry and emission spectrographic analysis of zirconium and stainless steel).

J. K. FOREMAN

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J. K. FOREMAN

Talanta, 1960, Vol. 4, pp. 150 to 151. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The following meetings have been arranged:

Thursday 12 *May* 1960: **Society for Analytical Chemistry,** Midlands Section. Mr. D. Holness: *Applications of Gas-Liquid Chromatography in the Analysis of Essential Oils.* Gas Showrooms, Nottingham, England, 7.0 p.m.

Friday 13 *May* 1960: **Society for Analytical Chemistry,** North of England Section and Microchemistry Group. *Corrosion.* Hull, England.

Friday 20 *May* 1960: **Society for Analytical Chemistry,** Western Section and Physical Methods Group. *Atomic Absorption Spectroscopy.* Conference Room, Municipal Building, Poole, England, 6.30 p.m.

Friday 27 *May* 1960: **Society for Analytical Chemistry,** Western Section. **Royal Institute of Chemistry,** South Western Section. Dr. W. H. N. Cooper: *Trace Elements in Sea Water.* Plymouth.

Wednesday–Friday 8–10 *June* 1960: **Society for Analytical Chemistry, Institute of Petroleum:** Discussion Group of the Hydrocarbon Research Group. Symposium on *Gas Chromatography.* Assembly Rooms, Edinburgh, Scotland.

Wednesday 22 *June* 1960: **Society for Analytical Chemistry,** Microchemistry Group. London Discussion Meeting, "The Feathers", Tudor Street, London, E.C.4. 6.30 p.m.

The eighty-sixth Annual General Meeting of the Society for Analytical Chemistry was held at the Queen's Hotel, Birmingham, on Wednesday 2 March 1960, with the President, Mr. R. C. Chirnside in the Chair. The following Officers and Members of Council were elected for the forthcoming year:

President:	R. C. Chirnside
Past Presidents serving on the Council:	J. W. Hamence, D. W. Kent-Jones, J. R. Nicholls, K. A. Williams
Vice-Presidents:	D. C. Garrett, Magnus A. Pyke, J. G. Sherratt
Hon. Treasurer:	A. J. Amos
Hon. Secretary:	R. E. Stuckey
Hon. Assistant Secretaries:	L. Brealey (Programmes), S. A. Price
Other Members of Council:	N. L. Allport, D. M. W. Anderson, B. Bagshawe, E. Bishop, H. E. Brookes, C. H. R. Gentry, E. Q. Laws, W. M. Lewis, R. F. Milton, F. C. J. Poulton, C. Whalley, J. T. Yardley.
Ex-Officio Members:	J. R. Edisbury (Chairman, North of England Section), A. N. Harrow (Chairman, Scottish Section), G. V. James (Chairman, Western Section), S. H. Jenkins (Chairman, Midlands Section), F. Holmes (Chairman, Microchemistry Group), G. W. C. Milner (Chairman, Physical Methods Group), J. I. M. Jones (Chairman, Biological Methods Group).

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The Meeting was followed immediately by the sixth Bernard Dyer Memorial Lecture, given by Professor A. C. Frazer, M.B., B.S., Ph.D., D.Sc., F.R.C.P., M.D., Professor of Medical Biochemistry and Pharmacology in the University of Birmingham. Professor Frazer's subject was *Chemical Analysis and Medical Progress.*

The sixteenth Annual General Meeting of the Microchemistry Group of the Society for Analytical Chemistry was held on Friday 19 February 1960 in the Postgraduate Medical School, Ducane Road, London, W.12. The chair was taken by the Chairman of the Group, Mr. F. Holmes.

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

Chairman: Mr. F. Holmes

Vice-Chairman: Mr. C. Whalley

Hon. Secretary: Mr. D. W. Wilson, Sir John Cass College,
Jewry Street, Aldgate, London, E.C.3.

Hon. Treasurer: Mr. G. Ingram.

The fifth Annual General Meeting of the Midlands Section of the Society for Analytical Chemistry was held on Wednesday 23 March 1960 in the Technical College, Nottingham. The Chairman of the Section, Dr. S. H. Jenkins, F.R.I.C., F.Inst.S.P., presided.

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

Chairman: Dr. S. H. Jenkins

Vice-Chairman: Dr. H. C. Smith

Hon. Secretary: Mr. G. W. Cherry, 48, George Frederick
Road, Sutton Coldfield, Warwickshire,
England.

Hon. Treasurer: Mr. F. C. J. Poulton

Hon. Asst. Secretary: Mr. R. Adkins.

The Chemical Society of London is co-operating with the British Department of Scientific and Industrial Research in providing complete translations of the *Russian Journal of Inorganic Chemistry* (from Jan. 1959), the *Russian Journal of Physical Chemistry* (from July 1959), and *Russian Chemical Reviews* (from Jan. 1960). Subscription rates per annum for the first two of these are (beginning with the Russian January issue) £30 or $90, with a reduction of 25 per cent for College or University Libraries. The price for the first six issues of the *Russian Journal of Physical Chemistry* is *pro rata.* The subscription rate for *Russian Chemical Reviews* per annum is £12 or $36 (£9 or $27 for College or University Libraries.)

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Vice-Chairman:	Mr. C. WHALLEY
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Hon. Treasurer:	Mr. F. C. J. POULTON
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PAPERS RECEIVED

Radio-frequency methods in analytical chemistry: M. F. C. LADD and W. H. LEE. (2 *March* 1960).

A new procedure in the low-temperature wet oxidation of organic compositions: Perchloric and periodic acids as oxidants: The "Periodic acid liquid fire reaction". G. FREDERICK SMITH and HARVEY DIEHL. (9 *March* 1960).

The estimation of the stabilities of bivalent transition metal complexes and deviations from the Irving-Williams order: D. L. LEUSSING. (11 *March* 1960).

Liquid-liquid extraction of iron^{III} with tributylphosphate: Separation from mixtures: SANTOSH K. MAJUMDAR and ANIL K. DE. (14 *March* 1960).

UV Spectrophotometric determination of trace amounts of selenium with *o*-phenylenediamine: HISAE ARIYOSHO, MICHIO KINIWA and KYOJI TOEI. (14 *March* 1960).

Organic analysis, XXVI: Determination of reducing sugars with 3:6-dinitrophthalic acid: TSUTOMU MOMOSE, YOSHIKO MUKAI and MITSUKO WATANABE. (15 *March* 1960).

Thiazolyl analogues of 1-(2-pyridylazo)-naphthol: V. SVOBODA. (18 *March* 1960).

Amperometric determination of glucose, fructose and saccharose without additional external voltage: E. MICHALSKI, K. CZARNACKI and M. IGNACZEK. (18 *March* 1960).

Analytical applications of 3-acetyl-4-hydroxycoumarin—II: Spectrophotometric determination of iron^{II}: A. N. BHAT and B. D. JAIN. (18 *March* 1960).

Applications of metallochromic indicators in colorimetry—I: Spectrophotometric determination of minute amounts of copper with analogues of glycine thymol blue. M. KOCH, V. SVOBODA and J. KÖRBL. (23 *March* 1960).

Lithium chloride in non-aqueous potentiometric titrations: E. L. GROVE. (26 *March* 1960).

PUBLICATIONS RECEIVED

Modern Methods of Analysis of Copper and its Alloys: CHARLES M. DOZINEL. Translated by GEORGE R. ANDRASO. Ets. Georges Thone, Liege, 1960. Pp. 239. $32.00.

Instrumental Methods of Chemical Analysis, 2nd Edition. GALEN W. EWING. McGraw-Hill Publishing Co., London: McGraw-Hill Book Co., Inc., New York, 1960. Pp. viii + 454. 69s.

Quantitative Inorganic Analysis, 2nd Edition. R. BELCHER and A. J. NUTTEN. Butterworths Scientific Publications, London, 1960. Pp. x + 390. 35s.

Separation and Identification of Food Colours permitted by the Colouring Matters in Food Regulations, 1957. Association of Public Analysts, Bank Chambers, 16, Southwark Street, London, S.E.1, 1960. Pp. vi + 31. 21s.

Heterometry. M. BOBTELSKY. D. Van Nostrand Company, Ltd., London: Elsevier Publishing Company, Amsterdam, 1960. Pp. viii + 229. 42s.

Automatic Titrators. J. P. PHILLIPS. Academic Press Inc., New York, 1959. Pp. viii + 225. $6.00.

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THE SEPARATION OF CARRIER-FREE ^{234}THORIUM (UX_1) FROM URANIUM BY ANION-EXCHANGE

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Division of Applied Chemistry, National Research Council,
Ottawa, Canada

(*Received* 30 *November* 1959)

Summary—A relatively simple procedure for the preparation of large quantities of carrier-free ^{234}thorium for use as a tracer has been devised. A 9·6*M* hydrochloric acid solution of uranium is fed into an anion-exchange column. The uranium complex is adsorbed and the daughter thorium is washed through the resin bed, resulting in a substantially quantitative separation of UX_1 from as much as 50 g of uranium. The uranium may be readily recovered by elution with 0·1*M* hydrochloric acid solution, or may be left on the column to be periodically washed with 9·6*M* hydrochloric acid solution to produce fresh batches of UX_1.

INTRODUCTION

IN the course of investigations in this laboratory it was found desirable to employ a radioactive tracer to follow the behaviour of thorium in various analytical procedures. ^{234}Thorium (UX_1) has proved to be an excellent isotope for this purpose for three reasons: (*i*) it can be prepared in the laboratory from readily available materials, (*ii*) its half-life of 24·1 days allows for convenient handling, and (*iii*) its short-lived (1·18 min) daughter, ^{234}protoactinium (UX_2), is a very energetic β emitter so that the detection of UX_1 is greatly facilitated.

^{238}Uranium disintegrates according to the familiar uranium series with the following first three steps:

$$^{238}U \xrightarrow[4{\cdot}51 \times 10^9\,yr]{\alpha} {}^{234}Th(UX_1) \xrightarrow[24{\cdot}1\,d]{\beta} {}^{234}Pa(UX_2) \xrightarrow[1{\cdot}18\,min]{\beta} {}^{234}U.$$

The third product, ^{234}uranium, has a half-life of $2{\cdot}48 \times 10^5$ years. Thus any uranium compound obtained from a chemical supplier will, in effect, contain only ^{238}U, equilibrium quantities of UX_1 and UX_2, and ^{234}U, since the original decay products of the uranium series will have been removed in the purification process, and the build up of new products arrested at ^{234}U due to its long half-life. Since 1 gram atomic weight of uranium produces an equilibrium amount of $3{\cdot}5 \times 10^{-3}$ micrograms of UX_1, the preparation of UX_1 becomes a problem of separating a submicro quantity of thorium from a macro amount of uranium.

About 10 minutes after a separation has been effected an equilibrium amount of UX_2 will again be present. This is a fortunate occurrence in our case since this constant companion of UX_1 produces a very hard β emission (2·3 Mev) which can be counted, instead of the soft β radiation (0·19, 0·10 Mev) of UX_1. Thus all weak emitters which may be present can be screened out and the detection of UX_1 greatly enhanced.

The separation of UX_1 from uranium has been the centre of much interest since its discovery by Crookes [1] in 1900 and an excellent review of the work in this field up to

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* Present address: Department of Oncology, University of Wisconsin, Madison, Wisconsin.

1950 is given by Dyrssen[2]. The methods are generally based on the solvent extraction of uranium into ether, precipitation of UX_1 with a carrier, or adsorption of UX_1 on charcoal or some other adsorbent. None of these procedures is quantitative and only the involved and lengthy method of Erbacher, Herr and Wiedemann[3], which employs both ether extraction and carrier precipitation, produces a substantially carrier-free isotope.

Recently, several ion-exchange procedures have been proposed for this separation. Bane[4] adsorbed the UX_1 from a uranyl nitrate solution on a cation-exchanger, allowing the uranium to pass through the bed. The UX_1 was eluted with a sodium bisulphate solution. A similar procedure has been developed by Dyrssen[2] who removed the thorium isotope with an oxalic acid solution. Chen[5] adsorbed the UX_1 on an anion-exchanger from a 7·5*M* nitric acid solution, and later washed it off with water. Forty grams of uranyl nitrate (19 g uranium) could be handled in this manner in comparison with the 1-gram uranyl nitrate samples processed by Dyrssen. Recoveries of greater than 85% of the original UX_1 are reported.

The authors, after a brief examination of some of the above procedures, decided that ion-exchange would probably yield the most efficient and simple method for producing relatively large quantities of the carrier-free thorium isotope. Attempts to utilise the methods of Dyrssen and Chen were unsuccessful. In order to produce large yields of UX_1 fairly concentrated solutions (1·3*M*) of uranium were used. Considerable leakage of UX_1 in the feed effluent occurred and great difficulty was encountered in removing much of the isotope from the resin in both cases.

In view of the recent success of several workers[6–8] in separating thorium from uranium by anion-exchange in hydrochloric acid solution it was decided to investigate this approach. It was felt that the apparent disadvantage of having to adsorb the major component on a very large bed would be balanced by the fact that there would be no problem of removal of the UX_1 from the resin.

APPARATUS AND METHODS OF ANALYSIS

The ion-exchange column used was of conventional design, 3·1 cm in internal diameter and 1 metre high. The bed consisted of 500 ml (approx. 1 lb) of 20–50 mesh Amberlite IRA-400 anion-exchange resin of analytical grade supported on a wad of glass wool. The resin was stirred for 1 hour with 2*M* hydrochloric acid solution before transferring it to the column, to ensure complete conversion to the chloride form.

The column volume above the resin bed (250 ml) served as a reservoir and was closed off by a rubber stopper through which a glass tube was inserted which extended almost to the resin bed. Flow rates of solutions were controlled by regulating the influx of air into the reservoir through this tube. The outlet tube of the column was fitted with a stop-cock so that the flow could be arrested at any time.

Activity measurements were made on suitable aliquots which were evaporated to dryness on aluminium dishes 1 inch in diameter. Hydrochloric acid solutions were evaporated to dryness in glassware and taken up in nitric acid before this step. Measurements were made with an appropriately shielded Nuclear-Chicago D34 end-on GM tube with a 1·4 mg/cm² mica window. The output of this tube was fed into an Atomic Instrument Company Model 1070B multiscaler unit. In each case the sample was covered with an aluminium absorber of 32 mg/cm² thickness which served to screen out all soft radiations, including that of the UX_1 itself, so that only the strong β emission of the UX_2 was registered.

Analysis of uranium effluents was done gravimetrically. Suitable aliquots were treated with carbonate-free ammonia solution to precipitate ammonium diuranate which was then filtered, washed, ignited at 800°, and weighed as U_3O_8.

The uranium used was the yellow trioxide, which, on analysis, was found to be quite free of other metals but hydrated as $UO_3 \cdot 0.5\ H_2O$.

EXPERIMENTAL

Initial experiments with a small ion-exchange column (1·0 × 20 cm) verified that uranium can be adsorbed on an anion-exchanger from concentrated hydrochloric acid solutions while UX_1 passes through into the effluent. Since maximum adsorption of uranium was desired, 4:1 (9·6*M*) hydrochloric acid solution was used throughout this work because, at this concentration, the distribution coefficient between the uranium-chloro complex and the exchanger is at its maximum[9]. These experiments also indicated the ease of removal of uranium from the resin with 0·1*M* hydrochloric acid solution and showed that 500 ml of resin should be able to adsorb at least 65 g of uranium before leakage occurred. This is approximately 120 times the amount indicated by Tomic *et al.*[7] who adsorbed uranium from a 6·5*M* hydrochloric acid solution.

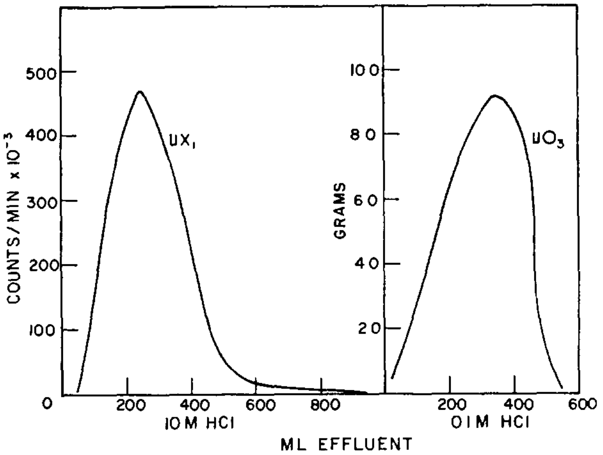

FIG. 1.—Typical elution curves for UX_1 and uranium.

Before feeding the uranium solution on to the large column, the resin bed was washed with 9·6*M* hydrochloric acid solution until the effluent was of this concentration. Sixty g of the uranium trioxide (48·4 g uranium) were dissolved in 150 ml of the hydrochloric acid solution, and the solution was poured into the column with the effluent stopcock closed. As the dense uranium solution came into contact with the resin, particles rose through the solution until about two-thirds of the bed had been displaced. At this point sufficient uranium had been adsorbed on the resin to (*i*) lower the density of the solution and (*ii*) increase the density of the particles so that the bed quickly resettled. This displacement provided excellent contact between the two phases, ensuring optimum adsorption of the uranium complex. Once the bed had resettled the effluent stopcock was opened, and the bleeder tube was adjusted so that the uranium solution, now much depleted in concentration, passed through the bed at the rate of about 4 ml per minute. Very little further movement of the uranium band was observed.

Elution of the UX_1 was continued with three 250-ml portions of the acid solution. The effluent was usually collected in 50-ml fractions which were analysed radiometrically for UX_1. A typical elution curve is shown in Fig. 1. Much tailing is noted in this elution, with the activity never dropping to zero. This may be explained by the fact that the uranium in the column is continually producing UX_1 at a rate which makes it impossible to wash the resin free of thorium activity. For example, during the hour it takes to pass 250 ml of eluent through the bed new UX_1 has been produced in sufficient amount to cause an increased activity of $4 \cdot 3 \times 10^4$ disintegrations per minute.

A sample of UX_1 in hydrochloric acid solution was passed through the column following the procedure described above, except that the total effluent was collected, evaporated and analysed radiometrically. This experiment indicated recovery of at least 99% of the UX_1.

Fractions of UX_1 effluents from a sample which had been separated from uranium by the above method were evaporated to dryness and the residues (mainly small quantities of organic matter from the resin) were examined spectrographically and were all found to be free of uranium, indicating complete separation of the thorium isotope.

The uranium could be eluted quite simply from the resin with 0·1M hydrochloric acid solution. The column was first washed with 250 ml of the acid solution at the rate of 5 ml per minute, and the effluent was discarded, as it contained no uranium. Elution with another 600 ml of this eluent produced a complete recovery of the uranium (Fig. 1). This elution curve was prepared from gravimetric analyses of 50-ml fractions of the effluent. The beginning and end of the uranium elution can be easily noted by eye because of the sharpness of the leading and trailing edges of the band and the intense yellow colour imparted to the solution by the metal.

The uranium, however, need not be removed from the column if a continuous supply of UX_1 is desired. Depending on the needs of the laboratory the column may be "milked" periodically to produce UX_1. For example, 14 days after the removal of UX_1 from the uranium another quantity of the isotope, which will have one-third the activity of the original batch, may be recovered by elution with the 9·6M hydrochloric acid solution. With each elution of the bed the uranium band moves less than 1 inch down the column, and since the band has a very sharp leading edge several "milkings" are possible before any uranium appears in the effluent. We were able to recover 5 batches of UX_1 from a column which was "milked" at two-week intervals, before any uranium was found in the effluent. In this way one column supplied our needs for 2 months before it was necessary to remove the uranium and recharge the resin bed with a fresh uranium solution. Eluted uranium solutions are evaporated to dryness and stored for re-use since in 4 months 97% of the equilibrium quantity of UX_1 is regenerated and 99% in 5½ months.

Impurities in the uranium should not present too much of a problem if a fairly pure reagent is used. Rare earths, alkali metals, alkaline earths and other elements such as Al, Ni and Cr, which are not adsorbed from concentrated hydrochloric acid solutions, will appear in the effluent with the UX_1. However, they will be removed with the first batch of the thorium isotope and future batches should not contain them. Other elements which are adsorbed or partially adsorbed (e.g. Fe^{III}, Cu, Mo^{VI}, Zn, Cd, etc.) may appear in various batches but their concentration will be very low, and since only a very small percentage of a batch of UX_1 is usually used in any one tracer experiment, the interference of any of these metals in any particular experiment would probably be negligible.

RECOMMENDED PROCEDURE

Dissolve approximately 50 g (0·2 mole) of uranium, as the oxide or chloride (but not the nitrate), in 150 ml of 9·6M hydrochloric acid solution. Transfer the solution to the ion-exchange column which has previously been washed with the acid solution. When the resin has resettled allow the solution to pass through the bed at the rate of 4 ml per minute. When the level of the liquid has just reached the top of the resin bed add another 250 ml of the acid. Repeat with another 250 ml of this solution and collect the total 650 ml of effluent, which will contain about 97% of the UX_1 present in the original uranium solution. More activity may be eluted with another batch of acid but the increased yield is generally not worthwhile.

The column may then be periodically eluted with 750 ml of the acid solution until it is noticed that the uranium band has almost reached the bottom of the resin bed. The interval between elutions is determined by the needs of the laboratory and the 24·1 day half-life of UX_1.

To remove the uranium the column is washed with 250 ml of 0·1M hydrochloric acid solution at the rate of 5 ml per minute. This effluent is discarded. Elution is continued with 600 ml of this solution, resulting in the quantitative recovery of the metal.

Zusammenfassung—Eine relativ einfache Methode zur Derstellung grösserer Mengen von trägerfreiem ^{234}Th wird beschrieben. Eine 9·6-m salzsaure Lösung von Uran wird durch eine Anionenaustauschersäule geschickt. Der Urankomplex wird absorbierbt und das Tochter-Thorium wird durchgelassen. Hierbei wird eine praktisch quantitative Trennung des UX_1 von bis zu 50 g Uran erzielt. Das Uran kann leicht wiedergewonnen werden, indem man mit 0·1-m Salzsäure eluiert. Man kann es aber auch auf der Säule belassen und in periodischen Eluierungen mit 9·6-m Salzsäure weitere Mengen von frisch gebildetem UX_1 gewinnen.

Résumé—On a imaginé un procédé relativement simple pour la préparation de grandes quantités de ^{234}Th libre d'entraîneur utilisable comme traceur. On introduit une solution d'uranium dans de l'acide chlorhydrique 9,6 M dans une colonne échangeur d'anions. L'uranium complexé est fixé et le Thorium issu par descendance, est éliminé par lavage de la résine, fournissant une séparation pratiquement quantitative de UX_1 de quantités aussi importantes que 50 g d'uranium. L'uranium

peut être récupéré facilement par élution avec une solution d'acide chlorhydrique 0,1 M, ou peut être laissé sur la colonne pour être lavé périodiquement à l'acide chlorhydrique 9,6 M produisant de nouveaux échantillons de UX_1

REFERENCES

[1] W. Crookes, *Proc. Roy. Soc. Lond.*, 1900, **A66**, 409.
[2] D. Dyrssen, *Svensk Kem. Tidskr.*, 1950, **62**, 153.
[3] O. Erbacher, W. Herr and M. Wiedemann, *Z. anorg. Chem.*, 1944, **252**, 282.
[4] R. W. Bane, U.S. Atomic Energy Comm., CC-3336, Nov. 1945.
[5] Y. Chen, *J. Chinese Chem. Soc.*, Ser. II, 1957, **4**, 47.
[6] K. A. Kraus, G. E. Moore and F. Nelson, *J. Amer. Chem. Soc.*, 1956, **78**, 2692.
[7] E. Tomic, I. Ladenbauer and M. Pollak, *Z. analyt. Chem.*, 1958, **161**, 28.
[8] O. A. Nietzel, B. W. Wessling and M. A. DeSesa, *Analyt. Chem.*, 1958, **30**, 1182.
[9] K. A. Kraus and F. Nelson, *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva* 1955, 1956, **7**, 113.

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UTILISATION OF TERNARY AND ION-ASSOCIATION COMPLEXES IN CHEMICAL ANALYSIS—II

POLAROGRAPHIC DETERMINATION OF INDIUM

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Laboratory of Analytical Chemistry, Chemical Institute, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

(*Received* 8 *December* 1959)

Summary—Conditions have been found for the formation of phenanthroline-thiocyanate complexes of indium, cadmium and other metals and their compositions have been determined. The influence of EDTA on the formation of these complexes has been observed. At pH 3 indium remains bound in the soluble EDTA complex, while cadmium, zinc, copper and other ions form water-soluble phenanthroline-thiocyanate complexes which can be separated from the aqueous phase into butanol. It is then possible, after acidification with hydrochloric acid, to determine indium polarographically in the aqueous phase. Using this method it is possible to determine from 0·05% of indium in metallic cadmium.

WITHIN the framework of the systematic study of analytically utilisable ternary complexes, further attention has been paid to certain complexes of the type metal-phenanthroline-thiocyanate. As is known, phenanthroline with bivalent and tervalent cations forms complex ions of the type $Me^{II}(Phen)_2^{2+}$ and $Me^{III}(Phen)_2^{3+}$, which, in contrast to similar pyridine complexes, behave as chelates. They are characterised by increased stability and, in the presence of halides or thiocyanate, they form insoluble compounds for which the composition $Me(Phen)_mX_n$ can be assumed. Their most significant property is their slight solubility in water and their solubility in organic solvents. Therefore they are suitable—as has been shown with the complex phenanthroline-iron-iodide[1]—for the extraction of certain metals and their separation.

It has been proved that a number of cations, in the presence of thiocyanate, also form insoluble precipitates over a wide pH range with phenanthroline. Some of these are readily extractable by an organic solvent; others can be thoroughly dispersed (e.g. in butanol) without making impossible a subsequent separation of the aqueous and organic phase. The presence of other complex-forming substances, principally EDTA, through the formation of other complexes, decreases the number of reacting cations so that it is possible to obtain a selective separation. So, for example, at pH 3 indium is firmly bound by EDTA against phenanthroline and thiocyanate whereas other elements occurring with it may continue to exist in the form of phenanthroline-thiocyanate complexes. This fact makes possible the separation of indium from cadmium and zinc and its determination in the aqueous phase, either polarographically or complexometrically. In this work the conditions have been elaborated for this separation of indium when it is subsequently determined polarographically.

EXPERIMENTAL

Reagents and solutions

Standard indium solution was prepared from reagent grade indium metal. Its titre was determined complexometrically.

A solution of 1:10-phenanthroline (0·05M) was prepared by dissolution of a precisely calculated and weighed quantity of 1:10-phenanthroline, Guaranteed Reagent (Lachema, Brno) in warm redistilled water acidified by a minimum quantity of nitric acid. The pH of the solution resulting was 3 to 4.

The disodium salt of ethylenediaminetetra-acetic acid (EDTA) was prepared in 0·05M concentration. The product "Chelaton 3" (Lachema, Brno) was employed.

Solutions of various metal salts were prepared from reagent grade chemicals. The concentrations of these solutions were controlled complexometrically.

A 30% solution of ammonium thiocyanate was prepared from the reagent grade chemical.

The indicator used was a 0·1% Xylenol Orange solution (Chemapol, Praha).

The buffer solution was prepared from formic acid and ammonium formate.

Apparatus

Adjustment of the pH of the solution was controlled potentiometrically with a glass electrode. The measurement was carried out with an electronic pH meter (Kovodružstvo, Praha).

Polarographic measurements were carried out by a photoregistering polarograph of the type LP-55 (Laboratorní přístroje, Praha) and in a polarographic cell with a separate calomel electrode.

RESULTS AND DISCUSSION

Phenanthroline-thiocyanate complexes of cadmium, indium and zinc

In solutions containing phenanthroline complexes of cadmium, indium and zinc, in the range of pH 1 to 5, on addition of thiocyanate in excess, a white voluminous precipitate is produced. The formation of this precipitate is not greatly influenced by the pH of the solution; for example, in the case of cadmium the precipitate is formed in strongly acidic solutions (1*N* HCl), in neutral, or in weakly alkaline solutions. It may be assumed that a change in acidity of the solution may influence the structure of the resulting complex. In the present work the structures of the complexes were studied in the range of pH 3 to 3·5 since this pH value, as will later be shown, is the most suitable for the separation of indium from the interfering elements.

The phenanthroline-thiocyanate complexes of cadmium, indium and zinc were prepared by the addition of solid ammonium thiocyanate (50 times the amount of the metal nitrates) to solutions of nitrates of these metals after adjusting the pH of the solutions with formate buffer to 3. This solution was then treated with saturated phenanthroline solution until precipitate no longer formed. The solution was then allowed to stand for 2 to 3 hours, and was then decanted and filtered. The precipitate on the filter was washed with water until the washings gave no reaction with silver ions. The material thus obtained was dried *in vacuo*. In the case of indium, the phenanthroline-thiocyanate complex of which is partly soluble in water, the precipitated complex was washed with ether and then also dried *in vacuo*.

Analysis was carried out by oxidative melting of the prepared complex with sodium peroxide in a sintered corundum crucible; after extraction of the melt with water, the content of sulphur was determined gravimetrically by precipitation with barium chloride in the presence of EDTA;[2] the metal constituent was then determined chelatometrically and polarographically.

Determination of the ratio of metal to phenanthroline in the complexes studied was carried out by amperometric titration. Since these materials are water-insoluble, the dependence of the concentration of the thiocyanate complex of cadmium (or indium or zinc) on the quantity of added phenanthroline has been studied. Since the metals in thiocyanate medium yield polarographic waves,[3] it is possible to follow the development of the complex amperometrically. The amperometric titration can easily be carried out using a rotating platinum electrode—the titration curve has, in this case, a normal course, and the current drops during the titration; at the point of equivalence it reaches a constant value. The employment of a mercury dropping electrode is less suitable—the reading of the equivalence point of the titration is inaccurate because of the influence of deformations which occur in the diffusion currents of cadmium, indium or zinc in the presence of phenanthroline.

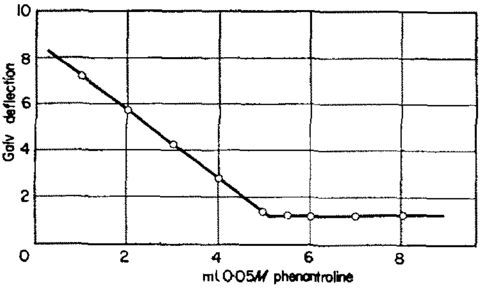

FIG. 1.—Amperometric titration of cadium thiocyanate complex with phenanthroline. Titrated solution: 5 ml of 0·05M $Cd(NO_3)_2$, 5 ml of 30% NH_4CNS solution in a 50-ml volume, pH 3·1; recorded at −0·80 V vs. S.C.E., rotating platinum electrode.

The titrations were carried out as follows: the metal nitrate solution in 1M ammonium thiocyanate solution was adjusted with formate buffer to a pH value of 2·5–3 and, after the removal of oxygen by nitrogen, the titration was carried out with 0·05M phenanthroline solution at an applied voltage for zinc of −1·10 mV, for cadmium of −0·75 mV and for indium of −0·80 mV vs. S.C.E. Fig. 1 shows the course of this type of titration.

On the basis of these titrations it was ascertained that in the case of phenanthroline-thiocyanate complexes of cadmium, indium and zinc the ratio of the metal to phenanthroline under the conditions described is always 1:1. From the content of sulphur and metal and using the determined ratio of phenanthroline to metal, it is possible to determine the formula of the compounds studied:

Zn complex

	found	*calculated*
S	15·45%	16·10%
Zn	16·73%	16·46%

Phen : Zn = 1:1

Formula: $Zn(Phen)(CNS)_2{\cdot}2H_2O$

Cd complex

	found	*calculated*
S	14·76%	14·45%
Cd	25·95%	25·53%

Phen : Cd = 1:1

Formula: $Cd(Phen)(CNS)_2{\cdot}2H_2O$

In complex

	found	*calculated*
S	18·85%	18·20%
In	22·42%	24·50%

Phen : In = 1:1

Formula: $In(Phen)(CNS)_3$

Similar complexes are formed under similar conditions with a number of other metals. Their compositions have not been studied in detail since it does not belong to the framework of this paper. In the majority of cases the complexes concerned are substances slightly soluble in water but soluble in certain organic solvents. As the aim of this work was to find the conditions for the separation of indium from the accompanying elements, the extraction of indium in the form of the phenanthroline-thiocyanate complex has been studied first. This complex can readily be extracted by butanol, methyl propyl ketone or other ketones but this method of extraction is not very selective and it is less suitable than, for example, extractions of the thiocyanate[4] or iodide[5] complexes of indium.

TABLE I.—DEVELOPMENT AND SOLUBILITY OF PHENANTHROLINE-THIOCYANATE COMPLEXES AT pH 3

Metal	Solubility in water	Formation of complexes in the presence of EDTA
Cd^{II}	insoluble	insoluble
Zn^{II}	insoluble	insoluble
Pb^{II}	insoluble	no complex develops
Mn^{II}	insoluble	insoluble
Cu^{II}	insoluble	insoluble
Ni^{II}	insoluble	insoluble
Fe^{III}	insoluble	no complex develops
Fe^{II}	insoluble	insoluble
Al^{III}	insoluble	no complex develops
Th^{IV}	no complex develops	no complex develops
Tl^{I}	no complex develops	no complex develops
Bi^{III}	insoluble	no complex develops
V^{V}	insoluble	no complex develops
Ti^{IV}	insoluble	no complex develops
UO_2	insoluble	no complex develops
Mo^{VI}	insoluble	insoluble
W^{VI}	no complex develops	no complex develops
Cr^{VI}	no complex develops	no complex develops

Separation of indium from cadmium and other metals

The influence of the presence of EDTA on the development of phenanthroline-thiocyanate complexes was further studied. It was ascertained that in the range of pH 2–3, the compound $In(Phen)(CNS)_3$ does not develop and indium remains bound in the form of the soluble EDTA complex. Under the same conditions, on the other hand, the insoluble complexes of cadmium, zinc, copper and other metals are formed. Table I contains a survey which summarises the formation of phenanthroline-thiocyanate complexes at pH 3 in the presence and absence of EDTA. From this survey it is evident that indium can be separated from a number of elements by the utilisation of the formation of phenanthroline-thiocyanate complexes. A suitable organic solvent for the complete extraction of phenanthroline-thiocyanate complexes has not been found. But in butanol, which does not dissolve the phenanthroline-thiocyanate complexes, they readily disperse without hindering the separation of the aqueous and organic phase.

The experiments were carried out as follows: 50 ml of aqueous solution containing 2 ml of the standard indium solution, 4 ml of 30% ammonium thiocyanate solution and 2 ml of 0·05M phenanthroline solution, were stirred rapidly by a magnetic stirrer with 50 ml of butanol, and then the two phases were separated in a separatory funnel. In preliminary experiments the content of indium in the aqueous phase was determined by complexometric back-titration with a standard thorium nitrate solution, using Xylenol Orange as indicator.

In this manner it was ascertained that indium remains quantitatively in the aqueous phase as an EDTA complex and in this way it can be separated from cadmium, zinc and other metals. Further, it was observed that phenanthroline alone forms with thiocyanate an insoluble ion-association complex which also disperses in butanol. Therefore, it is possible to remove phenanthroline quantitatively from the aqueous phase by addition of thiocyanate and by separation of the complex which is formed in butanol. From the structure of the cadmium complex of phenanthroline thiocyanate it is evident that the same molar quantity of phenanthroline is necessary for its precipitation. But since the thiocyanate complex of cadmium is extracted into butanol, it is evident from a number of experiments that, for the separation of cadmium into butanol in the presence of excessive thiocyanate, two-thirds of the stoichiometric quantity of phenanthroline is sufficient.

Polarographic determination of indium after separation of interfering elements in the form of phenanthroline-thiocyanate complexes

Since indium is a good depolariser and the determination of low concentration of this element is frequently required, special attention has been paid to its polarographic determination. A number of methods have been elaborated in which, almost always, the interfering influence of cadmium is considered. Some authors solve this problem by precipitation,[7,8] others by extraction,[9] or by chromatographic separation;[14] others use complex-forming electrolytes.[11–15]

If indium is separated from cadmium and other elements, as described above by means of the formation of phenanthroline-thiocyanate complexes in the presence of EDTA, the indium remains in the aqueous phase as a stable soluble EDTA complex which does not manifest itself polarographically. But on acidification of the solution it decomposes, and indium can then be determined polarographically. For this reason hydrochloric acid solutions of different molarity were tested as base electrolyte. The development of the polarographic wave of indium in hydrochloric acid medium depends on the existence of chloro-indic complexes as has been proved by Kolthoff[16] and Schufle[17] who studied the polarographic behaviour of indium in 1M to 8M HCl.

The influence of *o*-phenanthroline on the wave of indium in 1M HCl was studied further. It was ascertained that in this base electrolyte *o*-phenanthroline yields a double wave. The first (more positive) wave is badly developed and its height is about one-sixth of the total height of the wave. The half-wave potential of the more negative wave is —0·71 V vs. S.C.E. This wave is shown in Fig. 2, curve 1.

o-Phenanthroline influences very unfavourably the otherwise well-developed wave of indium in 1M HCl. If the ratio of indium to phenanthroline is 1:3 or greater, the current drops steeply after the limiting current for indium is reached; for ratios of 1:2 and 1:1 this decline is not so obvious and a residue of the wave of phenanthroline is still maintained. A similar drop of the current in the polarographic curves of indium has been explained by Bulovová[14] as an effect of slightly deformable anions.

This explanation could be applied equally well to the reduction of the phenanthroline complex of indium but, since in the presence of phenanthroline the development of the minimum on the polarographic curve occurs also in the waves of other cations (copper, cobalt), the half-wave potential of which is substantially different from the potential at which the dropping mercury electrode has no charge, the explanation of this feature will require further study. The presence of *o*-phenanthroline in the solution to be analysed therefore makes a polarographic determination of indium impossible. It is necessary, in consequence, in removing the phenanthroline-thiocyanate complexes of cadmium and other metals into butanol, to use thiocyanate in excess so as to transfer the total phenanthroline to the organic phase as described earlier. The aqueous solution with the separated indium then still contains excess of EDTA, thiocyanate and a residue of butanol dissolved in water (the solubility of butanol in water[18] is 79 g/litre at 20°). This solution is acidified with hydrochloric acid so as to make the resulting concentration of HCl 3*M* and, after removing oxygen by nitrogen, the polarogram of the solution is recorded, beginning at —0·30 V vs. S.C.E. In this medium indium produces a well-developed step with a half-wave potential of —0·64 V vs. S.C.E. This must result from the reduction of chloro-indic complexes, since in such a strongly acidic solution the existence of thiocyanate complexes cannot be assumed. Proof of this is also provided by the value of the half-wave potential, which in reduction of the indium thiocyanate complex is —0·717 V vs. S.C.E.[3]

TABLE II.—DEPENDENCE ON TIME OF HEIGHT OF THE POLAROGRAPHIC WAVE OF INDIUM IN 3*M* HCl AND 0·1*M* NH_4CNS (SOLUTION SATURATED WITH BUTANOL).

time, *min*	height, *mm*	$E_{\frac{1}{2}}$
10	40	—0·644
60	39·5	—0·644
120	40	—0·644
180	42	—0·644
240	44	—0·662
300	46	—0·662
900	53	—0·696

$E_{\frac{1}{2}}$ = half-wave potential in V vs. S.C.E. t = 0 is the mixing time of the solution after separation with hydrochloric acid.

On acidification of the aqueous phase after the separation of cadmium and other elements an interesting feature may be observed. The solution becomes faintly pink in colour and this colour disappears after about 3 hours. During this time the solution has a slight odour of hydrogen sulphide, and the presence of this gas can be confirmed by a paper impregnated with lead acetate solution. This reaction can be accelerated by increasing the temperature. At room temperature its course is slow and it can be explained by assuming reduction of thiocyanate. This reaction influences both the height and the half-wave potential of the indium wave. For 2 hours after acidification, the height of the wave remains constant; the half-wave potential then shifts to more negative values and the height of the wave increases slightly. The results indicating this phenomenon are presented in Table II.

Because of the high solubility of butanol in water, the diffusion coefficient of the analysed solution differs from that of an aqueous solution of hydrochloric acid and the wave of indium in 3*M* HCl solution, saturated with butanol, is somewhat lower. For the evaluation of polarograms it is therefore necessary either to prepare solutions for the construction of a calibration curve for indium by the procedure used for the sample, or to use the standard addition method.

Procedure for the determination of indium after separation of cadmium

In a solution containing the mixture of the two ions adjust the pH to a value of 3 by addition of buffer (formic acid and ammonium formate, pH 3), then add 0·02*M* EDTA solution at a concentration which will produce EDTA in excess, in comparison with the concentration of indium. To the solution adjusted in this manner add 30% ammonium thiocyanate solution to make its total concentration amount to 2–3% and then add 0·05*M* *o*-phenanthroline solution for as long as a precipitate of $CdPhen(CNS)_2$ is produced. Now add the same volume of butanol and stir the mixture thoroughly for 3 min by a magnetic stirrer. Separate the two phases in a separatory funnel and repeat the stirring with half the volume of butanol for 2 min. Normally the organic phase will then be clear. Again separate the two phases in the separatory funnel, pour the bottom (aqueous) layer into a 50-ml volumetric flask, wash the butanol twice with 5 ml of water, and add this water to the volumetric flask. Acidify the solution in the volumetric flask with 12 ml of concentrated HCl, add 1 ml of 1% glucose solution and make up with water to the mark. It is necessary to carry out the polarographic recording of indium within 2 h after mixing. The wave height for indium is compared, for the evaluation of the analysis, with the wave height for a standard indium solution prepared by the same procedure, or the determination is carried out by the standard addition method. Several curves obtained after separation of a larger amount of cadmium are shown in Fig. 3, and Table III presents the results of several analyses of indium after its separation.

TABLE III.—POLAROGRAPHIC DETERMINATION OF INDIUM AFTER SEPARATION OF CADMIUM

Present		In found, *mg*	Error, %
Cd, *mg*	In, *mg*		
39·2	0·55	0·57	+5
39·2	1·90	1·96	+3
39·2	2·70	2·67	−1
39·2	3·50	3·48	−0·6
196	1·90	1·95	+3
196	0·80	0·83	+4
294	0·80	0·78	−3
588	0·80	0·82	+3

Procedures for the determination of indium after separation of other metals

It is also possible to separate zinc, copper, manganese, cobalt, nickel, iron^{II} and molybdenum^{VI} from indium in the same way. For the polarographic determination of indium, the most important of these elements is copper which, it is true, does not interfere polarographically; but at high concentration (in comparison with indium) it interferes in the determination because of its more positive half-wave potential. Iron^{II} can be separated from indium in the form of the phenanthroline-thiocyanate complex; since, however, iron^{II} does not interfere in the polarographic determination, it is simpler not to carry out a separation, but merely, before the polarographic determination proper, to reduce iron^{III} with hydroxylamine (or iron powder, reduced by

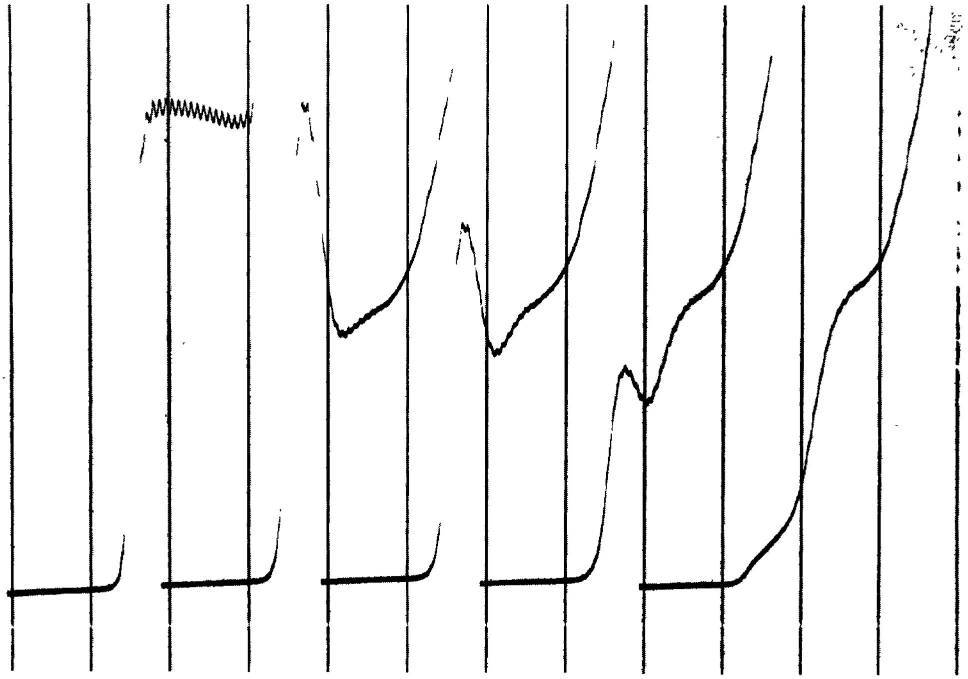

FIG. 2.—Influence of phenanthroline on the wave of indium in $1M$ HCl

(1) 10 ml of $1M$ HCl, 1 ml of 1% glucose, 1 ml of $0{\cdot}05M$ phenanthroline.
(2) the same solution as (1) with 0·5 ml of $0{\cdot}01M$ $In(NO_3)_3$
(3) the same solution as (1) with 0·5 ml of $0{\cdot}01M$ $In(NO_3)_3$
(4) the same solution as (1) with 0·5 ml of $0{\cdot}01M$ $In(NO_3)_3$
(5) 11 ml of $1M$ HCl, 1 ml of 1% glucose, 1 ml of $0{\cdot}01M$ $In(NO_3)_3$

[All the curves begin at —0·30 V, 200 mV/abscisse, sensitivity 1/70, S.C.E., the curves (1)–(5) from right to left.]

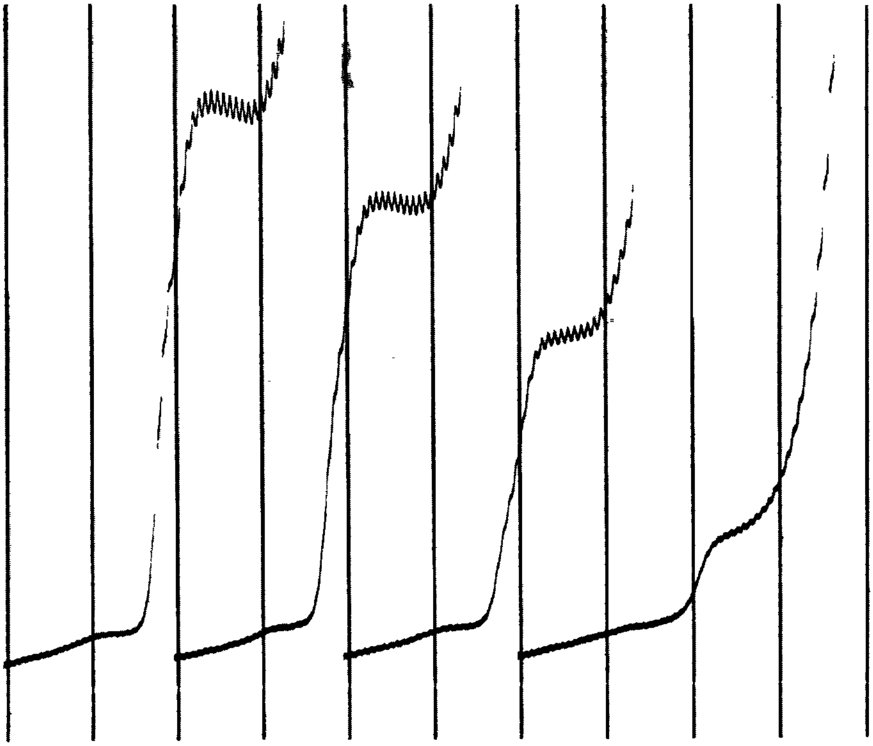

FIG. 3.—Polarographic curves of indium after separation of cadmium
Before separation 50 ml of solution contained
(1) 0·55 mg of In, 39·2 mg of Cd
(2) 1·90 mg of In, 39·2 mg of Cd
(3) 2·70 mg of In, 39·2 mg of Cd
(4) 3·50 mg of In, 39·2 mg of Cd
[All the curves start at —0·30 V, 200 mV/abscisse, sensitivity 1/70, S.C.E., the curves (1)–(4) from right to left.]

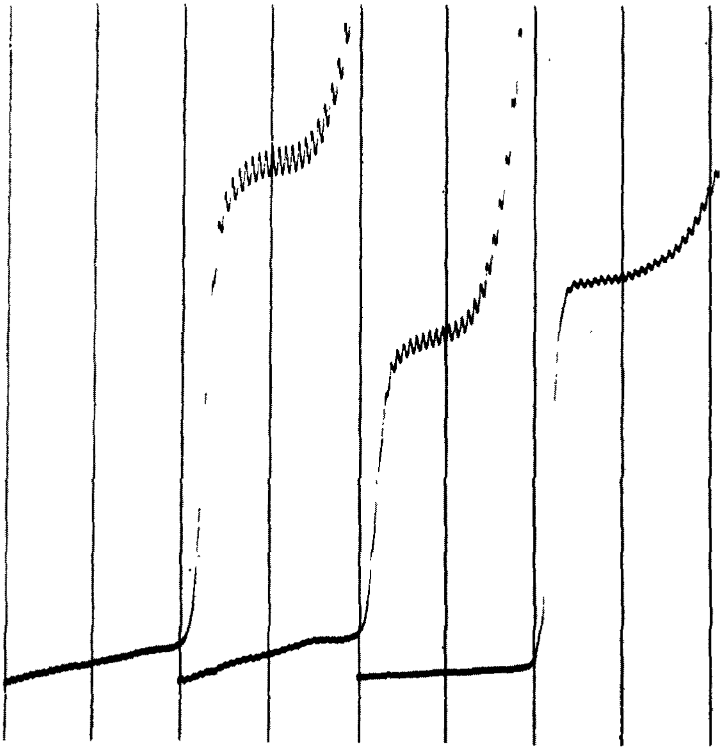

FIG. 4.—Polarographic curves of indium after separation of cadmium, copper and zinc

(1) Before separation, 50 ml of solution contained 2·70 mg of In, 294 mg of Cd, 32 mg of Zn
(2) Before separation, 50 ml of solution contained 1·68 mg of In, 196 mg of Cd, 63 mg of Cu, 65 mg of Zn
(3) Curve of indium in 3*M* HCl without separation
[All the curves start at −0·30 V, 200 mV/abscisse, sensitivity 1/30, S.C.E., the curves (1)–(3) from right to left.]

hydrogen). Fig. 4 shows polarographic curves obtained after the separation of copper, zinc, cobalt, nickel and cadmium.

In the analyses of synthetic samples containing cadmium as the principal component, with an indium content of 0·05–0·5%, the error of determination varies from ±3 to ±5%; when the indium content ranged from 0·5 to 5% results were obtained with the normal accuracy of polarographic analysis, *i.e.* ±2%. The sample weights were chosen in such a manner that the quantities of indium involved in the separation were at least 0·8 mg (at 0·1% content of indium in metallic cadmium). Only higher concentrations of lead and bismuth in the analysed sample interfere in the determination of indium carried out in this manner, because the half-wave potentials of these metals are more positive than the half-wave potential of indium.

Zusammenfassung—Die Bedingungen für die Bildung der Phenanthrolin-Thiocyanate-Komplexe von Indium, Cadmium und anderen Elementen wurden studiert und die Zusammensetzung der Komplexe wurde bestimmt. Der Einfluss von EDTA auf die Bildung der Komplexe wurde untersucht. Bei pH 3 bleibt Indium als EDTA-komplex gebunden, während Cadmium, Zink, Kupfer und andere Ionen wasserlösliche Phenanthrolin-Thiocyanate-Komplexe bilden, die mit Butanol ausgeschüttelt werden können. Nach Ansäuern der verbleibenden wässerigen Phase kann Indium polarographisch bestimmen werden. Mit dieser Methode ist es möglich, noch 0·05% Indium in Cadmiummetall zu bestimmen.

Résumé—Les auteurs ont établi les conditions dans lesquelles on peut former les complexes phénanthroline-thiocyanate de l'indium, du cadmium et d'autres métaux; la composition de ces complexes a été déterminée et l'influence de l'EDTA sur la formation de ceux-ci a été observée. A pH 3 l'indium reste engagé dans un complexe soluble de l'EDTA, tandis que le cadmium, le zinc, le cuivre et d'autres ions forment des complexes phénanthroline thiocyanate solubles dans l'eau, qui peuvent être séparés de la phase aqueuse par extraction dans le butanol. Il est alors possible, après acidification par l'acide chlorhydrique, de doser l'indium polarographiquement dans la phase aqueuse. En utilisant cette méthode il est possible de doser jusqu'à 0,05% d'indium dans le cadmium métallique.

REFERENCES

[1] F. Vydra and R. Přibil, *Talanta*, 1959, **3**, 72.
[2] R. Přibil and D. Maričová, *Coll. Czech. Chem. Comm.*, 1953, **18**, 309.
[3] J. W. Grenier and L. Meites, *Analyt. Chim. Acta*, 1956, **14**, 482.
[4] H. Irving and F. J. C. Rossotti, *J. Chem. Soc.*, 1955, 1946.
[5] R. Bock, *Z. analyt. Chem.*, 1951, **133**, 110.
[6] J. Kinnunen and B. Wennestrand, *Chemist-Analyst*, 1957, **46**, 92.
[7] N. V. Akselrud and V. B. Spivakovskij, *Zhur. analit. Khim.*, 1957, **12**, 78.
[8] A. S. Mukchina, *Zavodskaya lab.*, 1948, **14**, 354.
[9] M. Ostanek, *Repts. J. Stefan Inst.*, 1957, **4**, 147.
[10] W. Kemula, *Przemysl Chem.*, 1954, **10**, 453.
[11] S. I. Sinjakova, *Zhur. analit. Khim.*, 1946, **1**, 241.
[12] J. Doležal, *Coll. Czech. Chem. Comm.*, 1956, **21**, 251, 844.
[13] J. Doležal, *Chem. Listy*, 1955, 49, 1237.
[14] M. Bulovová, *ibid.*, 1954, **48**, 655.
[15] L. Treindl, *ibid.*, 1956, **50**, 534.
[16] I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, 1939, **24**, 1.
[17] J. A. Schufle *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 1013.
[18] G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*, J. Wiley, New York, 1957, Appendix.

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ACID CHLORIDES OF SUBSTITUTED SUCCINIC AND GLUTARIC ACIDS AS HYDROLYTIC REAGENTS FOR THE DETERMINATION OF WATER

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Summary—Some alkyl substituted succinyl and glutaryl chlorides have been examined as hydrolytic reagents for the determination of water. The best reagents are methylethylglutaryl and dimethylglutaryl chlorides; the former compound is recommended because it is less volatile.

Water of crystallisation in several hydrates has been determined satisfactorily using this reagent.

Naphthalyl chloride and *cyclo*hexyl diacetyl chloride were also examined, but were unsuitable.

THE method of determining water in a gas stream by passing it through an acid chloride and titrating the hydrochloric acid formed was first used by Lindner[1] in his titrimetric procedure for the determination of carbon and hydrogen in organic compounds. Lindner's original reagent was α-chloronaphthyldichlorophosphine oxide, but later he used naphthyldichlorophosphine oxide.[2] Hydrogen chloride produced from the hydrolysis is absorbed in water contained in a bubbler and is determined alkalimetrically. A few other reagents have been suggested by later investigators.[3]

In the course of an examination of titrimetric procedures for the determination of carbon and hydrogen, it was found that succinyl chloride had advantages over earlier reagents in speed of reaction.[4,5] Although succinyl chloride reacts rapidly with water and yields hydrogen chloride almost immediately, it would be desirable to have available a reagent which yields lower blank values. A number of alkyl substituted succinyl chlorides have now been examined because it was expected that they would be less volatile and that the nature of the alkyl groups would lead to acid chlorides of greater reactivity. Glutaryl chloride and alkyl substituted glutaryl chlorides were also examined because it was envisaged that the six membered ring of the acid anhydride formed in the reaction would possess a stability similar to that of the five membered anhydride ring of the succinic acid series. The stable nature of these anhydrides probably has some influence on the efficiency of the reaction.

The following compounds were therefore prepared and examined:—

Succinyl chloride
α:α-Dimethylsuccinyl chloride
α:α-Diethylsuccinyl chloride
Glutaryl chloride
β:β-Dimethylglutaryl chloride
β-Methyl-β-ethylglutaryl chloride
β:β-Diethylglutaryl chloride
*Cyclo*hexyl-1′:1′-diacetyl chloride
Naphthalyl chloride

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Attempts to make tetramethylsuccinyl chloride and di*cyclo*hexyl-1:1-diacetyl chloride were unsuccessful.

Barium chloride dihydrate was used for most of the tests. Samples obtained from different sources were checked gravimetrically; in all cases their water content varied only slightly (±0·07%) from the theoretical value of 14·75%. Sodium acetate trihydrate, copper sulphate pentahydrate and cadmium chloride ($CdCl_2.2{\cdot}5H_2O$) were also used in some experiments and were satisfactory. These hydrates were heated in a stream of dry nitrogen which was passed through a reaction vessel containing the reagent. The hydrogen chloride liberated from the reagent passed over and was collected in an absorber containing distilled water.

To obtain the best results from a given reagent it is necessary to keep the gas bubbles in the reaction vessel as small as possible. This is best achieved by passing the gas directly upwards into the liquid through a sintered-glass disc, but limitations are imposed by the back pressure of the gas. When a No. 3 glass sinter-disc (20 mm diameter) was used a pressure of about 80–120 mm Hg was required to maintain a flow rate of 50 ml/min. The pressure was considerably lower and the bubble size was still reasonably small with a No. 2 sinter-disc. However, the surface area exposed to the reagent increases with the square of the radius of the bubble and the volume with the cube of diameter, whereas the efficiency of the reaction depends on the size of *active* interface per unit volume.

For each reagent the time of contact depends mainly on the viscosity and therefore on the temperature. Surface-tension and the formation of foam also have to be considered.

It was found that a spiral path inside the reaction vessel did not markedly improve the results, and a possible explanation seems to be that the small bubbles emerging from the sinter-disc usually combine when they ascended the spiral. The increased contact time thus obtained appears to offset the decrease in surface area caused by the merging of the small bubbles.

Two other factors which require consideration are the amount of hydrogen chloride retained by the reagent and the time taken for it to pass over from the reaction vessel to the absorber. The most favourable conditions were established experimentally.

The column of reagent used in the reaction vessel must be long enough to allow sufficient contact time. This factor depends on the shape of the reaction vessel and the dead space enclosed between reagent and absorbent. It is desirable to keep the quantity of reagent small, to minimise retention of hydrogen chloride.

A volume of about 5 ml of the reagent is suitable in most cases. This amount of reagent is usually sufficient for at least 700–800 mg of water. Special care was taken to design the reaction vessel in such a way that the maximum amount of the reagent was in permanent contact with the gas-stream. The gas-bubbles themselves gave the necessary stirring effect.

The reproducibility of results and, of course, of blanks, depends essentially on the volume of gas which is passed, and varies only slightly with the flow rate. This means that for a given volume of gas, the flow rate may be altered over rather a wide range without undue effect on the constancy of blanks, provided that the cooling-system used to counteract the volatility of the reagents is efficient. It is also necessary to ensure that aerosol formation does not lead to the passage of reagent into the absorbing vessel. Glass-wool or silica-wool filters inserted in the cooling trap are not very

TABLE I.—COMPARISON OF ACID CHLORIDES AS REAGENTS FOR WATER

Reagent and b.p.	Reagent temp, °*C*	Blank analyses, *ml* of 0·05*N* NaOH		Amt. of H_2O, *mg*	Time required, *min*	Accuracy (Deviation from 100% recovery)	Comments
		No trap	Cooling trap				
Succinyl chloride 75°/12 mm	70	1·0–4·0	0·3–0·5	3–10	30	−2·7%	High blanks Slow removal of HCl
α:α-Dimethylsuccinyl chloride 88–92/12 mm	20–50	2·0–3·0	1·6–1·9				High blanks Difficult conditions
α:α-Diethylsuccinyl chloride 117°/12 mm	20–50	0·8–1·2					Sluggish at low temp.
	90	1·5–1·7	0·7–1·0				High blanks at elevated temp.
Glutaryl chloride 101–104/14 mm	20	1·5–1·7					High blanks
	70–90	1·4–1·7	0·1–0·45	3–10	60	0–11%	Low blanks with cooling trap but slow removal of HCl.
β:β-Dimethylglutaryl chloride 122–125°/15 mm	70–100	0·4–0·8		10	30	±1%	Low and stable blanks Recommended. Flow rate up to 30 ml/min
			0·1–0·2	10–20	60		
β-Methyl-β-ethyl-glutaryl chloride 115°/12 mm	40–70	0·2–0·3	Not necessary	25	30	±2%	Highly recommended Flow rate 30–50 ml/min
β:β-Diethylglutaryl-chloride 127°/11 mm		0·6–0·7	0·4–0·5				High blanks
*Cyclo*hexane-1:1-diacetyl chloride 141°/12 mm		0·1	Not necessary	5	30	−10%	Low capacity. Slow release of HCl.

useful, as their surface is rather big and it may be that hydrogen chloride as well as the reagent is retained.

Examination of reagents

The behaviour of the various reagents examined during this investigation is summarised in Table I. As already mentioned, the use of succinyl chloride has been described elsewhere[4] but it is included in the table for the sake of comparison. The chief comment to be made on this reagent is that the blank values, though reproducible, are large in comparison to those of other reagents described below. They were reduced by means of a cooling trap and a more efficient design has since improved them further. Results obtained invariably tend to be low. α:α-Dimethylsuccinyl chloride gives higher blanks, even with a cooling trap, and possesses no advantage over succinyl chloride. The corresponding diethyl-substituted succinyl chloride reacts very sluggishly with water so that only 40–60% recovery was obtained. In the glutaryl chloride series the parent substance yielded promising results when maintained at 70–90° and used in conjunction with an ice-salt cooling trap to counteract the volatility of the reagent. However, the release of hydrochloric acid gas is rather slow. β:β-Dimethylglutaryl chloride proved to be an extremely satisfactory reagent, superior to any yet examined. When maintained at 70–100° and used in conjunction with an ice-salt trap, low and reproducible blanks were obtained under a variety of conditions of flow rate up to 30 ml/min. In almost all cases the recovery of water was quantitative (*cf.* Table II.) β-Methyl-β-ethylglutaryl chloride gave more variable results, but it has the advantage of being much less volatile and not requiring a cooling trap. Flow rates of up to 50 ml/min can be used and the evolution of hydrogen chloride is rapid and quantitative (*cf.* Table III.) The corresponding diethyl-substituted glutaryl chloride was, rather surprisingly, found to be inferior. It gave low recoveries, and high blanks, and was sluggish in its reaction. The substitution of the carbon atom of a *cyclo*hexane ring in place of the β-methylene group of glutaryl chloride yielded the *cyclo*hexyl-1 : 1-diacetyl chloride. It was thought that the higher molecular weight would decrease the volatility of the reagent and that the tendency for hydrogen chloride to be retained would be minimised, but the removal of hydrogen chloride was

TABLE II.—DETERMINATION OF H_2O IN $BaCl_2.2H_2O$ USING DMGC

Analysis No.	H_2O, *mg*		Recovery, %
	Taken	Found	
1	5·032	5·056	100·5
2	6·328	6·315	99·8
3	8·557	8·503	99·4
4	9·894	9·917	100·2
5	12·03	11·98	99·6
6	14·61	14·57	99·7
7	16·96	16·98	100·1
8	19·98	20·00	100·1

Analyses 1–4 Flow rate 15–20 ml/min. Volume of gas passed 500 ml. Blank deducted 0·07 mg H_2O
Analyses 5–8 Flow rate 20–30 ml/min. Volume of gas passed 1000 ml. Blank deducted 0·14 mg H_2O

slow; although the blanks were low under normal conditions they increased considerably with rise of temperature. The reagent has a low capacity (<1 mg/H_2O per ml). Naphthalyl chloride (not shown in Table I) was used in the molten form at 80°, but it is unstable and gives recoveries of water varying from 40–70%. The deposited anhydride is difficult to remove.

TABLE III.—ANALYSIS OF HYDRATES BY MEANS OF MEGC; FLOW RATE 5–30 ML/MIN

Hydrate	Gas volume	H_2O, *mg* Taken	H_2O, *mg* Found	Recovery, %
$BaCl_2{\cdot}2H_2O$	500 ml	3·647	3·687	101·2
		5·580	5·626	100·8
		7·846	7·830	99·8
		10·02	10·07	100·5
$BaCl_2{\cdot}2H_2O$	1000 ml	12·23	12·16	99·4
		15·60	15·57	99·8
		17·88	18·04	100·9
		20·12	20·20	100·4
$NaC_2H_3O_2{\cdot}3H_2O$	500 ml	2·334	2·320	99·2
	1000 ml	9·665	9·656	99·9
$CuSO_4{\cdot}5H_2O$	500 ml	3·099	3·117	100·6
	1000 ml	15·85	16·01	101·0

Blank on 500 ml gas volume ≡ 0·09 mg H_2O
Blank on 1000 ml gas volume ≡ 0·14 mg H_2O

Discussion of results

Table I shows that there is no apparent pattern in the behaviour of the various reagents. It was expected that under comparable conditions, the blank analyses would at least bear a direct relationship to the vapour pressure or boiling point of the reagents. It is surprising to note, therefore, that $\alpha:\alpha$-dimethylsuccinyl chloride gave blank analyses of 1·6–1·9 ml of 0·05*N* sodium hydroxide as compared to 0·3–0·5 ml for succinyl chloride although the respective boiling points are 88–92°/12 mm and 75°/12 mm. Even $\alpha:\alpha$-diethylsuccinyl chloride (117°/12 mm) gives twice the blanks of succinyl chloride.

As a result of this examination it appeared that the choice of reagent lay between $\beta:\beta$-dimethylglutaryl chloride (DMGC) and β-methyl-β-ethylglutaryl chloride (MEGC). The latter was selected because it was less volatile and eliminated the need for a cooling trap. Results obtained for the analysis of several hydrates using both reagents are shown in Tables II and III.

These results reveal that both MEGC and DMGC are suitable as reagents for the determination of water.

EXPERIMENTAL

Synthesis of reagents

The acid chlorides were prepared by treatment of the corresponding acids with a 20% excess of phosphorus pentachloride. After refluxing for several hours, the excess of PCl_5 was distilled off, first at atmospheric and then at slightly reduced pressure. The main fraction was eventually redistilled and the product stored in sealed tubes. The chlorine content of the reagents was determined by hydrolysing samples with 40% sodium hydroxide solution and applying the Volhard procedure.

The α:α-dialkyl substituted succinic acids and β:β-disubstituted glutaric acids were prepared by conventional procedures.[6,7] In the case of the β:β-diethylglutaric acid, however, a modified method was used owing to the failure of the ammonium salt of 4:4-diethyl-3:5-dicyanoglutarimide to separate. This was as follows.

200 Ml of anhydrous ethanol saturated with NH_3 at $-5°$ were treated with 1 mole of ethyl cyanoacetate (113 g) and 0·5 mole of diethyl ketone in a wide necked 750-ml stoppered bottle and stored in an ice box for 24 h. Subsequently the mixture was transferred to a distillation flask and the ammonia was removed by aspirating dry air through the mixture for 5 h. 250 ml of water were then added and 250 ml of the mixture were distilled. The residue was acidified with hydrochloric acid after being cooled and the free "Guareschi" imine which separated was purified and hydrolysed as described elsewhere.[7]

The *cyclo*hexyl-1:1-diacetic acid was prepared by the method described by Thole and Thorpe.[8]

Apparatus

The apparatus used is shown in Fig. 1. Nitrogen from a cylinder is fed through a side-arm into the combustion tube after passage through a scavenging train packed with Anhydrone and soda asbestos to remove moisture and acid gases. The working end of the delivery tube is provided with a B.14 cone and cap; this latter arrangement permits safe loading of the combustion boat into the tube without risk of contamination from grease. The combustion tube is supported horizontally, with an aluminium heating block mounted two thirds of the way along the tube. The delivery arm between the combustion tube and the reaction vessel is kept warm by means of an electrically heated tape, and the part of the reaction vessel below the condenser is similarly maintained at an appropriate temperature. Evaporation of the reagent is minimised by the water cooled condenser round the upper part of the vessel and by a cold-finger condenser as shown in Fig. 1. The gas stream is finally passed (where necessary) through a U-tube cooled in ice/salt and then through an absorber where the hydrochloric acid is removed by distilled water. The gas emerging from the absorbing vessel is then passed into a bottle so that it displaces an equal volume of water into a graduated 1-litre measuring cylinder.

When the apparatus is assembled the reaction vessel is charged with 5 ml of the appropriate acid chloride, the temperature of the heating tape is adjusted as necessary, and the absorber vessel is charged with a few ml of distilled water. The temperature of the heating block is raised to 150° and gas is passed at a rate of *ca.* 20 ml/min for 3–4 h. A blank analysis is then conducted to establish whether the reagent has been run-in sufficiently (*cf.* Table I.)

Method of analysis using β-Methyl-β-ethylglutarylchloride

The absorber is charged with *ca.* 6 ml of distilled water, and the sample of hydrate contained in a platinum micro-combustion boat is placed into the tube and pushed along into the heating zone whilst the nitrogen flushes out of the tube. The cap is then placed in position and the gas is allowed to flow through the train at a rate of *ca.* 18–22 ml per min. Dehydration of $BaCl_2 \cdot 2H_2O$ is said[9] to begin at 42° and to be complete at 110–120°. Thus the temperature of the heating block is raised quickly to 60° and then to 120° over the next 10 min and finally up to 150° during the last 10 min. At the end of the experiment (*ca.* 500 ml gas passed over 25–30 min) the absorber is detached and its contents are washed out into a conical flask. The hydrochloric acid content is determined by titration with 0·05*N* sodium hydroxide, with neutral red as indicator. The blank analysis is determined by carrying out an identical operation except that an empty platinum boat is used. It is not necessary to carry out a blank determination with each analysis, for the true blank value can be found in each case by correcting the standard blank for the volume of gas passed during a determination. This value is deducted from the appropriate titre.

$$1 \text{ ml } 0{\cdot}05N \text{ NaOH} \equiv 0{\cdot}45 \text{ mg } H_2O.$$

Acknowledgement—We wish to thank Dr. J. H. Thompson for his help and useful discussion during the early stages of this work; and we are indebted to the Austrian Institute for the award of a Fellowship to one of us (L. O.)

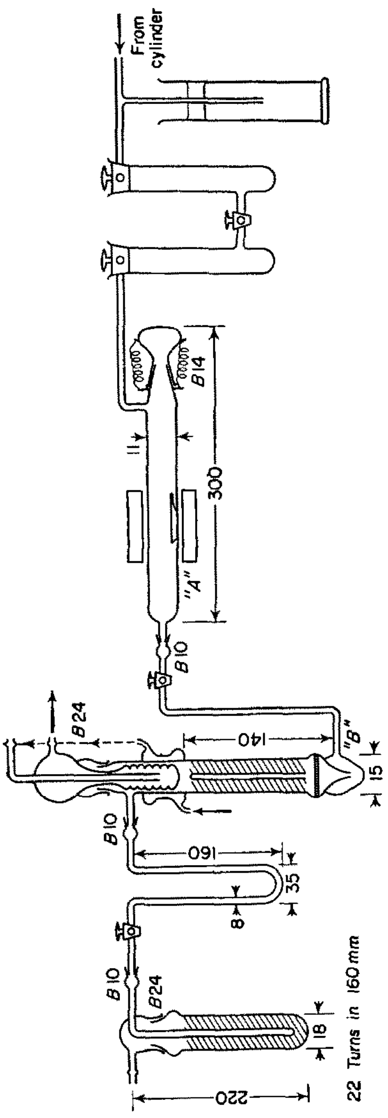

FIG. 1.—Apparatus used for determination of water. A heating tape is wound round the glassware from "A" to "B". All dimensions in mm.

Zusammenfassung—Einige alkylsubstituierte Succinyl- und Glutarylchloride wurden in Hinblick auf ihre Brauchbarkeit zur Bestimmung von wasser untersucht. Besonders studiert wurden Methyl-Äthyl-Glutarylchlorid und Dimethylglutarylchlorid. Die erstere ist mehr zu empfehlen wegen seiner geringeren Flüchtigkeit. Kristallwassergehalte in verschiedenen Hydraten wurde zufriedenstellend bestimmt. Naphthylchlorid und Cyclohexyldiacetyl chlorid wurden ebenfalls untersucht, sind jedoch ungeeignet.

Résumé—Quelques dérivés alkyl substitués de chlorures de succinyl et de glutaryl ont été étudiés comme agents hydrolitiques pour le dosage de l'eau. Les réactifs test sont les chlorures de méthyl éthyl glutaryl et de diméthyl glutaryl; le premier composé est recommandé comme étant moins volatil.

L'eau de cristallisation de certains hydrates a été déterminée d'une façon satisfaisante avec ce réactif.

Les chlorures de naphtalyl et de cyclohexyl-diacétyl ont aussi été étudiés mais ne convenaient pas.

REFERENCES

[1] J. Lindner, *Ber*, 1922, **55**, 2025.
[2] *Idem Z. analyt. Chem*, 1925, **66**, 305.
[3] J. Mitchell and D. M. Smith, *Aquametry*, Interscience Publishers, New York, 1948.
[4] R. Belcher, J. H. Thompson and T. S. West, *Analyt. Chim. Acta*, 1958, **19**, 148.
[5] *Idem*, *ibid.*, 1958, **19**, 309.
[6] A. I. Vogel, *Practical Organic Chemistry*, Longmans Green, 3rd Edition, London, 1956, p. 465.
[7] *Idem*, *ibid.*, p. 876.
[8] F. B. Thole and J. F. Thorpe, *J. Chem. Soc.*, 1911, **99**, 430.
[9] H. B. Baker and G. H. J. Adlam, *ibid.*, 513.

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ESTIMATION OF SMALL AMOUNTS OF AMINES BY MEANS OF CATIONITE PAPER

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Summary—The use of paper with an incorporated cation-exchanger for estimation of microgram amounts of amines is described. Several chain amines and carbocyclic amines have been estimated with an error of 1–3%.

INTRODUCTION

SINCE 1954, when the first report of the making and analytical use of filter paper with incorporated ion-exchangers was submitted,[1] this new chromatographic technique has been utilised for different analytical purposes.[3–16] The first reports[1] had shown the usefulness of such paper, not only for separating, but also for quantitative estimation of inorganic ions. Subsequently, organic ions *e.g.* alkaloids,[12–13] amines, heterocyclic bases, amino acids, amides of carbonic and sulphonic acids, urea and its derivatives were also successfully estimated. In the present paper the use of paper charged with cation-exchanger for estimation of chain amines and carbocyclic amines is considered.

As such paper will have wide applications it would be useful to shorten the term "paper with incorporated ion-exchanger" or "paper charged with ion exchanger". In the present communication the term "ionite paper" is used. To avoid any misunderstanding it is stressed that ionite paper must be distinguished from ion-exchanger paper with chemically changed cellulose fibres (*e.g.* sulphonated, phosphorylated or aminated cellulose fibres).

Ionite paper offers unlimited possibilities for estimation of small amounts of any kind of ionic substance. Ions differing sufficiently in affinity for the ion-exchanger have already been separated and estimated simultaneously on the same strip of ionite paper.[1] Adjacent zones may be determined when the colours of zones belonging to the separated ions are different. In the case of aniline and dimethyl- or diethylaniline, the yellow zone of the *p*-nitrosocompound belonging to the substituted aniline differs distinctly from the violet zone of the diazo compound of aniline with naphthylamine. Components of mixtures of these amines may be easily determined. Promising results were obtained when mixtures of compounds were first separated by partition chromatography on common chromatographic paper (*e.g.* Whatman No. 1) and then the single compounds were transferred to the ionite paper. The 5–10% error arising in direct determinations from partition chromatograms diminished to about 2% when, in addition, ionite paper was used.

EXPERIMENTAL

Ionite paper

The ionite paper[2] and the required phenolsulphonic ion-exchanger were prepared in our Institute. Ionite paper containing about 10% ion-exchanger in hydrogen form was generally used. In some cases less ion-exchanger (2%) was taken. A high percentage shows more brilliant colours but leaves smaller zone areas. Lower contents of ion-exchanger assures a sufficiently great zone area when very small amounts of substances are estimated.

The paper was cut into strips 80 mm long and 10 mm wide.

Reagents

Chemically pure amino compounds were used. The chain amines were estimated from aqueous solutions whilst benzidine was dissolved in 10% ethyl alcohol. The aminobenzoic acids were dissolved in 3 ml of ethyl alcohol and diluted with water to 100 ml. The remaining compounds enumerated in Table I were dissolved in water acidified with an equivalent amount of hydrochloric acid. The actual concentrations during the experiments correspond to the one,- two-, three- and fourfold weight units of amines in 1·0 ml of solution. The weight units are indicated in Table I. Lower amounts, down to 1 μg, were also estimated.

α-Naphthylamine (1% solution in butanol) was used for spraying.

TABLE I. AREA OF ZONE AS A FUNCTION OF AMOUNT OF AMINE

Amine	Value of one weight unit, μg	Zone–area, *mm*^{2}			
		Weight units, 1×	2×	3×	4×
Methylamine	38	28	64	108	150
Dimethylamine	45	61	131	202	270
Triethylamine	91	37	80	124	168
Ethanolamine	127	86	178	265	350
Triethanolamine	185	59	134	211	284
Aniline	34	70	126	187	247
Toluidine	50	57	90	123	152
Phenyldimethylamine	32	67	95	123	152
Phenyldiethylamine	31	75	109	138	170
α-Naphthylamine	78	76	132	184	238
o-Phenylenediamine	50	59	106	160	215
m-Phenylenediamine	50	101	188	278	362
Benzidine	100	61	106	145	192
o-Aminobenzoic Acid	100	149	247	352	442
p-Aminobenzoic Acid	100	106	184	262	340
Phenylhydrazine	93	107	189	270	362
Phenylhydroxylamine	100	94	171	237	307

Note: Different amines have been estimated on papers with different ion-exchange content.

General procedure

For analysis the samples of amine were placed on a spot test plate. On the same plate five standards of various concentrations were also placed. It is essential to use equal volumes (*e.g.* 1·0 ml) of all solutions. The ionite paper strips, joined with narrow (2–3 mm) feeding strips of Whatman No. 1 paper, were hung over the plate in such a way that the ends of the feeding strips dipped into the solutions. The feeding strips were used to diminish the speed of flow and to prevent static equilibrium on the lower end of the ionite paper (when dipped immediately into the solution). A piece of lignin lying on the upper ends of the strips soaked up all surplus liquid which travelled upwards. In a suitable arrangement the solutions may also travel to horizontally mounted ionite paper.[14] In both cases the whole system was enclosed in a glass chamber.

When the solutions had passed the strips, two drops of water or diluted acid of the same pH as the solution were added to wash away the excess of amines resting on the feeding strip and the lower parts of the zones. In order to visualise the zones occupied by amines, convenient reagents were spread on the strips. In all experiments coloured zones with sharp boundaries (Fig. 1) appeared.

After spraying, the strips were dried and the areas of the zones were measured by means of transparent mm-grid paper. As the strips were accurately 10 mm wide it was easy to define the areas with an accuracy of 1 mm^2. The areas of the standards were plotted against micrograms of compounds and the "unknown" was found graphically from the resulting graph. For different series of estimations papers with different contents of ion-exchanger were used. The areas were therefore comparable only within the same series *i.e.* in Table I in respect to one amine.

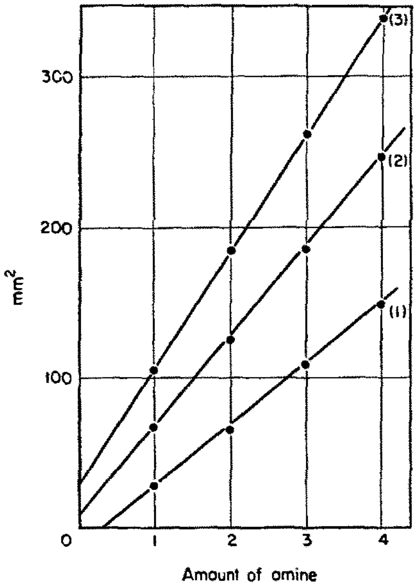

FIG. 2.—Graphs showing the linear dependence between area of zone and amount of amine. 1-Methylamine, 2-Aniline, 3-*p*-Aminobenzoic acid.

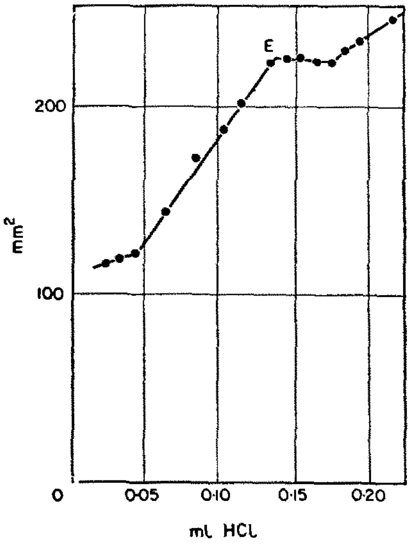

FIG. 3.—Areas of zones of toluidine as a function of added 0·05*M* hydrochloric acid. E—Equivalent point.

RESULTS AND DISCUSSION

Numerous estimations that were performed show, as expected, linear dependence between areas and μg of amines. Fig. 2 presents graphs illustrating this dependence. An error of 1–3% was found.

Ionite paper with less ion-exchanger (about 2%) enables one to estimate about 1 μg of amine with the same error.

In Table 1 one series of several estimations of each amino compound is cited. Chain amines enumerated in this table were estimated in the way just mentioned. The zones were made visible by means of Congo Red. The quantitative evaluation of the zones offers no difficulties.

Most of the aromatic amino compounds were estimated from acidified solutions. Benzidine and *o*- and *p*-aminobenzoic acids were absorbed from acid-free slightly alcoholic solutions. Phenyldimethylaniline and phenyldiethylaniline were rendered visible by means of gaseous nitric oxide which produced coloured *p*-nitroso compounds (brown fading to yellow). *o*-Phenylenediamine and benzidine were located by dipping in a 2% potassium dichromate solution acidified with sulphuric acid. The remaining aromatic compounds were diazotised on the moist strips by gaseous nitric oxide and covered with α-naphthylamine solution. Violet zones appeared.

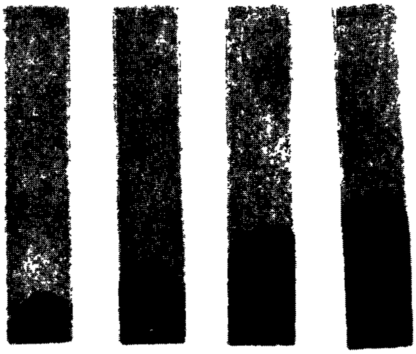

FIG. 1.—Zones of aniline on strips of cationite paper.

The areas of zones are influenced by the relative amounts of aromatic amine and hydrochloric acid. For equivalent amounts, less acid causes the appearance of smaller zones whilst a greater excess of acid causes the formation of larger zones. On graphs where areas are plotted against added acid (Fig. 3), there is a sharp change at the equilibrium point (E). In the presence of a small excess of acid the areas remain constant but grow when much acid is added. It may be mentioned that this behaviour has been utilised in our Institute in so called chromatographic titrations[17] of weak amines. The areas of the zones served as indicator. Details about this will be published elsewhere. Here, this fact must be taken into consideration when unknown concentrations of amines are to be estimated and the usual accuracy is desired.

In the case of estimation of unknown concentrations of weak (*e.g.* aromatic) amines a few equal samples of the unknown were placed in the cavities of a spot test plate and increasing volumes of hydrochloric acid were added. The final volume of the samples was adjusted to 10 ml by means of water. The resulting solutions were taken up by the ionite paper as mentioned above. For quantitative evaluation the zone appropriate to the equivalence point, *i.e.*, which demonstrated the greatest area resulting from increasing amounts of acid, was compared with the standards. Standards were obviously prepared with equivalent amounts of acid. As just quoted, a slight excess of acid causes no significant error.

Zusammenfassung—Die Verwendung von Papier mit einverleibten Jonenaustauschern zur quantitativen Bestimmung von verschiedenen organischen Aminen wird beschrieben. Mikrogrammengen wurden mit 1–3 % Fehler bestimmt.

Résumé—Les auteurs décrivent l'utilisation d'un papier avec échangeur d'ion incorporé pour le dosage des amines organiques. Microgrammes des amines sont dosées avec une erreur de 1–3 %.

REFERENCES

[1] A. Lewandowski and coworkers, *First Polish Chromatographic Symposium*, Krakow, May, 1954.
[2] A. Lewandowski and H. Witkowski, *Pol. Pat.* 38801, 1955.
[3] H. Witkowski, *Roczniki Chem.* 1956, **30**, 549.
[4] A. Lewandowski and J. Ignasiak, *ibid.*, 1956, **30** ,557.
[5] M. Lederer, *Analyt. Chim. Acta*, 1955, **12**, 142.
[6] D. K. Hale, *Chem. and. Ind.*, 1955, 1147.
[7] G. Illing, *Arch. Pharm.*, 1957, **290**, 581.
[8] M. M. Tuckerman, *Analyt. Chem.*, 1958, **30**, 231.
[9] M. M. Tuckerman, R. A. Osteryoung and F. C. Nachod, *Analyt. Chim. Acta*, 1958, **19**, 151.
[10] B. Borkowski and A. Lewandowski, *Przemysl Chem.*, 1957, **13**, 282,
[11] H. Witkowski, *Chem. Analit.*, 1958, **3**, 1049.
[12] *Idem. ibid.*, 1959, **4**, 312.
[13] A. Lewandowski and H. Witkowski *ibid.*, 1959, **4**, 321.
[14] A. Lewandowski, *ibid.*, 1959, **4**, 545.
[15] B. Sansoni, *Naturwiss.*, 1959, **46**, 228.
[16] J. Soboczyńska and W. Wawrzyczek, *Milchwissenschaft*, 1959, **14**, 528.
[17] H. Flood, *Discuss. Faraday Soc.*, 1949, **7**, 190.

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2:5-DIHYDROXY-*p*-BENZOQUINONE AS AN ANALYTICAL REAGENT FOR THE GRAVIMETRIC DETERMINATION OF THORIUM AND ZIRCONIUM

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Summary—2:5-Dihydroxy-*p*-benzoquinone precipitates thorium alone and completely from 1*N* hydrochloric acid solution even in presence of large quantities of cerium^{3+} and cerium^{4+}, lanthanum and uranium. It also precipitates zirconium alone and completely from 1*N* hydrochloric acid solution in presence of titanium^{4+}. The precipitate in each case can be ignited to oxide and weighed.

INTRODUCTION

2:5-DIHYDROXY-*p*-BENZOQUINONE is a yellowish-brown crystalline solid, soluble in alcohol and acetic acid. It is slightly soluble in cold water but appreciably so in hot water, giving a red solution and the colour of the solution changes to yellow at pH lower than 2.5. It is a dibasic acid, $pK_1 = 5.18$, $pK_2 = 2.73$.[1]

2:5-Dihydroxy-*p*-benzoquinone has been stated to give complexes with a large number of cations.[2] The thorium chelate has been shown to contain two dihydroxy-*p*-benzoquinone groups to one thorium.[3] We have now found that Th^{4+} is completely precipitated by this reagent from 1*N* hydrochloric acid solution, whereas Ce^{4+}, Ce^{3+} and La^{3+} are only precipitated at pH 2–3, and $UO_2{}^{2+}$ at pH 7. Th^{4+} can thus be readily separated from Ce^{4+}, Ce^{3+}, La^{3+} and $UO_2{}^{2+}$. Zr^{4+} is precipitated alone and completely by this reagent from 1*N* hydrochloric acid solution even in presence of $Ti.^{4+}$ The Th^{4+} and Zr^{4+} chelates on ignition give the corresponding oxides. Sulphate ions do not interfere in the above determinations.

For the determination of thorium and its separation from rare-earths (except Ce^{4+}) and from uranium, *m*-nitrobenzoic acid,[4] ferron,[5] tetrachlorophthalic acid,[6] and benzoic acid[7] have been used. 1-Hydroxy-3-methoxyxanthone separates thorium from a ten-fold excess of cerite earths and a five-fold excess of cerium^{4+} and uranium.[8] We have found that 2:5-dihydroxy-*p*-benzoquinone completely precipitates thorium even in the presence of fifteen times its weight of cerium^{3+}, lanthanum and uranium.

Propylarsonic acid[9] and mandelic acid[10] have been used for the determination of zirconium and for its separation from titanium. We have now found that 2:5-dihydroxy-*p*-benzoquinone completely precipitates zirconium even in the presence of ten times its weight of titanium.

EXPERIMENTAL

All reagents used were of A.R. quality.

2:5-Dihydroxy-*p*-benzoquinone was prepared by the oxidation of hydroquinone with hydrogen peroxide in the presence of sodium hydroxide.[11] The sodium salt of 2:5-dihydroxy-*p*-benzoquinone so formed was converted into the reagent by treatment with concentrated hydrochloric acid at 10°.

Procedure for the determination of thorium

One hundred and fifty ml of a solution containing 50 mg of thorium is treated with about 0·4 g of the solid reagent or its aqueous solution. The resultant solution is boiled for 1–2 min, cooled to room temperature and filtered through Whatman No. 40 filter paper. The precipitate is washed with 0·2% aqueous solution of the reagent, dried and ignited at 900° to the oxide. The results obtained from a standard solution of thorium nitrate by this method are shown in Table I.

TABLE I

ThO_2 taken, *mg* (Oxine method)	53·6	53·6	48·6	48·6	9·8	9·8
ThO_2 found, *mg*	53·6	53·6	48·6	48·6	9·8	9·8

Properties of the thorium chelate

The chelate is violet in colour; it is slightly soluble in water, dilute alcohol and dilute acetic acid. It is slimy at pH higher than 0.5 and crystalline at lower pH.

Effect of pH *on the precipitation of thorium*

The pH of the thorium solution was adjusted by adding various amounts of dilute hydrochloric acid. Thorium was then precipitated from the solution as described above. The results are recorded in Table II.

TABLE II

ThO_2 taken, *mg* (Oxine method)	53·6					
ThO_2 found, *mg*	53·6	53·6	53·6	53·6	53·6	53·6
pH	3	2	1	0·5	1*N* HCl	2*N* HCl

Precipitation of cerium^{4+} and the effect of pH on its precipitation

The procedure employed is the same as described for thorium. Cerium^{4+} is completely precipitated by this reagent at pH 3; at lower pH the precipitation is incomplete (Table III).

TABLE III

CeO_2 taken, *mg* (Oxine method)	17·6		
CeO_2 found, *mg*	17·6	15·1	1·6
pH	3	2	1

Properties of the cerium^{4+} chelate

The properties of the cerium^{4+} chelate are similar to those described for the thorium chelate.

Separation of thorium from cerium^{4+}, cerium^{3+}, lanthanum^{3+} and uranyl

After the addition of different amounts of cerium^{4+}, cerium^{3+}, lanthanum and uranyl salts to a thorium salt solution, its acidity was adjusted to 1*N* with hydrochloric acid and thorium precipitated as described above. The precipitate was then washed with about 200 ml of 0·2% solution of the reagent which had been made 1*N* with HCl. The results obtained are given in Table IV.

TABLE IV.

ThO$_2$ taken, *mg* (Oxine method)			48·6				
CeO$_2$ added (as Ce^{4+}), *mg*	ThO$_2$ found, *mg*	CeO$_2$ added (as Ce^{3+}), *mg*	ThO$_2$ found, *mg*	La$_2$O$_3$ added, *mg*	ThO$_2$ found, *mg*	U$_3$O$_8$ added, *mg*	ThO$_2$ found, *mg*
50	48·6	50	48·6	50	48·6	50	48·6
100	48·6	100	48·6	100	48·6	100	48·6
250	48·4	250	48·6	250	48·6	250	48·6
500	48·8	500	48·6	500	48·6	500	48·6
750	48·6	740	48·8	750	48·4	750	48·4

TABLE V.

ZrO$_2$ taken, *mg* (Oxine method)	38·4	38·4	35·0	35·0	9·6	9·6
ZrO$_2$ found, *mg*	38·4	38·4	35·0	35·0	9·6	9·6

TABLE VI.

ZrO$_2$ taken, *mg* (Oxine method)	35·0					
ZrO$_2$ found, *mg*	35·0	35·0	35·0	35·0	35·0	35·0
pH	3	2	1	0.5	1*N* HCl	2*N* HCl

TABLE VII.

ZrO$_2$ taken, *mg* (Oxine method)	35·0
TiO$_2$ added, *mg*	ZrO$_2$ obtained, *mg*
21·6	35·0
43·2	35·0
108·0	35·0
216·0	34·8
324·0	34·8

Precipitation of zirconium and the effect of pH *on the precipitation*

The procedure employed is the same as described for thorium. The results are presented in Tables V and VI.

Properties of the zirconium chelate

The properties of the zirconium chelate are similar to those described for the thorium chelate.

Separation of zirconium from titanium

After the addition of different amounts of titanium^{4+} solution to the zirconium solution, the acidity of the solution is adjusted to 1*N* hydrochloric acid and zirconium precipitated as described above. The precipitate is washed with about 200 ml of 0·2% solution of the reagent which has been made 1*N* with hydrochloric acid. The results are shown in Table VII.

Iron^{3+} interferes in the determination of zirconium by this method and must be absent.

Acknowledgements—Our thanks are due to Prof. T. R. Seshadri, F.R.S. for his keen interest and helpful discussions and to the Atomic Energy Commission, Government of India, for sponsoring a research scheme under which this investigation was carried out.

Zusammenfassung—2:5 dioxy-p-benzochinon fällt Thorium allein und vollständig aus 1N HCl selbst in Gegenwart grosser Mengen von Cer(III) und Cer(IV), La(III) und UO_2(II). Das Reagens fällt auch Zirkonium allein und vollständig aus 1*N* HCl Lösung neben Titan(IV). Die Niederschläge können in beiden Fällen versucht und die Oxyde gewogen werden.

Résumé—La 2,5 dihydroxy-p-benzoquinone précipite le thorium seul et complétement en solution HCl N, même en présence de grandes quantités de cérium III et cérium IV, La(III) et UO_2(II). Elle précipite aussi le zirconium seul et completement en solution HCl *N* en présence de titane IV. Dans chaque cas, le précipité peut être calcine jusqu'a obtention de l'oxyde et pesé.

REFERENCES

[1] G. Schwarzenbach and H. Suter, *Helv. Chim. Acta*, 1941, **24**, 617–38.
[2] R. L. Frank, G. R. Clark and J. N. Coker, *J. Amer. Chem. Soc.*, 1950, **72**, 1827.
[3] T. Moeller and E. H. Kobisk, *ibid.*, 1950, **72**, 2777.
[4] G. H. Osborn, Analyst, 1948, **73**, 381.
[5] D. E. Ryan, W. J. McDonnell and F. E. Beamish, *Analyt. Chem.*, 1947, **19**, 416–17.
[6] L. Gordon, C. H. Vanselow and H. H. Willard, *Analyt. Chem.*, 1949, **21**, 1323.
[7] M. Venkataramaiah, C. L. Rao and B. S. V. R. Rao, *J. Sci. Ind. Res., India*, 1951, **10B**, 254–55. *Idem*, *Analyst*, 1952, **77**, 103-5.
[8] G. M. Saxena and T. R. Seshadri, *Proc. Ind. Acad. Sci.*, 1958, **47A**, 238.
[9] F. W. Arnold, Jr., and G. C. Chandlee, *J. Amer. Chem. Soc.*, 1935, **57**, 8.
[10] C. A. Kumins, *Analyt. Chem.*, 1947, **19**, 376.
[11] R. G. Jones and H. A. Shonle, *J. Amer. Chem. Soc.*, 1945, **67**, 1034.

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CALCEIN BLUE—A NEW METALFLUORECHROMIC INDICATOR FOR CHELATOMETRIC TITRATIONS

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Summary—A new metal fluorechromic indicator is described for the chelatometric titration of metal ions. Calcein Blue (a condensation product of 4-methylumbelliferone, formaldehyde, and iminodiacetic acid) may be used for the chelatometric determination of metal ions which form highly coloured complexes with chelatometric reagents. A procedure based on reaction rates is given for the determination of nickel and chromium in mixtures without prior separations. Calcein Blue serves as an indicator for the direct titration of the alkaline earth elements as the result of the formation of an indicator-reversal complex.

THE colour of the complexes of EDTA with elements such as copper, cobalt, chromium, etc., has caused considerable difficulty in chelatometric titrations. The use of conventional and visual indicators is limited to solutions containing only a few milligrams of elements which form highly coloured complexes. The introduction of Calcein and Calcein W as metalfluorechromic indicators has eliminated much of the difficulty previously encountered with these elements.[2-4] An extensive study of metalfluorechromic indicators has led to the preparation of many new indicators similar to Calcein W. This paper deals with some applications of a new indicator, Calcein Blue,* which is a condensation product of 4-methylumbelliferone, formaldehyde and iminodiacetic acid. Although the metalfluorechromic properties of Calcein Blue and Calcein W are very similar, the former is a superior indicator for chelatometric titrations. Calcein Blue exhibits its maximum fluorescence when activated by a wavelength of 370 mμ (in alkaline solution) and 330 $m\mu$ (in acid solution), whereas Calcein W exhibits its maximum fluorescence when activated with light of much longer wavelengths. Since most sources of ultraviolet light exhibit a maximum output of radiation at 366 mμ or 250 mμ it can readily be seen that Calcein Blue, in alkaline solutions, approaches the ultimate in matching the maximum output of the ultraviolet source with the wavelength of maximum activation of fluorescence. This fortuitous circumstance leads to a much more sensitive indicator for titrations under ultraviolet radiation. The parent compound (4-methylumbelliferone) is an acid-base indicator of the coumarin series. The addition of a chelating functional group that is *ortho* to the phenolic oxygen imparts metafluorechromic properties to the resulting indicators. Calcein Blue exhibits a brilliant blue fluorescence (445 mμ) up to a pH of 11. The addition of copper ions to a solution of the free indicator at a pH from 4 to 10 results in the quenching of the blue fluorescence. Palladium also quenches the fluorescence over the pH range of 4 to 10, but the reaction is too slow to be of use in chelatometric titrations. Manganese, nickel and cobalt also quench the fluorescence of Calcein Blue, but this reaction is confined to the alkaline region in which the free indicator fluoresces.

If the pH of a solution containing Calcein Blue is raised above 12, the free indicator

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* G. Frederick Smith Chemical Co., Columbus, Ohio.

no longer fluoresces. The addition of calcium, barium or strontium ions to this solution results in the formation of a complex with the indicator which does fluoresce. It should be noted that this indicator complex exhibits the "acid colour" of the free indicator.[5] This phenomenon has been referred to as the formation of an indicator-reversal complex. The titration of metal ions which form highly coloured complexes with chelating agents is most conveniently carried out by adding a standard excess of the chelating agent and performing a back-titration with a standard copper solution. In this manner, macro amounts of nickel, cobalt, copper, iron and titanium (in the presence of peroxide), as well as elements which do not form highly coloured complexes such as aluminium, manganese, zinc and mercury, can be carried out with a single standard solution. The selection of an appropriate pH for the back-titration can be derived from pY-pH curves for the chelating agent in question.[1] Back-titrations with a standard copper solution are carried out by adding an excess of an appropriate chelating agent, for example, trien, EDTA or tetraethylenepentamine to a solution of the metal ion to be determined. The pH is then adjusted, a few drops of a 0.1% solution of Calcein Blue added, and the solution back titrated with a standard solution of copper to the quenching of the blue fluorescence of the free indicator.

METHODS

The determination of nickel and chromium mixtures

To an acid solution of nickel and chromium add a measured excess of EDTA over that which would be necessary to complex the nickel present in the solution. Dilute to 100–150 ml with water, add 10 ml of a sodium acetate-acetic acid buffer (pH approximately 4.8) and 2–3 drops of the indicator solution. Back-titrate the excess of EDTA with a standard copper solution to the quenching of the blue fluorescence of the free indicator. To the solution in which the nickel was just titrated add a measured excess of EDTA over that which would be necessary to complex the chromium present in the solution. Place the beaker on a hot plate and boil for 10–15 minutes in order to form the chromium–EDTA complex. Back-titrate the excess EDTA with a standard copper solution to the quenching of the blue fluorescence of the free indicator. Both titrations should be done with ultraviolet light as the sole source of illumination. From the two back titrations calculate the mg of nickel and chromium present.

The determination of calcium, strontium and barium

In the determination of these elements use is made of the formation of an indicator-reversal complex. To a solution containing calcium, barium or strontium, add a few drops of a 0.1% solution of Calcein Blue, adjust the pH to a value of 13–14 (in the case of strontium add a two-fold excess of potassium tartrate) and titrate the solution with standard EDTA. The end-point is characterised by the quenching of the fluorescence due to the alkaline earth-indicator complex.

DISCUSSION

The determination of nickel and chromium in mixtures without prior separation is based on the slow reaction rate for the formation of a chromium–EDTA complex. The solution containing the nickel and chromium should be maintained near room temperature until after the nickel determination is completed. The titration should be completed shortly after the addition of EDTA for the nickel determinations, since a long period of standing, even at room temperature, could lead to the formation of the chromium–EDTA complex or to the precipitation of chromium.

Other binary mixtures in which one of the ions to be determined is chromium^{III} may be analysed by the procedure given here for nickel-chromium mixtures. The criteria for the determination are that the second element must react with EDTA at room temperature, and must form a complex which can be back-titrated with a standard copper solution at a pH of 4.8.

In the determination of calcium, strontium and barium, the pH may be adjusted by the addition of a $1M$ solution of potassium hydroxide or by the addition of pellets of potassium hydroxide. In either case, one should use a low-carbonate potassium hydroxide, such as reagent grade potassium hydroxide, which contains approximately 2% potassium carbonate. The presence of an excessive amount of carbonate leads to a residual fluorescence after the end-point in the titration. The continued use over a period of several months of a large stock bottle of $1M$ potassium hydroxide or of potassium hydroxide pellets can lead to a selection of an excessive amount of carbonate, causing a gradual deterioration of the end-point. This can easily be avoided by maintaining a small stock bottle of alkali for daily use. In this manner the supply of alkali is consumed before an excessive amount of carbonate is accumulated. Potassium hydroxide is superior to sodium hydroxide for the adjustment of the pH in the determination of the alkaline earths. The use of sodium hydroxide leads to a high residual fluorescence after the end-point—an indication that sodium also forms a weak indicator-reversal complex.

Zinc, as well as some other elements which form indicator-reversal complexes, may also be determined by the procedure given for the alkaline earths. These elements, however, are conveniently determined by back-titration with a standard copper solution.

Zusammenfassung—Ein neuer metallfluorochromer Indicator zur chelometrischen Bestimmung von Metallionen wird beschrieben. "Calceinblau" (ein Kondensationsprodukt von 4-Methylumbelliferon, Formaldehyd und Iminodiessigsäure) kann für die chelometrische Bestimmung auch solcher Metallionen verwendet werden die mit dem chelometrischen Reagens stark gefärbte Komplexe bilden. Eine Vorschrift zur Bestimmung von Nickel und Chrom in einer Lösung ohne vorhergehende Trennung wird beschrieben. Das Verfahren beruht auf der Verschiedenheit der Reaktionsgeschwindigkeit beider Metalle bei der Komplexbildung. Calceinblau dient auch als indicator bei der direkten Titration von alkalischen Erden.

Résumé—L'auteur décrit un nouvel indicateur métallique fluorochromique pour le dosage des ions métalliques par complexométrie. Le bleu de calcéine (un produit de condensation de 4 méthyl ombelliferone, de formaldéhyde et d'acide iminodiacétique) peut être utilisé pour le dosage complexométrique d'ions métalliques qui forment des complexes fortement colorés avec les réactifs complexants.

Une méthode basée sur les vitesses de réaction est donnée pour le dosage de mélanges de nickel et de chrome sans séparations préalables. Le bleu de calcéine sert d'indicateur pour le dosage direct des alcalino-terreux, étant donnée la formation d'un complexe réversible de l'indicateur.

REFERENCES

[1] C. N. Reilley and R. W. Schmid, *Analyt. Chem.* 1959, **31**, 887.
[2] D. H. Wilkins, *Analyt. Chim. Acta*, 1959, **20**, 324.
[3] *Idem*, *Talanta*, 1959, **2**, 12.
[4] *Idem*, *ibid.*, 201.
[5] *Idem*, *ibid.*, 277.

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A NEW GENERAL PROCEDURE IN THE LOW-TEMPERATURE WET OXIDATION OF ORGANIC COMPOSITIONS

PERCHLORIC AND PERIODIC ACIDS AS OXIDANTS "THE PERIODIC ACID LIQUID FIRE REACTION"

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Summary—The substitution of periodic acid for nitric acid in the much employed "liquid fire reaction" for destructive oxidation of organic compositions is described. The advantages attained are extended general applicability, low temperature requirements, and the noteworthy reactivity of periodic acid in downgrading heavy, complex organic molecules to fragments more readily soluble in perchloric acid used as companion reagent. These fragments are more easily oxidised by 66 to 69 or 70% strengths of this acid. The reactions described cover organic compositions which are essentially cellulose, sugars and proteins. Coal, leather, polymerised products and other commercially important products may be readily oxidised. The reactions involved are hazard free.

INTRODUCTION

PERCHLORIC acid is the most adaptable oxidant in general use for the wet oxidation of organic compositions. With added nitric acid, these combined oxidants serve to constitute the "liquid fire reaction."[1] These mixed reactants are of extensive general applicability. Mixtures of sulphuric and perchloric acids have also been employed.[2,3] The highest oxidation potentials available are thus provided. A wide variety of wet oxidations result from the individual use of perchloric acid.[4] For such reactions the perchloric acid is employed at controlled concentrations and temperatures.

In all these wet oxidation procedures, conditions are defined, and suitable apparatus has been designed, to ensure hazard-free reaction kinetics.

Employing periodic acid in preferential applications, as a substitute for nitric acid, has marked advantages. This modification effects improvements in extensive general applicability. Lower reaction temperatures may be employed. Periodic acid serves not only as oxidant, but contributes to the ready fragmentation of large molecular species, by degradation, to smaller organic entities. The effective oxidation potentials cover the range 1.6 to 2.0 V. The present contribution describes the new procedure, designated "the periodic acid liquid fire reaction."

REACTIONS INVOLVED

The following reactions are fairly well established and appear to apply concurrently in the reaction mixture:

1. $2H_5IO_6 + (HClO_4 + \Delta) = 2HIO_3 + O_2 + 4H_2O$
2. $4HIO_3 + (HClO_4 + \Delta) = 2I_2 + 5O_2 + 2H_2O$

3. $HIO_3 + 2I_2 + 5HClO_4 = 5IClO_4 + 3H_2O$
4. $4HClO_4 + \Delta = 2Cl_2 + 7O_2 + 2H_2O$
5. $4IClO_4 + 2Cl_2 + 3O_2 + 6H_2O = 4HIO_3 + 4HCl + 4HClO_4$

The effective degradation of the large complex molecules of organic compositions by periodic acid, to form fragmentation products of lesser molecular weight, is of major importance to the reaction mechanism. Such reactions are extensively applied in a wide variety of reactions of practical analytical determinations and studies of related structural significance. The extent to which these reaction types contribute to the wet oxidation reactions being described, is not well established. The reactions in strong perchloric acid, at moderately elevated temperatures (150–200°), are undoubtedly much more extensive and complicated than those which apply in neutral or moderately acid solutions. Evidence will be submitted which demonstrates the reality and extent of the periodic acid fragmentation reactions which contribute effectiveness to the periodic acid liquid fire reactions.

In the reactions stated above the oxidants simultaneously operative are periodic, iodic and perchloric acids, iodine and iodine perchlorate, oxygen and chlorine.

Reaction (1), the thermal dissociation of periodic acid in hot concentrated perchloric acid, is relatively slow. Tests in boiling 70 % perchloric acid indicate that 3 to 5 min are required. In lesser strength acid, a longer interval is required. In the wet oxidation mixture, therefore, the periodic acid is available for a sufficient period to provide both for fragmentation and oxidation.

Reactions (2) and (3) occur simultaneously at low temperature (40–70°), in the presence of organic matter dispersed in concentrated (60–70 %) perchloric acid. These reactions are markedly exothermic. Perchloric acid concentrations should be selected which minimise reaction (2) to such rates that reaction (3) keeps pace with reaction (2). Both iodine and iodine perchlorate may be evolved. They may be retained by the use of a reaction apparatus of the vapour refluxing principle.

Reaction (4) increases in rate as the perchloric acid concentration is augmented from 60 to 72.5 % and at its boiling point.

Reaction (5) is slow, but intensifies with increases under the same conditions as reaction (4). Iodine is oxidised to iodic acid, following the intermediate formation of iodine perchlorate, under the same conditions. Total destruction of organic matter often occurs before reactions (4) and (5) have become jointly complete.

The standard reduction potential of the periodic-iodic acid couple[5]

$$H_5IO_6 + H^+ + 2e^- = IO_3^- + 3H_2O$$

has been estimated to be 1.6 V. The oxidising power of perchloric acid depends upon its concentration and temperature. Exact measurements of its reduction potential have not, and perhaps cannot, be made. Even the exact nature of the reduction products is not known with certainty. On the basis of its effects at different concentrations approximate values can be assigned. Thus, since in 58 to 60 % perchloric acid[3] at 150° to 160° ferrous iron is oxidised to ferric, the potential is estimated to be 0.8 V. For progressively increasing concentrations, from 60 to 72.5 %, the boiling temperature increases in almost direct proportion (to 203° at 760 mm for the 72.5 % water-perchloric acid azeotrope), and the oxidising power rises markedly and approximately in direct proportion, reaching an estimated value of 2.0 V.

In the periodic acid-perchloric acid mixture, the former brings about the initial reaction in oxidation of organic compositions at moderate temperature and with controlled intensity. Fragmentation of organic compositions by periodic acid is well known. It reacts rapidly upon organic material bearing hydroxyl or amino groups on adjacent carbon atoms, aldehydes and ketones being assumed to be hydrated. Degradation products, formic acid and probably oxalic acid among other simple formulations, are then readily oxidised to carbon dioxide through the medium of hot concentrated perchloric acid.

Fragmentation is more extensive in the reactions at hand owing to the presence of concentrated perchloric acid. As the temperature increases following initiation of oxidation by periodic acid, which is exothermic, the perchloric acid provides more extensive fragmentation before final conversion of carbon to carbon dioxide. The perchloric acid has an additional function. It effects dissolution of organic matter of a wide range of structures, both in hot or cold concentrated acid, without being accompanied by char formation. The periodic acid liquid fire reactions are thus seen to have many unusually effective reaction advantages.

EXPERIMENTAL

Reagents

Periodic acid: Colourless, crystalline, non-hygroscopic, reagent grade para-periodic acid, H_5IO_6. Free adsorbed water, at 85°, not more than 0.3 %. Non-volatile after ignition, not more than 0.01 %. Assay 99·98 %. Sulphate and heavy metal free. Commercially available.

Perchloric acid: Reagent grade vacuum distilled. Assay 66.0, 68.0, 70, and 72 %. Non-volatile matter, as sulphate, not in excess of 0.003 %. Sulphate, chloride phosphate and iron free. Intermediate concentrations are obtained by blending. Commercially available.

Vanadium: Used in mg amounts as catalyst. NH_4VO_3 or V_2O_5, reagent grade.

Apparatus

The most suitable apparatus has been previously described and its design designated by line drawings.[1,2,3,4] The Bethge apparatus serves best for general use. The apparatus employed in the liquid fire reactions may serve for many applications of the new periodic acid liquid fire reaction, for example in the determination of heavy metal trace elements in the wet ash residue. Vycor reaction flasks are preferable but Pyrex glass may be substituted. The Bethge apparatus provides for reflux retention of volatile products. This maintains a fixed concentration of the original perchloric acid employed. The complete retention of volatilised spray formation is assured. By use of the three-way stopcock of the Bethge apparatus, an increase in the concentration of perchloric acid wet ash residue is made operative.

Oxidation of cellulose

To 1.0 g of cellulose, in the 250-ml conical flask of the Bethge apparatus, was added 15.0 ml of 68 % perchloric acid and 1.5 g of para-periodic acid. The mixture (both reactants cellulose and periodic acid, being soluble in the perchloric acid) was heated gently to initiate the reaction, which began at 40 to 50°. The reaction was markedly exothermic and, in 15 to 20 sec after initiation, the temperature rose to 100 to 110° without further heating. Heat was again applied and the oxidation of the cellulose was complete in 2 to 5 min. Continued heating to the boiling point completed the conversion of the iodine perchlorate formed to iodic acid. The latter operation is favoured by cutting off the return of condensate. The course of the temperature during the operation is shown graphically in Fig. 1.

Oxidation of wool

Wool yarn was subjected to the periodic-perchloric acid treatment under the same conditions given above for cellulose. Wool is not measurably attacked by concentrated perchloric acid when cold, but it is dissolved when the acid is heated. The initial reaction is exothermic, but to a lesser degree than with cellulose. Little or no iodine was evolved. Oxidation was complete in 5 min, the final temperature being 170°. The course of the reaction temperature effects is shown in Fig. 2.

Oxidation of sucrose

Cane sugar is soluble, without charring, in concentrated perchloric acid. Its oxidation under conditions identical with those given above for cellulose followed. The reaction began at about 40° and was markedly exothermic. Iodine was liberated, then oxidised to iodine perchlorate. Oxidation was complete in 5 to 6 min, the final temperature being 190°, with most of the time taken to effect oxidation of the iodine perchlorate to iodic acid. The results are shown graphically in Fig. 3.

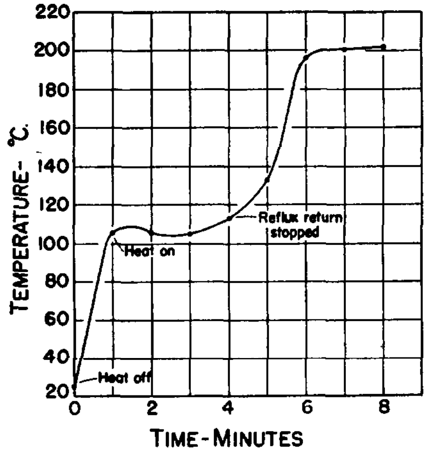

FIG. 1.—Cellulose oxidation.

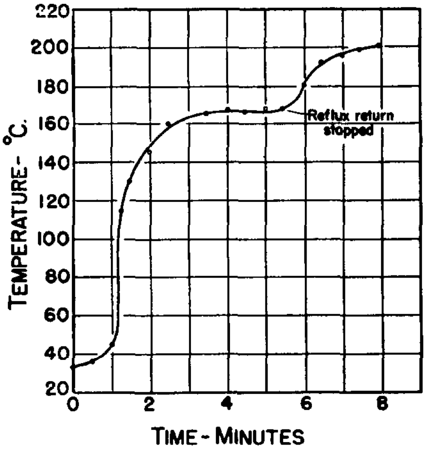

FIG. 2.—Wool oxidation.

Oxidation of vegetable and chrome tanned leather

Vegetable tanned leather was treated in duplication of conditions given for the oxidation of cellulose. The initial reaction occurred at approximately 40° and the reaction was complete in 14 to 15 min, the final temperature being 175°. In the initial reaction considerable iodine was formed, soon to be converted to iodine perchlorate. The results are shown in Fig. 4. Chrome tanned leather is often fortified by incorporation of such additives as paraffin and barium sulphate. The presence of 3 to 6% of chromium in the tanning process also increases the difficulty in its wet oxidation. The same method of attack was applied to a sample of such type chrome tanned leather as that applied to vegetable tanned leather, except that 2 mg of vanadium was added as catalyst. At the initial reaction temperature, 50°, the temperature rose rapidly to 150° in 4 min. At 5 min the solution of wet ash acids has a green colour, with considerable turbidity, and oxidation was essentially complete with the flask walls coated with paraffin still unoxidised. After 9 min the reflux was cut off and at 13 min and at 198° the reaction mixture was orange coloured from dissolved chromic acid, indicating complete removal of organic matter. The boiling wet ash solution was clear but, upon cooling, a precipitate of barium sulphate was present.

Wet oxidation of various types of coal

The wet oxidation of soft coal[2] (high and low V.C.M.) has recently been described. The major objective of the present study was to provide conditions of wet oxidation suited to the subsequent determination of arsenic. It was postulated that the periodic acid liquid fire reaction would provide more suitable reaction conditions than in the previously cited method. This was found to be the case. In the previous study, the wet oxidation procedure developed the condition that the volatile combustible matter of coal was evolved as in the case of the regularly applied V.C.M. determination in the standard (proximate analysis) analytical routine. By the use of the present procedure the volatile combustible matter in coal is oxidised rather than volatilised. In addition, the presence of periodic and iodic acids, as well as iodine perchlorate, ensures more favourable conditions for retention of arsenic in the wet ash residue.

Coal samples of all types may be boiled in contact with 70% perchloric acid for periods of 1 to 3 h before complete oxidation results. The presence of a few mg of chromium shortens the required boiling period to 30 min. The addition of 1 or 2 mg of vanadium in place of chromium catalytically shortens the required boiling period to 15 min. The reaction mechanism accounting for this valuable catalyst influence has been previously described.[1]

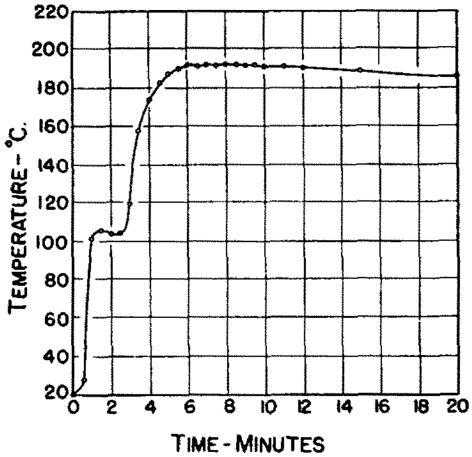

Fig. 3.—Sucrose oxidation.

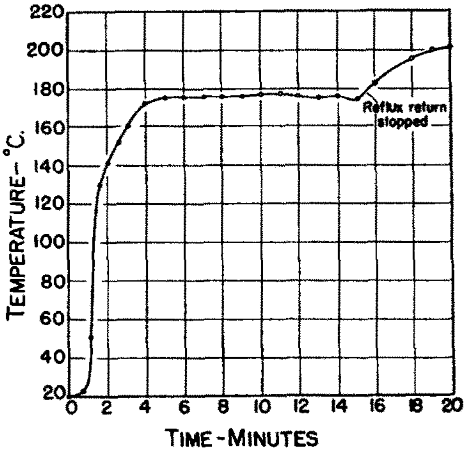

Fig. 4.—Vegetable-tanned leather oxidation.

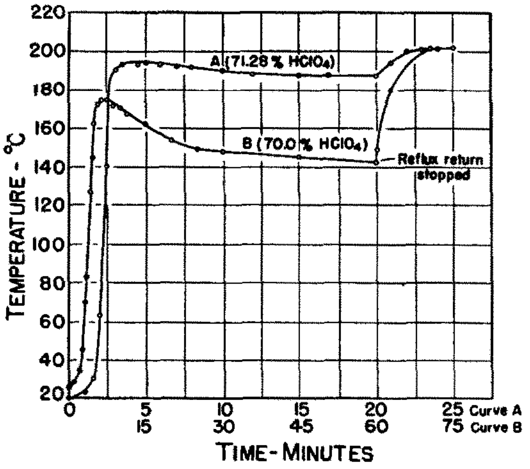

Fig. 5.—Anthracite coal oxidation.

The time required for the oxidation of coal by the new procedure varies to a large extent with the initial concentration of perchloric acid. Thus, for anthracite (see Fig. 5), a 1 h digestion was required using 70·0% perchloric acid concentration, but only 20 min using 71·28% concentration. With either concentration of perchloric acid, the initial reaction set in at 30 to 40° and was exothermic. For the lower acid concentration the formation of iodine perchlorate was very pronounced; at the higher concentration little was formed and its conversion to iodic acid was rapid. The results for the oxidation of anthracite coal are shown graphically in Fig. 5.

Soft coals containing a moderate amount of volatile combustible matter, such as Pocahontas coal, require less concentrated perchloric acid for their rapid oxidation. Considerable foam, a layer 25 to 40 mm thick, was formed but did not interfere. Relatively little iodine was formed. Starting with

69.5% perchloric acid, the reaction was practically complete in 5 min and assuredly complete in 10 min at 200°; with 69%, the time was about doubled. The results are shown in Fig. 6.

Bituminous coal containing high volatile combustible matter, such as the Orient coal of Southern Illinois, was oxidised expeditiously with high initial concentrations of perchloric acid, 70.0 and 71.28%. Considerable foam, a layer of approximately 50 mm thick, was present during the early stages of the reaction. Some iodine was formed in the 70% perchloric acid digestion but little or none in the 71·28% mixture. The effect of the initial acid concentration on the time required is shown in Fig. 7.

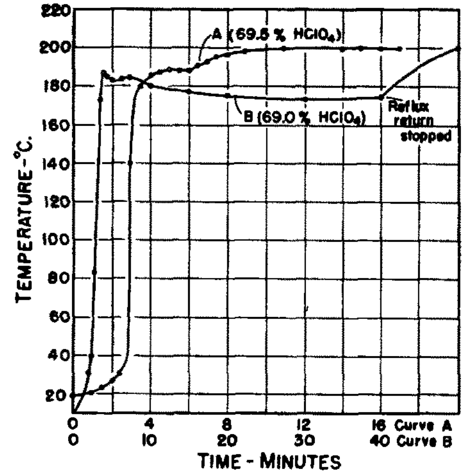

FIG. 6.—Pocahontas coal oxidation.

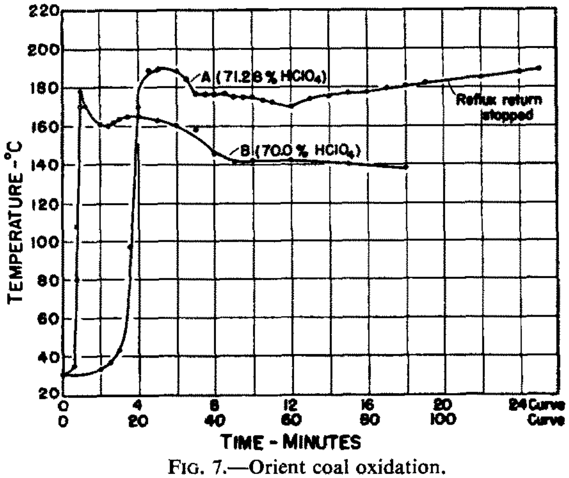

FIG. 7.—Orient coal oxidation.

As was expected, the ash remaining following the periodic-perchloric acid digestion of coal was less than that obtained by dry ashing: Pocahontas 6·83 and 9.72%, respectively; Orient coal 4.60 and 7.50%, respectively.

Oxidation of adipic acid

Because of the use of adipic acid in Nylon synthesis its wet oxidation was studied. The Bethge apparatus reactants were: 1.0 g of adipic acid, 15.0 ml of 65.5% perchloric acid, 1.5 g of para-periodic acid, both with and without vanadium. The results were as follows:

1. Without vanadium, the reaction was smooth and complete in 10 min. The maximum temperature was 162°. The evolution of iodine was excessive for best conditions.

2. With 1.0 mg of vanadium added, the reaction was smooth, more rapid and the evolution of iodine retarded in favour of iodine perchlorate. The oxidation was complete in 8 min at a maximum temperature of 159°.

3. With 2.0 mg of vanadium added, the best conditions were attained. The reaction was complete in 6 min and the maximum temperature was 157°.

The last of these conditions was applied to the oxidation of Nylon with the exception that the perchloric acid concentration was augmented.

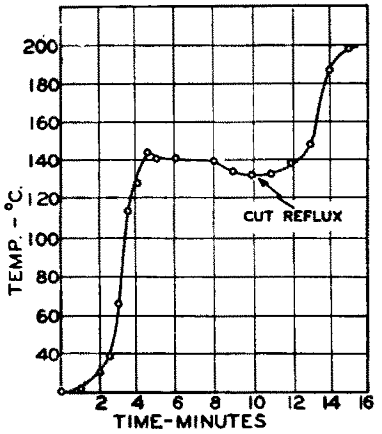

Fig. 8.—Nylon oxidation.

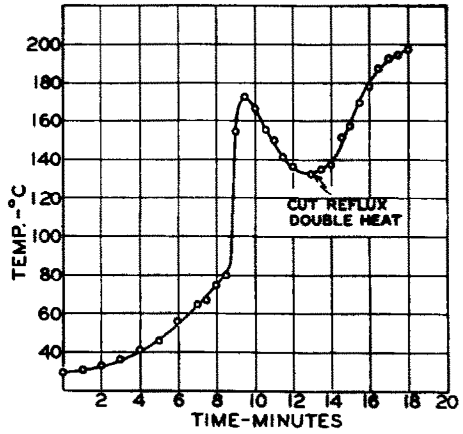

Fig. 9.—Methyl methacrylate oxidation.

Oxidation of nylon

For Nylon oxidation (polymerised adipic acid and hexamethylenediamine), the use of 69.5% perchloric acid was found to favour iodine perchlorate formation with little iodine. The data for this oxidation is given in Fig. 8. Nylon is seen to be completely oxidised at a maximum temperature of 145°. The ashed acid residue, upon cooling, deposited ammonium perchlorate. The wet ash was soluble in water, except for its titanium dioxide additive.

Oxidation of uric acid

Uric acid was investigated as an organic type involving heterocyclic ring nitrogen structure. Also, because it is a component of urine and of many types of faecal matter. One gram of uric acid with 1.5 g of periodic acid, 15.0 ml of 65.5% perchloric acid and 2 mg of vanadium, was digested in the Bethge apparatus. The initial exothermic reaction was at 45–50°, evolving a modest amount of iodine, followed by iodine perchlorate. Reaction was complete after 5 to 6 min at a maximum temperature of 150°. The cold wet ash residue deposited ammonium perchlorate and was completely soluble upon dilution with water.

Oxidation of methyl methacrylate or methyl methacrylate polymer P-1 and lucite

Methyl methacrylate is miscible with 68.5% perchloric acid. It is smoothly oxidised by the use of the periodic acid liquid fire reaction. Low temperature treatment retards foam formation. Vanadium, as catalyst, is effective. One gram samples were oxidised in 15 ml of perchloric acid in 17 min without vanadium. Ten minutes were required with 2 mg of catalyst. 1.5 g of para-periodic acid constitutes a generous excess. The polymer of methyl methacrylate, du Pont P-1, in the presence of vanadium, was similarly oxidised in 16 to 17 min. Lucite was similarly oxidised in the same time interval. The production of iodine perchlorate as the reduction product of periodic acid predominated. At a lesser perchloric acid concentration iodine was formed initially. The oxidation of polymerised methyl methacrylate is shown in Fig. 9.

As shown in Fig. 9 reaction is initiated exothermally at 80°. It would appear that, in all these reactions, the oxidation follows the same course as for methyl methacrylate. The initial exothermic reaction is followed by a second stage of oxidation contributed by perchloric acid. This latter oxidation accounts for the catalysis by vanadium.

Iodine perchlorate as the reduction product of periodic acid

A 60-g sample of the volatile orange coloured reduction product from the periodic acid oxidation of organic matter was collected for examination of its composition. Upon distillation the sample dissociated materially to liberate iodine. The most stable fraction had a constant boiling point of 112.5°. This fraction was subjected to analysis for iodine by titration of its solution in excess potassium iodide using sodium thiosulphate. A sample weight of 0.5261 g required 26.60 ml of 0.0930N thiosulphate, corresponding to 0.5770 g of $I(ClO_4)_3$. The problem was not studied further. The conclusion was postulated that the reduction products of periodic acid in the oxidation of organic matter consists of iodine monoperchlorate which dissociates to liberate iodine, thus accounting for random ratios of iodine to the perchloric acid anions. In the reactions as described, iodine and iodine perchlorate are oxidised to iodic acid by boiling with concentrated perchloric acid.

Polyethylene oxidation

Polyethylene is well known to be non-reactive in contact with hot concentrated perchloric and periodic acids. The periodic acid liquid fire reaction could thus be predicted to be uneffective. This was experimentally substantiated. Evidence was produced that oxidation was progressing due to the formation of iodine perchlorate and by the exothermic reaction properties, but the time that would be required for complete oxidation would be excessive.

The rapid oxidation of polyethylene is provided by boiling 70–72% perchloric acid with added ceric ion. This reaction, at 200°, is rapid (10 to 15 min), and the wet ash residue is completely soluble when hot and, after dilution, when cold. The low oxidation equivalent weight of cerium requires the use of considerable amounts. These tests indicate that polyethylene requires the application of 1.9 to 2.0 V for rapid destructive oxidation.

Procedural treatment of residual wet ash solution

If the removal of iodic acid from the wet ash solution is desirable, this is accomplished by its dilution by addition of an equal portion of water followed by a stream of sulphur dioxide from a small lecture demonstration pressure bottle. Boiling will remove the iodine, leaving a perchloric acid solution. If perchloric acid is objectionable, the addition of sulphuric acid and boiling to expel it may be easily provided. In many procedures for determination of wet ash concentrates neither iodic nor perchloric acids are interferences. An excess of sulphur dioxide causes the formation of hydriodic acid. It is, therefore, an advantage to add the sulphur dioxide to the boiling diluted wet ash residue. Small amounts of sulphuric acid only are formed by the sulphur dioxide reduction of iodic acid.

ADVANTAGES IN THE APPLICATION OF THE PERIODIC ACID LIQUID FIRE REACTION

The new procedure, herein described, is the most widely applicable of any process which may be applied in wet ashing techniques. It is seen to apply to the rapid wet oxidation of cellulose, sugars and other polyhydric organic compositions, proteins and protein rich materials.

The special feature of these reactions is the much lower temperatures required.

The most important reaction property is that of heavy molecular weight degradation reactions to produce smaller fragments which are readily destroyed through simultaneous contact with concentrated perchloric acid. The effective catalysis of the oxidation by very small amounts of vanadium is thus made operative to a greater extent.

The oxidation of coal at the lowest temperature which is effective in complete removal of organic matter is an attractive procedure in preparation for the determination of arsenic.

The special property of periodic acid in fragmentation of polymeric compositions has made the wet oxidation of such products as nylon, methyl methacrylate polymers and other comparable products easily operative.

Owing to the use of low strength perchloric acid it is postulated that all amino nitrogen of organic compositions is retained in the wet ash digestion residue. This assumption is now being investigated.

The wet oxidation of cellulose type products such as dried feeds, which is a much employed procedure in the determination of calcium, magnesium, sulphur, phosphorus and the alkali metals as applied by the routine animal nutritionists using the nitric acid liquid fire reaction almost entirely, may now be preferentially replaced with gains in many considerations.

The periodic acid wet oxidation procedure has been applied to cellophane, Dacron and Orlon fabrics, dried clover, corn leaves and ground corn stocks, honey, dried beef, Lucite, Du Pont Mylar, and starch, with equal success. Many other applications are deemed attractive.

Because of the use of much less highly concentrated perchloric acid in the reactions described, and the need for only lower temperatures of reaction, there is no tendency to encounter uncontrolled reaction rates.

Zusammenfassung—Der Ersatz von Salpetersäure durch Periodsäure zur nassen Veraschung organischer Substanzen wird vorgeschlagen. Die erzielten Vorteile sind: allgemeinere Anwendungsmöglichkeit, niederere Temperatur und eine bemerkenswerte Aktivität der Periodsäure bei der Zerstörung starke komplexer organischer Molekeln unter Bildung von Fragmente, die in der als weiteres Reagens anwesenden Perchlorsäure wesentlich leichter löslich sind. Diese verbindungen werden dann in 66–70%iger Perchlorsäure leichter oxydiert. Die beschriebenen Reaktionen beziehen sich Vorwiegend auf organische Verbindungen des Types Cellulose, Zucker und Eiweiss. Auch Kohle, Leder, polymere Produkte und ander handelsubliche wichtige Materialien werden ebenfalls leicht oxydiert. Die Reaktion ist ungefährlich.

Résumé—Les auteurs décrivent la substitution de l'acide périodique à l'acide nitrique dans la réaction très employée "liquid fire" pour l'oxydation destructrice des composés organiques. Les avantages obtenus sont les suivants: possibilité d'application générale étendue, nécessités de basse température, réactivité intéressante de l'acide periodique dans la dégradation de molécules complexes organiques lourdes en fragments plus facilement solubles dans l'acide perchlorique utilisé comme réactif d'accompagnement. Ceux-ci sont plus facilement oxydés par cet acide pour des concentrations de 66 à 69 ou 70%. Les réactions décrites s'appliquent à des composés organiques, en particulier à la cellulose, aux sucres et aux protéines. Le charbon, le cuir, les produits polymérisés et d'autres matériaux importants au point de vue commercial peuvent etrê facilement oxydés.

Les réactions mises en jeu ne dépendent pas du hasard.

REFERENCES

[1] G. Frederick Smith, *Analyt. Chim. Acta*, 1953, **8**, 397.
[2] G. Frederick Smith and Harvey Diehl, *Talanta*, 1959, **3**, 41.
[3] Harvey Diehl and G. Frederick Smith, *ibid.*, 1959, **2**, 209.
[4] G. Frederick Smith, *Analyt. Chim. Acta*, 1957, **175**, 1957.
[5] W. H. Latimer, *Oxidation Potentials*, Prentice Hall, Inc. 2nd Ed., 1952, p. 66.

Talanta, 1960, Vol. 4, pp. 194 to 200. Pergamon Press Ltd. Printed in Northern Ireland

THE DETERMINATION OF TANTALUM IN ROCKS BY NEUTRON-ACTIVATION ANALYSIS

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Summary—Neutron-activation analysis has been applied to the determination of traces of tantalum in rocks. Radiochemical separations, after the addition of carrier, have been based mainly on precipitations of tantalum as the hydrous oxide and on solvent extraction with tri-*n*-butyl phosphate. Radiochemically pure tantalum has been finally precipitated as the pentoxide and the chemical yield has been determined gravimetrically.

In order to avoid errors due to self-shielding, dilute aqueous solutions of tantalum were used as the standards irradiated simultaneously with the analytical samples.

Results for the tantalum contents of standard rock samples G1 and W1 are reported.

Tantalum may be classified geochemically as lithophile.[1,2] The element shows a close chemical and geochemical similarity to niobium. Both niobium and tantalum occur in Group Va of the Periodic Table, and as a result of the lanthanide contraction the ionic dimensions of the elements are nearly identical.[3] The close similarity in properties has led in the past to difficulties in the separation and determination of niobium and tantalum.

Neutron-activation analysis has been widely used for the determination of tantalum in ores, ferroniobium, and mixtures of oxides.[4–8] In these cases the tantalum has usually been a major constituent of the sample, and neutron-activation has been used in order to obviate difficulties which pertain with more conventional methods of analysis. However, the chief significance of radio-activation analysis generally lies in its contribution to the determination of trace elements,[9] and the technique has been used to determine traces of tantalum in pure silicon (transistor material[10,11]).

The sensitivity provided by neutron-activation has been utilised in the present work for the development of a new procedure for the determination of tantalum in rocks, The abundance of the element in igneous rocks has been estimated as 2·1 ppm.[1]

NEUTRON-ACTIVATION OF TANTALUM

Naturally occurring tantalum consists of two isotopes, ^{180}Ta (per cent abundance, $\theta = 0{\cdot}0123$) and ^{181}Ta ($\theta = 99{\cdot}9877\%$). On irradiation with neutrons of thermal energies the latter isotope gives rise to radionuclides.

$$\begin{tikzcd}
{}^{181}\text{Ta} \arrow[r, "{n,\gamma}"] \arrow[dr, "{n,\gamma}"'] & {}^{182m}\text{Ta}\ (t_{1/2} = 18{\cdot}5\text{ m.}) \arrow[d, "\text{IT}"] & \\
 & {}^{182}\text{Ta}(t_{1/2} = 115{\cdot}1\text{d.}) \arrow[r, "\beta^-"] & {}^{182}\text{W (stable)}
\end{tikzcd}$$

Isotopic activation cross-sections, σ, for the nuclear reactions are

$$^{181}\text{Ta}(n,\gamma)^{182m}\text{Ta} \qquad \sigma = 0{\cdot}03 \text{ barns}$$
$$^{181}\text{Ta}(n,\gamma)^{182}\text{Ta} \qquad \sigma = 21$$

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Using the flux of 10^{12} neutrons cm^{-2} sec^{-1} available in the Harwell Pile BEPO and measurement of the β^--activity of ^{182}Ta, it has been estimated that as little as 1×10^{-10} g of tantalum may be determined under ideal conditions.[12] The decay scheme for ^{182}Ta is shown in Fig. 1.

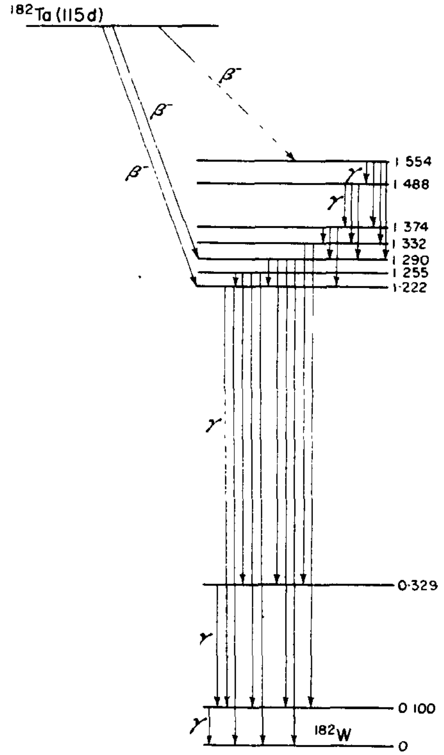

FIG. 1.—Decay scheme for ^{182}Ta, energies in MeV.

EXPERIMENTAL

Irradiation

Samples of the powdered rocks of about 0·5 g were accurately weighed out and sealed in 6-mm internal-diameter silica irradiation tubes. Standards were prepared by weighing out 0·1-ml aliquots of a dilute standard solution of tantalum^{V} (50 mg Ta/litre, in oxalic acid solution) into 4-mm internal-diameter silica irradiation tubes, which were then sealed. Samples and standards were packed together in a standard 3-in. × 1-in. screw-top aluminium can and sent for irradiation in the Harwell Pile BEPO. Irradiation was usually for a period of 1 week with pile factor 10.

Radiochemical separation

Following delivery from Harwell after irradiation, the samples and standards were left to "cool" for a few days, and then were assayed radiochemically for ^{182}Ta. A procedure involving carrier chemistry, precipitation, and solvent extraction, was employed for the separation of tantalum from the irradiated rock samples. Steps involving solvent extraction with tri-*n*-butyl phosphate were based on distribution data of Morris *et al.*[14,15]

Reagents

Ta carrier, 10 mg Ta/ml (see preparation of carrier)
KNO_3, solid
K_2CO_3, solid

HNO_3, conc
H_2SO_4–HF solution, 12*N* in H_2SO_4 and 10*M* in HF
HF, conc
HF, 0·5*M*
NH_4OH, conc
NH_4NO_3, solid
NH_4NO_3, 2% solution in H_2O
Tri-*n*-butyl phosphate (TBP), purified by the method of Alcock *et al.*[16]
Petroleum ether
Ethyl alcohol, absolute

Preparation of tantalum carrier

Dissolve a weighed quantity of "Specpure" Ta_2O_5 in a mixture of conc HNO_3 and conc HF. Make up to a volume with 5*M* HF to give 10 mg of Ta per ml of solution. Store in a stoppered polythene bottle.

Radiochemical separation procedure for tantalum in rocks

Step 1. Remove the irradiation tubes from the can, open them at the constriction, and transfer the powdered rock samples quantitatively to platinum crucibles. To each add 4 g of powdered K_2CO_3 and 0·1 g of KNO_3; mix thoroughly. Fuse in an electric muffle furnace, heating carefully at a low temperature first, and then at 850–900°. When decomposition is complete, remove the crucible from the furnace, allow it to cool somewhat, then grasp it with the tongs and carefully distribute the melt in a thin shell over the interior walls by imparting a slow rotary motion to the crucible as it cools. Transfer the cooled melt to a 250-ml polythene beaker, add 20 ml of H_2O and break up the melt with a glass rod flattened at one end. Acidify carefully with HF, add 2 ml of Ta carrier, and stir for 5 min with a polythene rod. Filter the supernate into a 50-ml polythene centrifuge tube and discard any residue.

Step 2. Add 1 g of solid NH_4NO_4, and make the solution just ammoniacal with conc NH_4OH. Centrifuge and discard the supernate. Wash the precipitate of hydrous tantalum^V oxide with two 10-ml portions of conc HNO_3. Centrifuge and discard the supernate.

Step 3. Dissolve the precipitate in 10 ml of a solution 12*N* in H_2SO_4 and 10*M* in HF. Add 10 ml of TBP and mechanically stir the phases for 2 min using a polythene stirring rod. Centrifuge, transfer the organic (upper) layer with a polythene transfer pipette to a clean 50-ml polythene centrifuge tube, and discard the aqueous layer. Wash the TBP phase with two 5-ml portions of 0·5*M* HF. Discard the aqueous washings.

Step 4. Add 10 ml of petroleum ether to the TBP phase and stir it with 10 ml of 6*M* NH_4OH. Centrifuge at high speed and separate and discard the organic and aqueous layers. Wash the precipitate twice with 10-ml portions of hot 2% NH_4NO_3 and transfer to a 50-ml glass centrifuge tube.

Step 5. Centrifuge and discard the supernate. Wash the precipitate twice with 10-ml portions of boiling conc HNO_3. Centrifuge and discard the supernate.

Step 6. Transfer the precipitate to a porcelain crucible with 2 ml of distilled water; heat to dryness. Ignite at 900° for 15–20 min, and allow to cool in a desiccator.

Step 7. Add 1 ml of ethyl alcohol to the Ta_2O_5 in the crucible and grind with the polished end of a stirring rod. Slurry the Ta_2O_5 with the ethyl alcohol on to a weighed aluminium counting tray (A.E.R.E. cat. no. 4–3/1068). Dry thoroughly under a radiant heater lamp taking care to ensure that the resulting deposit on the tray is uniform. Cool and weigh to determine the chemical yield. (The precipitate is very loose and powdery and great care is necessary). Fix the precipitate to the tray by the addition and evaporation of a few drops of collodion solution (2 mg/ml).

Treatment of the irradiated tantalum standards

At a suitable time open the irradiation tubes containing the tantalum standards. Using a polythene transfer pipette drawn out almost to a point, transfer the tantalum solution quantitatively to a 50-ml polythene centrifuge tube and rinse thoroughly with 5*M* HF. Add 2 ml of Ta carrier, mix thoroughly, then make just ammoniacal with conc NH_4OH. Proceed as from Step 5 of the radiochemical procedure for rock samples.

Counting of the Ta_2O_5 *precipitates*

In the present study final precipitates of Ta_2O_5 were counted through a standard Al-Pb sandwich absorber with a γ-scintillation counter type 1186A.

In order to check for the radiochemical purity of the radiotantalum, decay measurements on the final precipitates were performed. Decay curves obtained from a sample and a standard are shown in Fig. 2, and are straight lines corresponding well with published values[13] for the half-life of ^{182}Ta. *A* further check for radiochemical purity was made by measuring the γ-spectra of final precipitates with a single NaI(Tl) crystal γ-scintillation spectrometer. Typical results are shown in Fig. 3.

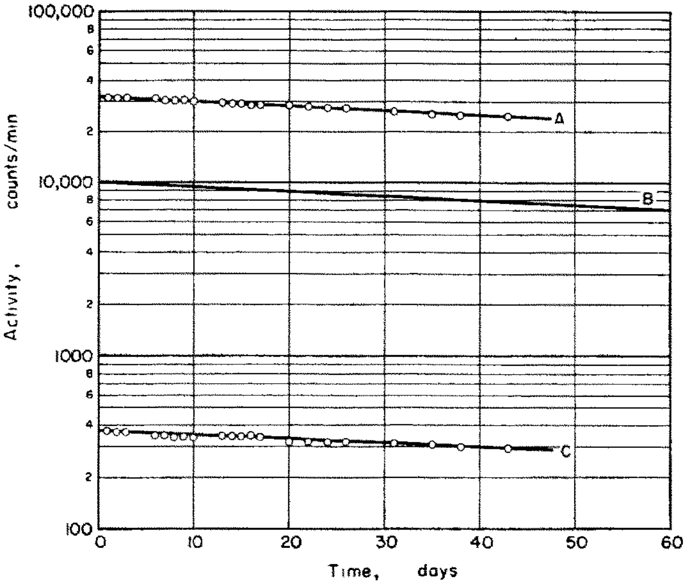

FIG. 2.—Decay curves: A, tantalum activity of a standard. B, line of slope corresponding to a nuclide of half-life 115 days. C, tantalum activity from a rock sample.

RESULTS

If A_1 is the activity (corrected for background and chemical yield) from a rock sample and A_2 is the corresponding activity from a tantalum standard, at a given time

$$\frac{A_1}{A_2} = \frac{w_1}{w_2}$$

where w_2 is the weight of tantalum in the standard and w_1 is the weight of tantalum in the rock sample.

Typical analysis results obtained by the radio-activation method are shown in Table 1. These refer to the standard granite G1 from Westerley, Rhode Island, and the standard diabase W1 from Centreville, Virginia, which have been distributed as standards for both major and minor constituents of igneous rocks.[17]

DISCUSSION

In the determination of tantalum by neutron-activation, consideration must be given to the possibility of formation of ^{182}Ta through nuclear reactions involving

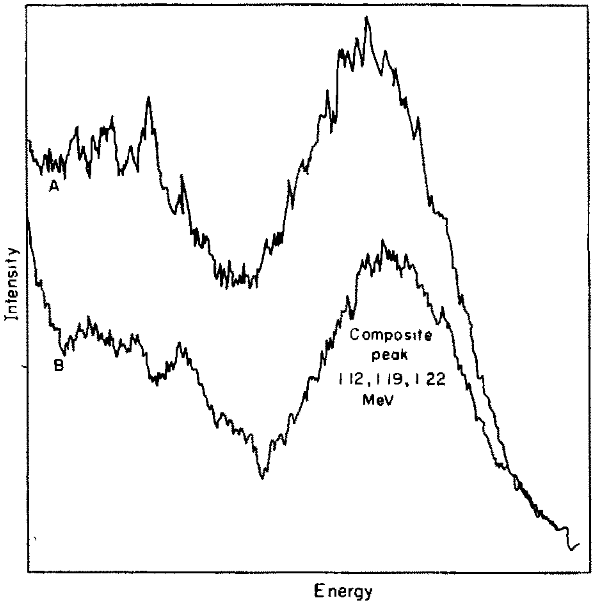

FIG. 3.—Gamma ray spectra: A, activity of a standard. B, activity from a rock sample

TABLE I.—TANTALUM CONTENTS OF THE STANDARD GRANITE G1 AND THE STANDARD DIABASE W1 DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

G1	W1
3·1 ppm	0·95 ppm
2·8	0·88
2·9	0·89
3·1	1·06
3·1	0·99
3·1	0·84
2·7	Average 0·93
2·9	
Average 3·0	

elements other than tantalum. For example, ^{182}Ta could be produced by the following reactions:

$$^{185}\text{Re}(n,\alpha)^{182}\text{Ta}$$

$$^{182}\text{W}(n,p)^{182}\text{Ta}$$

$$^{183}\text{W}(\gamma,p)^{182}\text{Ta}.$$

The first two of the above nuclear reactions may be brought about by the fast neutron flux in the pile, which flux Mellish *et al.*[18] calculated to be 0·17 of the slow flux in the centre of BEPO. The cross-sections for these reactions are likely to be very much lower than for the reaction ^{181}Ta(n,γ)^{182}Ta, and since the abundance of rhenium in igneous rocks is extremely low, 0·001 ppm,[1] the first reaction is clearly not troublesome in the present work.

To check on any possible interference arising from the production of ^{182}Ta from nuclear reactions of tungsten, samples of pure WO_3, together with pure Ta standards, were irradiated in the Pile for 1 week. The tantalum activity was separated and counted as before. The experimental results indicated that if a rock contained 70 ppm W (the crustal abundance of tungsten has been quoted[1] as 1·5–69 ppm), this could give rise to a maximum spurious tantalum content of only 10^{-5} ppm.

Any interference of importance due to the formation of radio-isotopes of tantalum other than ^{182}Ta would have been apparent from the decay and energy measurements on the final precipitates from analysis samples.

Note added in proof.

Since the acceptance of this paper, Atkins and Smales[19] have published details of the determination of tantalum by neutron-activation analysis. Our results for the tantalum content of G1 and W1 do not correspond with the values obtained by these investigators. Atkins and Smales point out and discuss the possibility of contamination of the rock samples during pulverisation, and this may account for the discrepancy. Our samples were provided in a powdered condition by the U.S. Geological Survey.

Acknowledgment—The authors wish to record their thanks to Mr. G. W. J. Kingsbury of the National Chemical Laboratory, Teddington, for the loan of "Specpure" tantalum pentoxide.

Zusammenfassung—Neutronenaktivierungsanalyse wurde zur Bestimmung von Tantal in Gestein angewandt. Radiochemische Abtrennung unter Verwendung von Trägern beruhte hauptsächlich auf der Fällung von Tantalhydroxyd und Solventextraktion mit Tri-n-butylphosphat. Radiochemisch reines Tantal wurde schliesslich als Pentoxid gefällt und der chemische Gehalt gravimetrisch ermittelt. Zur Verhinderung von Fehlern durch Selbstabschirmung wurden verdunnte Lösungen von Tantal als Standards verwendet und zugleich mit den Proben bestrahlt. Die Ergebnisse der Analysen von Standardgestein G1 und W1 werden mitgeteilt.

Résumé—L'analyse par activation des neutrons a été appliquée au dosage de traces de tantale dans les roches. Les séparations radiochimiques aprés addition d'entraineur ont été basées principalement sur la précipitation du tantale a l'état d'oxyde tantaleux, et sur l'extraction par solvant avec le phosphate de tri-n-butyl. On précipite finalement le tantale radiochimiquement pur à l'état de pentoxyde et le rendement chimique a été déterminé par gravimétrie.

Pour éviter les erreurs dues au phénomène d'auto-absorption on utilise comme étalons des solutions diluées de tantale irradiées simultanément avec l'échantillon à doser.

Les résultats relatifs à la teneur en tantale d'échantillons de roches étalons G_1 et W_1 sont indiqués.

REFERENCES

[1] K. Rankama and T. G. Sahama, *Geochemistry*, University of Chicago Press, 1950.
[2] V. M. Goldschmidt, *Geochemistry*, Clarendon Press, Oxford, 1954.
[3] L. H. Ahrens, *Geochim. Cosmochim. Acta*, 1952, **2**, 155.
[4] J. V. P. Long, *Analyst*, 1951, **76**, 644.
[5] G. G. Eichholz, *Nucleonics*, 1952, **10**, No. 12, 58.
[6] J. Beydon and C. Fisher, *Analyt. Chim. Acta*, 1953, **8**, 538 (1953).
[7] A. Kohn, Chimie et Industrie, 1954, **71**, 69.
[8] G. W. C. Milner and A. A. Smales, *Analyst*, 1954, **79**, 425.
[9] D. H. F. Atkins and A. A. Smales, *Adv. Inorg. Chem. and Radiochem.*, 1959, **1**, 315.
[10] A. A. Smales, D. Mapper, A. J. Wood, and L. Salmon, Atomic Energy Research Establishment Harwell Rept., A.E.R.E., C/R 2254, 1957.
[11] B. A. Thompson, B. N. Strause, and M. B. Leboeuf, *Analyt. Chem.*, 1958, **30**, 1023.
[12] E. N. Jenkins and A. A. Smales, *Quart. Rev. Chem. Soc.*, 1956, **10**, 83.

[13] D. Strominger, J. M. Hollander, and G. T. Seaborg, *Rev. Mod. Phys.*, 1958, **30**, 585.

[14] D. F. C. Morris, A. G. Wain, and J. M. Fletcher, Atomic Energy Research Establishment, Harwell Rept. A.E.R.E., C/R 1391, 1954.

[15] J. M. Fletcher, D. F. C. Morris, and A. G. Wain, *Trans. Inst. Mining Metal.*, 1956, **65**, 487.

[16] K. Alcock, S. S. Grimley, T. V. Healy, J. Kennedy, and H. A. C. McKay, *Trans. Faraday Soc.*, 1956, **52**, 39.

[17] H. W. Fairbairn, W. G. Schlecht, R. E. Stevens, W. H. Dennen, L. H. Ahrens, and F. Chayes, *U.S. Geological Survey Bull.* No. 980, 1951.

[18] C. E. Mellish, J. A. Payne, and R. L. Otlet, *Radioisotopes in Scientific Research*, Pergamon Press, London, 1958, **1**, 35.

[19] D. H. F. Atkins and A. A. Smales, *Analyt. Chim. Acta*, 1960, **22**, 462.

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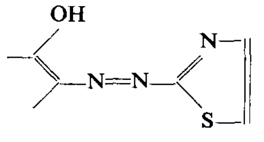
PRELIMINARY COMMUNICATION

Thiazolyl analogues of 1-(2-pyridylazo)-2-naphthol

(*Received* 9 *March* 1960)

AMONG the metallochromic indicators of the azo-dye series, 1-(2-pyridylazo)-2-naphthol (PAN)[1] has an outstanding position. In contrast to the analogous *o*:*o*′-di-substituted azo dyes of the Eriochrome Black T type—where the transforming functional groups[2] are represented by phenolic hydroxyls—the chelating grouping of the indicator PAN contains a heterocyclic nitrogen atom with a lone electron pair as one of the ligands. Due to this fact, pyridylazonaphthol possesses an increased ability to form coloured complexes with bivalent metal ions (*e.g.* with Cu^{II}, Cd^{II}, Ni^{II}, Co^{II}, Hg^{II}, Pb^{II} etc.) which display an especially strong affinity towards the nitrogen as a donor atom. The advantageous metallochromic properties of this substance have, in recent years, inspired several attempts to find other analogous indicators. In all these attempts the approach has been limited to modification of the phenolic part of the PAN molecule, resulting in the preparation of 4-(2-pyridylazo)-resorcinol (PAR),[3] and derivatives of H-acid and chromotropic acid.[4] From the analytical viewpoint, however, among all these substances only the indicator PAR may be considered successful.[3,5]

A novel and especially valuable group of analogues of the PAN and PAR indicators has now been found in thiazolyl azo dyes of the type I. With a view to studying the metallochromic properties of these substances the condensation products of diazotised 2-aminothiazole with a number of phenols, naphthols and naphthol-sulphonic acids have been prepared.



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Their preparation is very simple, since 2-aminothiazole (as opposed to 2-aminopyridine) requires no special conditions for diazotisation or condensation; and the products are obtained in relatively good yields and—in most cases—in a fairly pure form. Among all the substances synthesised, the best properties were displayed by derivatives of 2-naphthol, of Schäffer's acid, of R-acid, of chromotropic acid and especially of resorcinol. Some of these dyes were synthesised earlier by Traumann;[6] however, their metallochromic properties and the possibility of their analytical application have not so far been studied.* With the exception of the dye derived from 2-naphthol, all these substances (and especially their alkali salts) are readily soluble in water; 1-(2-thiazolylazo)-2-naphthol resembles its pyridine analogue in its solubility in water and other solvents.

In aqueous solution the substances studied behave as acid-base indicators with the point of colour change varying for individual compounds over the pH range 6–10. In the case of derivatives containing the naphthalene ring, the acid-base colour change is one from yellow (or wine-red in the case of the chromotropic acid derivative) to purple or even violet; 4-(2-thiazolylazo)resorcinol changes from yellow to bright red. In the acid region the thiazolyl azo dyes form complexes with a number of metal ions, *e.g.* Cu^{II}, Cd^{II}, Ni^{II}, Co^{II}, Zn^{II}, Pb^{II}, Hg^{II}, Fe^{III}, Tl^{III}, Sc^{III}, In^{III}, La^{III} etc., which are coloured purple to violet (naphthalene derivatives) or bright red to purple (derivative of

* After the completion of the present work two abstracts appeared in *Z. analyt. Chem.*, 1960, **171**, 435, 444 of papers by T. Yanagimara, N. Matano and A. Kawase, *Bunseki Kagaku*, 1959, **8**, 10, 14, describing the application of 2-(2-hydroxy-5-methoxyphenylazo)-4-methylthiazole to the determination of Zn, Ni and Co.

resorcinol). The condensation product of diazotised aminothiazole with chromotropic acid reacts with metal ions within a narrow range of pH only (5–7), and gives a distinct and practically applicable reaction only with copper (a pure blue coloration). With alkaline earth metals these substances show no colour reactions.

Most coloured metal complexes of 1-(2-thiazolylazo)-2-naphthol can be extracted with organic solvents such as amyl alcohol, chloroform, carbon tetrachloride etc. Metal complexes of the resorcinol derivative are extractable with more polar solvents only (amyl alcohol). Among the sulphonated dyes only the mercury complex of 1-(2-thiazolylazo)-2-naphthol-6-sulphonic acid is soluble in amyl alcohol and even this is insoluble in chloroform or carbon tetrachloride.

As far as their analytical application is concerned, the thiazolyl azo dyes referred to can be used almost in all instances where the use of the PAN or PAR indicators has been recommended. Moreover, the water-soluble sulphonated derivatives, which have not yet been prepared in the pyridine series (*cf.*[5]), may be used with advantage. Selected substances from this new group have fully met expectations as metallochromic indicators in chelatometric titrations of a number of metal ions. In this respect those dyes which are derived from Schäffer's acid, chromotropic acid and especially from resorcinol appear to be the most promising. The end-point colour change of the latter (from bright red or purple to lemon yellow), on titrating *e.g.* Cu^{II}, Cd^{II}, Zn^{II}, Pb^{II}, Tl^{III}, Sc^{III}, La^{III} and In^{III} with ethylenediaminetetra-acetic acid, equals in its distinctness and sharpness those of the best metallochromic indicators used hitherto. Although the applicability of these thiazolyl dyes as chromogenic reagents for spectrophotometry has not so far been studied in detail, successful applications may also be expected here owing to the high sensitivity of the reactions and the excellent colour properties.

Note added in proof—The author's attention has been drawn to an abstract dealing with some of these compounds (*Chem. Abs.*, 1960, **54**, 4541g) which appeared while the present paper was in the press.

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Summary—A new group of metallochromic indicators, the thiazolyl analogues of 1-(2-pyridylazo)-2-naphthol, is described. These can be used in almost all instances where PAN or PAR indicators have been recommended, and their water-soluble sulphonated derivatives are also of value. Other properties are being studied.

Zusammenfassung—Eine neue Gruppe metallochromer Indicatoren, die Thiazolylderivate des 1-(2-pyridylazo)-2-naphthols, wird beschrieben. Die Indicatoren konnen in nahezu allen Fällen verwendet werden, in denen PAN oder PAR empfohlen werden. Die wasserlöslichen, sulfonierten Derivate sind ebenfalls wertvoll. Andere Eingenschaften werden studiert.

Résumé—L'auteur décrit un nouveau groupe d'indicateurs métallochromiques, les dérivés thiazolyl du 1-(2 pyridylazo)-2 naphtol. Ces indicateurs peuvent être utilisés dans presque tous les exemples où les indicateurs PAN ou PAR ont été recommandés, et leurs dérivés sulfonés solubles dans l'eau sont aussi intéressants. D'autres propriétés sont étudiées actuellement.

REFERENCES

[1] K. L. Cheng and R. H. Bray, *Analyt. Chem.*, 1955, **27**, 782.
[2] J. Körbl and R. Přibil, *Ind. Chemist* 1958, **34**, 616.
[3] P. Wehber, *Z. analyt. Chem.*, 1957, **158**, 10.
[4] L. Sommer and M. Hniličková, *Naturwiss.*, 1958, **45**, 544.
[5] F. H. Pollard, P. Hanson and W. J. Geary, *Analyt. Chim. Acta*, 1959 **20**, 26.
[6] V. Traumann, *Ann.*, 1888, **249**, 31.

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SHORT COMMUNICATIONS

A self-sampling indicator tube for oxygen

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ALTHOUGH oxygen is not usually numbered amongst the toxic or dangerous gases, a local deficiency or excess of oxygen in the atmosphere can constitute a serious hazard. Irrespective of any simultaneous production of other gases, such as carbon dioxide, a reduction to 10–15% in the oxygen content of the air can cause a degree of distress varying with the individual. On the other hand, an increase in the oxygen content of the air to above 30% can greatly augment the fire hazard due to increase in the ease of ignition and rate of burning of combustible materials.

Instruments available for the determination of oxygen are usually too expensive, bulky or fragile for convenience, whilst chemical methods depending on the extraction of oxygen from air by absorbents and the measurement of the residue tend to be lengthy and to be awkward in manipulation. The need for a simple field test has now been met by the use of an evacuated glass tube containing an intimate mixture of silica gel and manganous oxide. Air is admitted to the tube by breaking the end and very rapidly changes the colour of the absorbent from green to brown. The oxygen content of the atmosphere is determined by measurement of the lengths of green and brown material. The evacuated silica gel tube acts as its own pump and no other sampling apparatus is required.

The nature and ubiquity of oxygen impose special problems in the design of a field test which do not normally arise in the determination of toxic gases, usually present in small proportions in the atmosphere. Since the oxygen content may be large, the sample must be small enough to be commensurate with the absorptive power of the reagent, and the absorbent must be very reactive and capable of dealing with a wide range of oxygen content in the sample. Air must be excluded from the absorbent before sampling and from the unused portion of it after sampling.

A suitable absorbent was found in manganous oxide, which can be prepared in a suitable form by heating manganous carbonate, by the method of Schulek and Pungor,[1] who have used this oxide in gas analysis because of its high sensitivity to oxygen. The problems of protecting the manganous oxide from oxidation before sampling, and of providing the means of taking a small sample of air, were solved simultaneously by preparing the reagent *in situ* by heating manganous carbonate with a silica gel base in the tube, under reduced pressure, then vacuum sealing.

Manganous carbonate is prepared by pouring a solution of manganous chloride into a solution of sodium bicarbonate, filtering, washing successively with water, 96% alcohol, and pentane, and drying.[1] The manganous carbonate is then thoroughly mixed in an atmosphere of carbon diideox in a rotating drum with eight times its own weight of silica gel (chromatographic grade, 50–100 mesh) previously dried at 430°. The gel granules are now completely covered with an adherent layer of carbonate. The granules, still maintained in an atmosphere of carbon dioxide, are transferred to glass tubes of 5-mm bore, sealed at one end, to a height of about 20 cm, and plugged with a disc of asbestos paper and steel gauze. The tubes are evacuated, heated *in vacuo* at 430° for 45 min and sealed.

The actual determination of oxygen in the atmosphere can be carried out in less than 1 min. The end of the sample tube is broken and, after 20 sec, the length of the brown layer, y, and the total length of the brown and green layers, L, are measured. The percentage of oxygen, P, is

$$P = \frac{100cy}{s(L - y) + cy} \qquad (1)$$

where c = volume of oxygen in ml absorbed per cm length in the brown layer,
and s = volume of nitrogen in ml per cm length in the green layer.

Equation (1) can be more conveniently expressed as

$$P = \frac{100aF}{1 - F + aF} \tag{2}$$

where a, the batch constant, $= \dfrac{c}{s}$,

and $F = \dfrac{y}{L}$.

Actual measurement of the layer lengths in each determination can be avoided by placing the tube on a specially constructed chart and reading off the ratio F directly. From the value for F, the percentage of oxygen, P, can be read off on a batch calibration curve based on equation (2). A knowledge of the actual volume of sample taken is not necessary.

As the sample of air enters the evacuated tube, the oxygen component is rapidly absorbed by the manganous oxide, which it turns brown, and the nitrogen passes to the end of the tube containing unchanged green reagent. The boundary between brown and green layers is always sharp and well-defined. This process, which is extremely rapid at first, slows down slightly towards the end, but is complete, for practical purposes, within 20 sec. If the tube is now allowed to stand, air slowly percolates through the packing and the whole tube becomes brown at the end of 10 to 30 min. The difference between the rates of the initial rush and of the diffusion process is normally so great, however, that the error due to diffusion is negligible when the oxygen content does not exceed 40%.

Evacuated silica gel was found capable of adsorbing about 0·8 ml per g of gel of either air, oxygen or nitrogen. In the operation of the field test, it is probable that nitrogen is adsorbed throughout the length of the tube. The validity of equation (1) did not appear to be affected by this complication. Presumably s measures the nitrogen content of the air sample denuded of oxygen, irrespective of what proportion of this nitrogen content occupies the free space above the unused portion of reagent mixture, or is adsorbed by it.

Carbon dioxide is adsorbed by the silica gel far more avidly than nitrogen and, if a few per cent of carbon dioxide is present in the atmosphere, it will be adsorbed in the first few cm of granules. In these circumstances, P in equation (1) will express the oxygen content not of the atmosphere, but of the atmosphere denuded of carbon dioxide. If an appreciable amount of carbon dioxide is present in the sample, this gas should be separately determined.

At ordinary indoor temperatures and at pressures varying little from 760 mm, the field test gives results reproducible within 1 part in 20 of the oxygen content of the air. An increase in the ambient temperature results in an apparently lower oxygen concentration, whereas an increase in pressure gives an apparently higher oxygen concentration. If more exceptional temperatures and pressures are encountered, the following empirical formula can be used

$$P = P_1\left(\frac{100}{120 - t}\right)\left(\frac{980}{p + 220}\right) \tag{3}$$

where P = percentage of oxygen (corrected),
P_1 = apparent percentage of oxygen,
t = temperature (°C),
and p = barometric pressure (mm).

The method shares the drawback of batch calibration with most tests using tubes containing reagent based on silica gel. The necessity of excluding air during the preparation of the tubes is somewhat onerous. In operation, however, the field test could not be simpler, the sole apparatus required being the tube itself and a blue pencil to mark the colour boundary. The tubes appear to suffer no deterioration on keeping for at least two years.

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Summary—Oxygen is absorbed by manganous oxide which has been prepared *in situ* on a silica gel base. The percentage oxygen is found in less than one minute.

Zusammenfassung—Sauerstoff wird an Manganooxyd absorbiert, welches in situ auf einer Silicagelgrundlage erzeugt wurde. Der Prozentgehalt an Sauerstoff wird in weniger als einer Minute ermittelt.

Résumé—L'oxygène est absorbé par de l'oxyde manganeux qui a été préparé in situ sur un support de silica gel. Le pourcentage d'oxygène est trouvé en moins d'une minute.

REFERENCES

[1] E. Schulek, and E. Pungor, *Mikrochim. Acta*, 1956, 7–8, 1116.

Lithium chloride in non-aqueous potentiometric titrations

(*Received* 26 *March* 1960)

INSTRUMENT instability is often a problem in the use of non-aqueous solvents in potentiometric measurements or titrations. Various means have been used, such as special electrode holders and special cells with the tips of the electrodes placed very close together, to help stabilise the instrument. Lithium chloride was used by Fritz and Lisciki[2] as a means of reducing the resistance between the electrodes and thus increasing the stability of the instrument. This fact appears to be little known, and its limits of use are apparently much less known.

Equipment

The Beckman Model H-2 pH meter and the Leeds and Northrup pH Indicator were used for these observations. The glass-calomel electrode combination was used in all of the titrations. In addition the glass-silver:silver chloride electrode combination was also used when chlorobenzene, dioxane, and benzene were used as individual solvents.

Discussion

Glacial acetic acid was used as the solvent for the titration of aluminium oxinate,[3] salts,[4] and pyridine[1] with $0.1N$ perchloric acid. The instruments were reasonably stable and the use of lithium chloride did not appreciably improve their stability. Actually its use in these cases was undesirable, since the change in potential per increment of titrant near the inflection point of the potentiometric curves was much less when lithium chloride was used. The same results were observed for the use of lithium chloride when chlorobenzene[1] was used as the solvent for the titration of pyridine with perchloric acid. When the G-H mixture[5] was used as the solvent, lithium chloride had no effect on the stability of the instrument or the shape of the titration curves. The attempted titration of pyridine in inert solvents such as dioxane and benzene, with or without lithium chloride, failed.

The real usefulness of lithium chloride was found in the titration of weak acids with sodium methoxide in neutral or weakly basic solvents. In benzene-methanol solutions at a ratio of 3 : 1 or lower, the pH meters were stable due to the influence of the methanol. For the titration of acids such as benzoic or stearic in benzene-methanol solutions in a ratio of 4 : 1 or greater, the lithium chloride definitely increased the stability of the instruments. With the 8 : 1 benzene-methanol solution the instrument was extremely unstable, but stabilised when lithium chloride was added. Actually the instrument was stable enough to start a titration and obtain a reasonably good potentiometric curve with benzoic acid in 50 : 1 benzene-methanol solution titrated with sodium methoxide. However, titrations of these weak acids in pure benzene were not possible.

In these titrations, the change in potential per increment of titrant near the inflection point was also increased by approximately a factor of two. This may have been because the lithium chloride prevented the ionisation of the salt formed during the titration, thus reducing the common-ion effect

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The presence of lithium chloride also improved the stability of the instrument and increased the rate of change in potential per increment of titrant near the end-point when benzoic acid was dissolved in dimethylformamide and titrated with sodium methoxide.

The lithium chloride improved the stability of the pH meters using the glass-calomel electrode combination and caused an increase in $\Delta E/\Delta V$ near the end-point when using solvent mixtures with high ratios of benzene to methanol, and dimethylformamide. It was of no value or was detrimental in acidic solvents such as glacial acetic acid.

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Summary—The use of lithium chloride for improving instrument stability in non-aqueous potentiometric titrations is discussed, and its limitations are indicated.

Zusammenfassung—Der Gebrauch von Lithiumchlorid zur Erhöhung der Stabilität des Instrumentes bei potentiometrischen Titrationen in nichtwässrigem Medium wird diskutiert. Grenzen der Einsatzmöglichkeiten werden aufgezeigt.

Résumé—L'auteur discute l'utilisation du chlorure de lithium pour l'amélioration de la stabilité des instruments dans les titrages potentiométriques en milieu non aqueux, et indique ses limitations.

REFERENCES

[1] James S. Fritz, *Analyt. Chem.*, 1950, **22**, 1028.
[2] James S. Fritz and N. M. Lisciki, *ibid*, 1951, **23**, 589.
[3] C. H. Hill, Han Tai, A. L. Underwood and R. A. Day, Jr., *ibid*, 1956, **28**, 1688.
[4] Peter G. Markunas and James A. Riddick, *ibid*, 1951, **23**, 337.
[5] S. R. Palit, *Ind. Eng. Chem. Anal.*, 1946, **18**, 246.

Determination of carbon disulphide by chloramine-T

(*Received* 12 *April* 1960)

IT has been shown that chloramine-T brings about a rupture between S—S and N—S linkages and oxidises all the sulphur quantitatively to sulphuric acid.[1] It was of interest to find out whether the oxidant can break a C—S linkage and bring about a similar oxidation. Experiments carried out by the present authors indicated that carbon disulphide, after treatment with alcoholic potash, could easily be oxidised by chloramine-T quantitatively converting all the sulphur to sulphuric acid. This oxidation is described as an analytical procedure in this paper.

EXPERIMENTAL

Chloramine-T: About 15 g of a recrystallised sample of pure chloramine-T were dissolved in 1 litre of water and stocked in an amber coloured bottle. The solution was standardised iodimetrically in an acid medium as described earlier.[2,3]

Carbon disulphide: A weighed amount (about 0·200 g) of pure redistilled carbon disulphide, free from elemental sulphur, taken in a sealed thin-walled glass bulb, was broken under 5–6 ml of freshly prepared alcoholic potash (10%) in a stoppered conical flask. The carbon disulphide, on reacting with alcoholic potash, gave the corresponding amount of potassium ethyl xanthate. The yellowish white product was dissolved in water and filtered to remove the glass pieces, and the solution was made up in a standard volumetric flask (250 ml.). Aliquots of this solution were used for oxidation reactions.

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[2] James S. Fritz and N. M. Lisciki, *ibid*, 1951, **23**, 589.
[3] C. H. Hill, Han Tai, A. L. Underwood and R. A. Day, Jr., *ibid*, 1956, **28**, 1688.
[4] Peter G. Markunas and James A. Riddick, *ibid*, 1951, **23**, 337.
[5] S. R. Palit, *Ind. Eng. Chem. Anal.*, 1946, **18**, 246.

Determination of carbon disulphide by chloramine-T

(*Received* 12 *April* 1960)

It has been shown that chloramine-T brings about a rupture between S—S and N—S linkages and oxidises all the sulphur quantitatively to sulphuric acid.[1] It was of interest to find out whether the oxidant can break a C—S linkage and bring about a similar oxidation. Experiments carried out by the present authors indicated that carbon disulphide, after treatment with alcoholic potash, could easily be oxidised by chloramine-T quantitatively converting all the sulphur to sulphuric acid. This oxidation is described as an analytical procedure in this paper.

EXPERIMENTAL

Chloramine-T: About 15 g of a recrystallised sample of pure chloramine-T were dissolved in 1 litre of water and stocked in an amber coloured bottle. The solution was standardised iodimetrically in an acid medium as described earlier.[2,3]

Carbon disulphide: A weighed amount (about 0·200 g) of pure redistilled carbon disulphide, free from elemental sulphur, taken in a sealed thin-walled glass bulb, was broken under 5–6 ml of freshly prepared alcoholic potash (10%) in a stoppered conical flask. The carbon disulphide, on reacting with alcoholic potash, gave the corresponding amount of potassium ethyl xanthate. The yellowish white product was dissolved in water and filtered to remove the glass pieces, and the solution was made up in a standard volumetric flask (250 ml.). Aliquots of this solution were used for oxidation reactions.

Procedure

An aliquot portion of the xanthate (carbon disulphide) solution (about 5 ml) was added to a known excess of acidified chloramine-T solution (20 ml of 0·1*N* chloramine-T with 10 ml of 2*N* HCl) in a stoppered conical flask. To the mixture was added 10 to 25 ml of ethyl alcohol. The reactants in the flask were set aside for at least half-an-hour. At the end of this period, 10 ml of 10% potassium iodide solution were added and the liberated iodine was titrated against thiosulphate solution. The amount of chloramine-T consumed by the xanthate was thus obtained from the titre value and the number of equivalents of the oxidant required per mole of carbon disulphide was calculated. With freshly prepared alcoholic potash no blank correction was necessary.

The analytical values were found to be reproducible and the results of a few representative experiments are given in Table I.

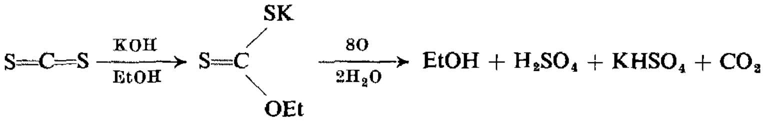
TABLE I. OXIDATION OF CARBON DISULPHIDE BY CHLORAMINE-T

Expt. No.	Amount of carbon disulphide taken × 10⁵, *moles*	No. of equivalents of oxidant consumed × 10⁵	No. of equivalents of oxidant per mole of carbon disulphide	Oxidant
1	5·367	74·86	13·94	Chloramine-T
2	5·590	78·20	13·99	Chloramine-T
3	10·61	149·60	14·10	Chloramine-T
4	11·26	11·20	0·995	Iodine
5	11·26	11·20	0·995	Iodine

Similar experimental results were obtained when the reaction was carried out at 50° for 1 hour by immersing the flask containing the reactants in a hot water bath, except for a small correction in the blank experiment (about 0·5 ml).

RESULTS AND DISCUSSION

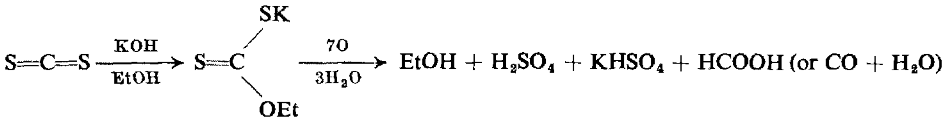
It can be seen from the results quoted in Table I that 14 equivalents of chloramine-T are consumed by 1 mole of carbon disulphide. If the carbon disulphide were to be oxidised completely, resulting in the conversion of carbon to carbon dioxide and sulphur to sulphuric acid, it would take 16 equivalents of oxidant, according to the equation:



$$S{=}C{=}S \xrightarrow[\text{EtOH}]{\text{KOH}} S{=}C\begin{matrix}\diagup SK\\ \diagdown OEt\end{matrix} \xrightarrow[2H_2O]{8O} EtOH + H_2SO_4 + KHSO_4 + CO_2$$

Ethyl alcohol is regenerated and is not oxidised by chloramine-T under the experimental conditions as described in the present investigation.[1]

As observed in the actual experiments carried out, only 14 equivalents of the oxidant are consumed by carbon disulphide converted to the form of xanthate. The probable products of oxidation may, perhaps, be sulphuric acid and formic acid or carbon monoxide. Formic acid or its salt are not oxidised further by chloramine-T. Such an oxidation can be represented by the equation

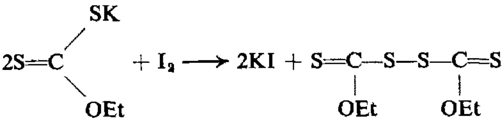


$$S{=}C{=}S \xrightarrow[\text{EtOH}]{\text{KOH}} S{=}C\begin{matrix}\diagup SK\\ \diagdown OEt\end{matrix} \xrightarrow[3H_2O]{7O} EtOH + H_2SO_4 + KHSO_4 + HCOOH\ (\text{or } CO + H_2O)$$

The fact that formic acid was not oxidised further to carbon dioxide and water by chloramine-T was established by separate experiments. Aliquots of chloramine-T, with and without formic acid (2 ml), when standardised against thiosulphate, gave the same titre.

It is well known that xanthic acid is liberated on acidifying a xanthate, and the free acid easily decomposes into ethyl alcohol and carbon disulphide. Carbon disulphide is found to be oxidised by hypochlorous acid, alkali hypochlorite or alkali hypobromite. The resulting solution was observed to contain sulphide, sulphate, formate and carbonate[4,5] but no quantitative data are available as the reaction appears to be too complicated. Chloramine-T resembles hypochlorite in many oxidation reactions. The procedure resulting from the present investigations offers a better and a more accurate method of determination of carbon disulphide, since 14 equivalents of the oxidant are consumed for every mole of carbon disulphide.

Iodimetric oxidation of xanthate in neutral solution to dixanthogen is a quantitative reaction which at present is used quite generally for the determination of xanthate or carbon disulphide.[6,7] The oxidant consumed in such a reaction is only 1 equivalent for 1 mole of xanthate or carbon disulphide, since the oxidation proceeds to the stage of formation of dixanthogen according to the equation:



$$2S{=}C\begin{matrix}\diagup SK\\ \diagdown OEt\end{matrix} + I_2 \longrightarrow 2KI + S{=}\underset{OEt}{\underset{|}{C}}{-}S{-}S{-}\underset{OEt}{\underset{|}{C}}{=}S$$

Experimental results obtained for the determination of xanthate by this method are also given in Table I.

The dixanthogen produced in the above reaction remains in suspension since it is insoluble in water, and further oxidation does not take place with iodine. However, in the homogeneous medium produced by the addition of the alcohol, chloramine-T brings about further oxidation of dixanthogen. The chloramine-T method has therefore several advantages over the conventional methods.

Chloramine-T has been suggested[8] as a suitable oxidant for xanthates, the titrations with chloramine-T being taken to a bleached end-point, with methyl red as indicator for clear solutions and indigo carmine for coloured solutions. In this oxidation Afanasev observes that 1 equivalent of chloramine-T is consumed per mole of xanthate. In the light of the present observation it is more convenient to treat the xanthate with excess of chloramine-T and determine the excess iodimetrically than to use direct titration of xanthate against chloramine-T.

The determination of carbon disulphide in an aqueous solution can also be carried out as accurately as by the method described by Bang and Szybalski.[9] For instance the solubility of carbon disulphide at 25° in water was found to be 203 mg per 100 g of saturated solution by the chloramine-T method. This compares favourably with the value reported in literature[10] (217 mg/100 g of saturated solution at 20° and 195 mg/100 g of saturated solution at 30°). It should be noted that for carbon disulphide in aqueous medium it is necessary to add a fairly large amount of alcoholic potash to convert it into xanthate. In the present experiment 5 ml of a saturated solution of carbon disulphide in water were treated with 20 ml of alcoholic potash.

Acknowledgement—The authors wish to express their grateful thanks to Prof. M. R. A. Rao for his keen interest in this work.

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Summary—Carbon disulphide, on treatment with alcoholic potash, can readily be oxidised quantitatively by chloramine-T, converting all the sulphur to sulphuric acid. Fourteen equivalents of the oxidant are consumed for every mole of carbon disulphide. Since excess of chloramine-T may be determined iodimetrically, this reaction may be used for the determination of carbon disulphide. It may also be applied to the determination of xanthates.

Zusammenfassung—Schwefelkohlenstoff, in alkoholischer Kalilauge, wird leicht durch Chloramin-T oxydiert. Die Oxydation ist quantitativ und führt zur Bildung von Schwefelsäure wobei 14 Aquivalente Oxydans per Mol Schwefelkohlenstoff verbraucht werden. Da ein Überschuss von Chloramin-T leicht iodometrisch bestimmt werden kann, ist die Reaktion eine geeignete Grundlage zur Titration von Schwefelkohlenstoff. Auch Xanthate können auf diesem Wege bestimmt werden.

Résumé—Le sulfure de carbone, traité avec la potasse alcoolique, peut être facilement oxydé de manière quantitative par la chloramine T, tout le soufre étant transformé en acide sulfurique. Quatorze équivalents de l'oxydant sont consommés par chaque mole de sulfure de carbone. Comme l'excès de chloramine T peut être déterminé par iodométrie, cette réaction peut être utilisée pour le dosage du sulfure de carbone. Elle peut aussi être appliquée au dosage des xanthates.

REFERENCES

[1] K. Sharada and A. R. Vasudeva Murthy, paper in preparation.

[2] A. R. Vasudeva Murthy and B. Sanjiva Rao, *Proc. Ind. Acad. Sci.*, 1952, **35A**, 7.

[3] E. Bishop and V. J. Jennings, *Talanta*, 1958, **1**, 197.

[4] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. VI, Longmans Green and Co. London, 1925, 111.

[5] W. M. Dehn, *J. Amer. Chem. Soc.*, 1909, **31**, 1229.

[6] M. P. Matuszak, *Ind. Eng. Chem. Anal.*, 1932, **4**, 98.

[7] S. Dal Nogare, *Organic Analysis*, Vol. I, Interscience Publishers, New York, 1953, p. 364.

[8] B. N. Afanasev, Zavodskaya Lab., 1949, **15**, 1271. *Chem. Abs.*, 1950, **44**, 3843.

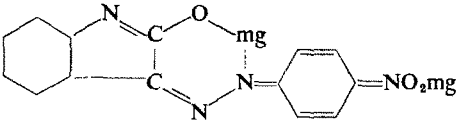
[9] N. H. Bang and W. Szybalski, *Acta Chemica Scand.*, 1949, **3**, 926.

[10] A. Seidell, *Solubilities of Inorganic and Metal Organic Compounds*, Vol. I. D. Van Nostrand Co. Inc., New York, 1940, p. 238.

A selective spot test for isatin

(*Received* 11 *April* 1960)

It has been observed that a blue precipitate is formed by addition of the violet alkaline solution of isatin-β-4-nitrophenylhydrazone to an aqueous solution of a magnesium salt. This reaction, which occurs also in ammoniacal medium, seems to be specific for magnesium ions.* It is probable that the essential part of the blue product is the chelate compound where the enolised CO and NO_2 groups



(mg = $\frac{1}{2}$Mg)

of isatin and 4-nitrophenylhydrazine, respectively, react with magnesium. A chelate binding of this kind may also be established through chemical adsorption of the hydrazone on the surface of magnesium hydroxide or oxide leading to a colour lake. It is consonant with this assumption that moist $Mg(OH)_2$ or ignited MgO turns blue in contact with an alcoholic or ethereal solution of isatin-β-4-nitrophenylhydrazone.

Due to the fact that this hydrazone reagent for magnesium is easily obtained by interaction of 4-nitrophenylhydrazine with isatin, a selective spot test for the latter can be based on the formation of the blue product. It may be expected that derivatives of isatin which condense with 4-nitrophenylhydrazone will behave like the parent compound.

Procedure: Heat, in a test tube, a small amount of the solid test material or a drop of its solution with 1 drop of an alcoholic solution of 4-nitrophenylhydrazine for 5–10 min. After cooling, add 1 drop of 10% sodium hydroxide and 1 drop of 1% magnesium nitrate solution. A positive response is indicated by the appearence of a blue precipitate. When the amount of isatin is less than 20 μg, extraction with ether, to dissolve the excess nitrophenylhydrazine, is recommended.

Limit of identification: 0·5 μg isatin.

The procedure given here also permits the detection of 2 μg of 4-nitrophenylhydrazine after condensation with excess isatin.

Acknowledgement—We thank the Conselho Nacional de Pesquisas for financial support.

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Résumé—Le sulfure de carbone, traité avec la potasse alcoolique, peut être facilement oxydé de manière quantitative par la chloramine T, tout le soufre étant transformé en acide sulfurique. Quatorze équivalents de l'oxydant sont consommés par chaque mole de sulfure de carbone. Comme l'excès de chloramine T peut être déterminé par iodométrie, cette réaction peut être utilisée pour le dosage du sulfure de carbone. Elle peut aussi être appliquée au dosage des xanthates.

REFERENCES

[1] K. Sharada and A. R. Vasudeva Murthy, paper in preparation.
[2] A. R. Vasudeva Murthy and B. Sanjiva Rao, *Proc. Ind. Acad. Sci.*, 1952, **35A**, 7.
[3] E. Bishop and V. J. Jennings, *Talanta*, 1958, **1**, 197.
[4] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. VI, Longmans Green and Co. London, 1925, 111.
[5] W. M. Dehn, *J. Amer. Chem. Soc.*, 1909, **31**, 1229.
[6] M. P. Matuszak, *Ind. Eng. Chem. Anal.*, 1932, **4**, 98.
[7] S. Dal Nogare, *Organic Analysis*, Vol. I, Interscience Publishers, New York, 1953, p. 364.
[8] B. N. Afanasev, Zavodskaya Lab., 1949, **15**, 1271. *Chem. Abs.*, 1950, **44**, 3843.
[9] N. H. Bang and W. Szybalski, *Acta Chemica Scand.*, 1949, **3**, 926.
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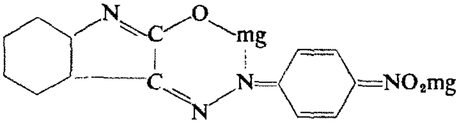

(mg = ½Mg)

of isatin and 4-nitrophenylhydrazine, respectively, react with magnesium. A chelate binding of this kind may also be established through chemical adsorption of the hydrazone on the surface of magnesium hydroxide or oxide leading to a colour lake. It is consonant with this assumption that moist $Mg(OH)_2$ or ignited MgO turns blue in contact with an alcoholic or ethereal solution of isatin-β-4-nitrophenylhydrazone.

Due to the fact that this hydrazone reagent for magnesium is easily obtained by interaction of 4-nitrophenylhydrazine with isatin, a selective spot test for the latter can be based on the formation of the blue product. It may be expected that derivatives of isatin which condense with 4-nitrophenylhydrazone will behave like the parent compound.

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The procedure given here also permits the detection of 2 μg of 4-nitrophenylhydrazine after condensation with excess isatin.

Acknowledgement—We thank the Conselho Nacional de Pesquisas for financial support.

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Summary—Isatin may be detected by conversion to isatin-β-4-nitrophenylhydrazone and reaction of the product with magnesium hydroxide to give a blue precipitate. The limit of identification of the test is 0·5 μg isatin.

Zusammenfassung—Isatin kann nachgewiesen werden durch Überführung in Isatin-β-4-nitrophenylhydrazon und Umsetzung dieses Produktes mit Magnesiumhydroxyd unter Bildung eines blauen Niederschlages. Die Nachweisgrenze ist 0·5 μg Isatin.

Résumé—L'isatine peut être décelée par transformation en isatine-4- nitrophénylhydrazone et réaction du produit obtenu avec 'hydroxyde de magnésium pour donner un précipité bleu. La limite d'identification de l'essai est de 0,5 μg d'isatine.

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* A paper on this subject will be presented by D.G. after finishing pertinent experiments.

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LETTERS TO THE EDITOR

Quantitative oxidations by potassium ferricyanide

SIR:

WITH the enormous progress of analytical chemistry, reviews of its various fields become more and more important. It is very necessary, however, that these reviews should reflect correctly the progress in the branches of analytical chemistry with which they are concerned, and their present state. The paper by B. R. Sant and S. B. Sant in *Talanta*[1] repeatedly gives rise to misunderstandings, regarding which we feel it necessary to comment.

In the first part of the Review the authors mention that oxidations by ferricyanide are slow and incomplete, but that they can *generally* be accelerated by using osmium tetroxide as a catalyst. Here they refer to the work of K. Gleu. It is well known, however, that K. Gleu observed the catalysing effect of osmium tetroxide only in the case of the reaction between ferricyanide and arsenite. The general catalysing effect of osmium tetroxide was dealt with elsewhere[2] by the present author.

Determinations by ferricyanide are divided by Sant and Sant into two groups, direct and indirect measurements. They have erroneously classified methods recently developed for the determination of various inorganic sulphur compounds[3,4] within the group of indirect determinations, although from papers published on this subject it is quite obvious that these are direct procedures. The Reviewers' statement regarding simultaneous determination of sulphur compounds is somewhat surprising. They write: "It is not clear if the above sulphur compounds can be analysed when present together." But in the short communication referred to[3] there is a clear description of the method applied to simultaneous determination of a variety of sulphur compounds.

The section dealing with the arsenometric determination of ferricyanide also calls for comment. The present author has described[5] the arsenometric determination of ferricyanide in presence of OsO_4. But one of the reviewers, B. Suseela Sant, while referring to our earlier paper, has again described the arsenometric determination of ferricyanide[6], with the only "modifications" that titration of ferricyanide is carried out, not in 2-3*N* NaOH, but in 1-2*N* NaOH concentration, and at room temperature instead of at 50°-55°. (The citation of the original paper is not correct.[6])

The question arises as to whether such slight changes in a procedure warrant a fresh scientific publication, when the only result of the modification is that the rate of the reaction between ferricyanide-arsenite becomes *slower* and the determination requires *a longer time* (instead of 5-6 min, 15-20 min!). And yet the Reviewers[1] write that S. B. Sant first applied the catalytic effect of OsO_4 to the arsenometric determination of ferricyanide and that this procedure is "*simpler and more rapid*".

In conclusion, it may be noted that the determination of selenite by ferricyanide was first published, not by the present author, as the Reviewers state,[1] but almost simultaneously and, in fact, a few months earlier, by their compatriots, G. S. Deshmukh and M. G. Bapat.[7]

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8 *April* 1960

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REFERENCES

[1] B. R. Sant and S. B. Sant, *Talanta*, 1960, **3**, 261.
[2] F. Solymosi, *Naturwiss.*, 1957, **44**, 374.
[3] F. Solymosi and A. Varga, *Analyt. Chim. Acta*, 1957, **17**, 608.
[4] *Idem, Acta Chim. Hung.*, 1959, **20**, 295, 339.
[5] F. Solymosi, *Magyar Kémiai Folyóirat*, 1956, **62**, 318; *Acta Chim. Hung.*, 1958, **16**, 267.
[6] S. B. Sant, *Z. Analyt. Chem.*, 1959, **168**, 112.
[7] G. S. Deshmukh and M. G. Bapat, *ibid.*, 1957, **156**, 273.

Quantitative oxidation by potassium ferricyanide

SIR,

IN the first part of our article,[1] only Gleu's reference was cited in order to draw attention to the fact that he, in 1933, first observed the catalysing effect of osmium tetroxide in ferricyanide oxidation. All other references, based essentially upon this observation, were cited at relevant places when considered necessary. In 1955, B. Suseela[2] reported in detail the use of osmium tetroxide as a catalyst to initiate and catalyse the quantitative oxidation of thiocyanate by ferricyanide to sulphate and cyanate. After Gleu's observation, this was perhaps the first report on the application of osmium tetroxide as a catalyst in quantitative ferricyanide oxidation. It is surprising that this article is not referred to in a note[3] by F. Solymosi in 1957.

The short communication[4] suggesting analysis of sulphur compounds when present together does not contain any data in support of the suggestion.

The paper by S. B. Sant[5] in 1959 on electrometric titration of ferricyanide by hydrazine sulphate and arsenic^{III} was a result of her independent investigations carried out during 1953–1956 and formed a part of her Ph.D. thesis. This fact is clearly mentioned as a footnote in the article.[5] Naturally, the above work is not a "modification" of an earlier procedure. Furthermore, nowhere in the article[1] is it written or even implied that "S. B. Sant first applied the catalytic effect of OsO_4 to the arsenometric determination of ferricyanide." In our opinion, an electrometric titration, and for that purpose any titration, is undoubtedly more convenient and easier to manipulate if it can be performed at room temperature (25–30°).

In addition to the question raised by F. Solymosi "whether slight changes in a procedure warrant a fresh publication", a further question arises, *viz.*, whether the same work by the same author need be published in two different journals.[6,7]

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REFERENCES

[1] B. R. Sant and S. B. Sant, *Talanta*, 1960, **3**, 261.
[2] B. Suseela, *Z. analyt. Chem.*, 1955, **145**, 175.
[3] F. Solymosi, *Naturwiss.*, 1957, **44**, 374.
[4] F. Solymosi and A. Varga, *Analyt. Chim. Acta*, 1957, **17**, 608.
[5] S. B. Sant, *Z. analyt. Chem.*, 1959, **168**, 112.
[6] F. Solymosi, *Analytical applications of the sodium arsenite-ferricyanide reaction catalysed by osmium tetroxide*, *Magyar Kém. Foly.*, 1956, **62**, 318.
[7] F. Solymosi, *Analytical applications of the reaction between sodium arsenite and iron(III) cyanide catalysed by osmium tetroxide*", *Acta Chim. Hung.*, 1958, **16**, 267.

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BOOK REVIEWS

Contributi Teorici E Sperimentale Di Polarografia: Volume IV. Pp. 361. Italian National Research Council, Rome, 1959. Lire 2,500.

THIS is the fourth volume of collections of papers on theoretical and experimental polarography, relating to work in the Polarographic Centre of the Italian National Research Council at the University of Padua and to the papers read at courses organised, at Bressionone, by the Polarographic Centre.

The introduction to the volume is by Professor Giovanni Semerano, the Director of the Polarographic Centre and is given in four languages (Italian, French, English and German). Twenty-one papers are included of which ten are in Italian, five in English, four in French and two in German. Each paper is accompanied by adequate summaries in the four languages.

The first paper, by Semerano, is a report on the work of the Polarographic Centre, from 1952 to 1958. It includes details of the diverse subjects on which research has been carried out and lists the resulting publications. The work of the Research Institutes and laboratories in Italy in the field of polarography is also mentioned. The second paper describes the well-known summer courses at Bressionone and gives lists of lecturers, participants and subjects discussed. The third paper is concerned with the purposes and organisation of the specialist schools of analytical and nuclear chemistry in relation to the summer course. The other papers deal with polarographic methodology and instrumentation, theoretical and kinetic studies, the behaviour of inorganic and organic substances and analytical applications. Finally, a number of surveys of advances in the application of polarography to various fields of analytical chemistry are presented.

The high standard of the work is assured by the presence in the list of authors, among others, of authorities such as Delahay (U.S.A.), Milner (Great Britain), Tirouflet (France) and Berg (Germany). All the original papers are good and, although there is little new in the reviews, they form a comprehensive collection. The book will be valuable to polarographers and should also prove a useful source of information for the non-specialist.

G. F. REYNOLDS

Trace Techniques using the K·1000 Cathode Ray Polarograph. Volume I, by J. HETMAN, F.R.I.C. Pp. 48. Southern Instruments Limited, Camberley, Surrey. 25s.

THIS book is a collection of thirty methods, developed by the author, for the determination of trace constituents and impurities in a wide variety of materials. Both inorganic and organic substances have received attention. Many of the methods contain novel features and will be of wide interest. They include a number of importance to food and public analysts, such as the determination of vitamin C in fruits and fruit juices, saccharin in non-alcoholic drinks, arsenic in plant materials, lead (in the presence of copper) in cocoa, cyanide in water and iron in blood serum and liver. Metallurgical methods include the simultaneous determination of copper, nickel and cobalt impurities in iron, of copper, lead and zinc in manganese brass, copper and lead in leaded steel, lead in brasses and bronzes and the simultaneous determination of beryllium, aluminium and lead. Those of interest to the Plastics Industry are the simultaneous determination of fumaric and maleic acids, the determination of *p*-chlorobenzyl cyanide in a polymerisation mixture and trace metal impurities in P.V.C. There are also methods connected with explosive and pyrotechnic materials. A bibliography, giving some background information and references to methods of allied interest, is appended.

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The introduction to the volume is by Professor Giovanni Semerano, the Director of the Polarographic Centre and is given in four languages (Italian, French, English and German). Twenty-one papers are included of which ten are in Italian, five in English, four in French and two in German. Each paper is accompanied by adequate summaries in the four languages.

The first paper, by Semerano, is a report on the work of the Polarographic Centre, from 1952 to 1958. It includes details of the diverse subjects on which research has been carried out and lists the resulting publications. The work of the Research Institutes and laboratories in Italy in the field of polarography is also mentioned. The second paper describes the well-known summer courses at Bressionone and gives lists of lecturers, participants and subjects discussed. The third paper is concerned with the purposes and organisation of the specialist schools of analytical and nuclear chemistry in relation to the summer course. The other papers deal with polarographic methodology and instrumentation, theoretical and kinetic studies, the behaviour of inorganic and organic substances and analytical applications. Finally, a number of surveys of advances in the application of polarography to various fields of analytical chemistry are presented.

The high standard of the work is assured by the presence in the list of authors, among others, of authorities such as Delahay (U.S.A.), Milner (Great Britain), Tirouflet (France) and Berg (Germany). All the original papers are good and, although there is little new in the reviews, they form a comprehensive collection. The book will be valuable to polarographers and should also prove a useful source of information for the non-specialist.

G. F. REYNOLDS

Trace Techniques using the K·1000 Cathode Ray Polarograph. Volume I, by J. HETMAN, F.R.I.C. Pp. 48. Southern Instruments Limited, Camberley, Surrey. 25s.

THIS book is a collection of thirty methods, developed by the author, for the determination of trace constituents and impurities in a wide variety of materials. Both inorganic and organic substances have received attention. Many of the methods contain novel features and will be of wide interest. They include a number of importance to food and public analysts, such as the determination of vitamin C in fruits and fruit juices, saccharin in non-alcoholic drinks, arsenic in plant materials, lead (in the presence of copper) in cocoa, cyanide in water and iron in blood serum and liver. Metallurgical methods include the simultaneous determination of copper, nickel and cobalt impurities in iron, of copper, lead and zinc in manganese brass, copper and lead in leaded steel, lead in brasses and bronzes and the simultaneous determination of beryllium, aluminium and lead. Those of interest to the Plastics Industry are the simultaneous determination of fumaric and maleic acids, the determination of *p*-chlorobenzyl cyanide in a polymerisation mixture and trace metal impurities in P.V.C. There are also methods connected with explosive and pyrotechnic materials. A bibliography, giving some background information and references to methods of allied interest, is appended.

The methods are in note form giving, in addition to brief details of procedure and interpretation of results, essential information such as preparation of sample, base electrolyte, reference electrode employed and instrumental settings. Specimen polarograms are included in each case.

The methods are easy to follow and contain sufficient details for direct application. Inevitably, however, they suffer in some cases from the brevity of the treatment and a number of errors are present. The most persistent is the use of "basic" instead of "base" electrolyte, which is an error sometimes encountered in papers in English in foreign journals. The heading "Basic Electrolyte" is itself sometimes misleading, since the materials listed under it in several methods do not have this function. It is also incorrect to refer to the current flowing at the peak of the wave as the diffusion current, since the current flowing at this point is not diffusion controlled. It is more usual to use the term "peak current".

The book would have been improved by the inclusion of an Introduction, setting out objectives and giving brief details of the principles and advantages of cathode ray polarography. The omission of this is not important to the specialist, but it would have helped non-specialist and potential users to realise that this is not concerned with a new method involving special and exclusive principles, but is an advance in polarographic instrumentation offering greatly increased sensitivity and rapidity of operation. The very low limits of detection that can be achieved in the determinations described have not been emphasised in the methods themselves and can only be inferred from the specimen polarograms and concentrations of the calibration solutions.

No previous collection of general methods for a single polarographic technique has been published in this way and the author is to be congratulated on his initiative. It makes an important contribution to the literature of the subject and he will undoubtedly receive the compliment of imitation. The book will be of great value, not only to the specialist, but also to polarographers and analytical chemists in general, who will find much of the information applicable outside the present field.

G. F. REYNOLDS

Instrumental Methods of Chemical Analysis: GALEN W. EWING. Second Edition, McGraw-Hill Publishing Company Ltd., New York, Toronto, London, 1960. 69s. Pp. 437. Name and subject indexes.

THE first edition of this book appeared in 1954; that a second edition has been called for is an indication that it has fulfilled its author's aim—"To describe the important analytical methods with sufficient theory for their comprehension and to present significant design features of representative apparatus." The book has been generally brought up to date and sections on nuclear magnetic resonance, spectroscopy, gas chromatography, electro-chromatography (*i.e.* electrophoresis) and electronic circuitry are now included.

The book is not intended as a reference work on "instrumental analysis." It is planned for use in colleges by "upper level undergraduates or first year graduate classes." For this reason each chapter includes a series of questions, mostly numerical in nature, and any student who conscientiously reads the text, carries out the recommended practical exercises and finally works through some of the problems will acquire a firm grip on the principles involved. The bibliography to each chapter gives some general guidance to the best monographs and reviews as well as a selection of references to original papers. This is a most useful feature, particularly in a students' book.

Not all the chapters are equally good and this is inevitable, as no one man can be expert in every field of instrumental analysis. The chapters on chromatography and ion-exchange, on extraction analysis, on polarimetry and on refractivity and optical dispersion are not up to the level of some of the others and one would guess the author's real interest is in the more complex types of apparatus. An unusual and commendable feature is a chapter on "General considerations in analysis"; this gives diagrams showing the relative sensitivity of various methods for a number of inorganic elements and very rightly includes "personal preference" as a valid factor in deciding what method to employ. The author does not sufficiently emphasise the fact—well-known to practising analysts, and often ignored by instrument men and other enthusiasts—that most of the methods described require

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The re-issue in U.S.A. of this undoubtedly successful book raises once again, in the mind of an English reviewer, the difficult query "How much instrumentation should be taught to university chemical students?" When one considers a modern research establishment, in which almost every laboratory seems to have its quota of electronic instruments, one is inclined to say that every graduate ought to have some knowledge of the subject; perhaps the proper place for teaching it is in the physics course. No doubt the physics curriculum is as over-loaded as the chemistry curriculum but it seems appropriate to teach the use of instruments that simply make physical measurements as part of physics, even though their applications are so largely chemical. This would raise great difficulties in co-ordinating chemistry and physics courses, and from a practical point of view it might seem that the chemistry course is the proper place. The tutor or the professor in either case will presumably say "Yes, we can arrange to teach the elements of instrumentation, but what would you like us to leave out? Qualitative analysis, perhaps, or preparative organic chemistry, or the phase rule, or even the quantum theory; after all very few chemists ever make any use of it. But we shall have to leave *something* out."

Chemistry is still an experimental science for most practising chemists. Few of them in the early stages of their career succeed in deserting the laboratory entirely, and nowadays, when physical instruments have become tools of the trade as important as the burette or the crucible, it seems desirable that the graduate should know something about them. The reviewer has not the temerity to suggest what should be left out so that this new subject can be carried by the already over-loaded curriculum. (It is, of course, arguable that it is the business of the university to teach fundamentals and to leave the practical aspect in a secondary position.) For the post-graduate student who proposes to become an analyst, some aquaintance with the physical instruments available to him seems essential and he should have a real appreciation of the potentialities of these devices before he leaves college. In fact, he is probably wasting his time if his post-graduate course is in "pure" analytical chemistry. The classical methods are certainly not obsolete, but inevitably occupy a much smaller percentage of the analyst's time and thoughts than they did twenty or even ten years ago and any system of training must take this into account. The number of useful non-specialised textbooks is quite small. Professor Ewing's work is certainly among the number; it is perhaps inevitable that at the present time it should be somewhat expensive. It would be desirable in the British part of the English-speaking world if a similar book were available in which the instruments described are those currently in use in this country.

H. N. WILSON

Proceedings of the International Symposium on Microchemistry: Held at Birmingham University, August 1958. Symposium Publications Division, Pergamon Press, London and New York, 1960. Pp. xxvi + 583. 100s.

THIS substantial volume contains the material of sixty-one papers which were presented at the Birmingham Symposium. These have been arranged into groups, although, as is stated, many papers could be included in more than one group. The headings of these groups are, qualitative microanalysis, the decomposition of organic matter, weighing, the determination of elements and groups in organic materials, the determination of physical constants, biochemical methods, chromatography and ion-exchange, polarography, radiochemical methods, spectrochemical methods, titrimetry, complexometry, industrial applications of microchemistry, teaching, apparatus, and Great Britain's contribution to microchemistry.

The contents of the majority of the papers are of a high standard, as is to be expected, since many were contributed by leading world authorities in their respective fields. For example, the plenary lectures were delivered by Feigl, Lieb, Benedetti-Pichler and Belcher.

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Many items of "stop press" news at the time of the symposium have since appeared in other journals and it is unfortunate that the Proceedings could only now be published, eighteen months after the symposium. This delay detracts somewhat from the value of the book.

However it is well-produced and the format good. It is relatively free from errors, although in a book of this size some are to be expected, and do occur. Mistakes which require correction are formula C on p. 12 where there is a tervalent carbon atom, "pertitanic acid" on p. 44 (last paragraph) which presumably should be replaced by "pervanadic acid", and Fig. 1 on p. 480 where material mentioned in the text is not shown in the figure.

The price is rather high for the pockets of many chemists, but, for those who wish to acquaint themselves with recent developments in microchemistry, the book is certainly recommended. It should prove to be a popular acquisition for most scientific libraries.

J. B. HEADRIDGE

Separation and Identification of Food Colours Permitted by the Colouring Matters in Food Regulations 1957. Association of Public Analysts, Bank Chambers, 16, Southwark Street, London S.E.1., England. Pp. vi + 31. 1960. 21s., postage 9d.

THE object of this monograph is to present the results of work carried out by a committee of Members of the Association of Public Analysts on the separation and identification of colours used in foodstuffs following the coming into force in Great Britain of the "Colouring Matter in Food Regulations 1957". Before the introduction of this legislation manufacturers were at liberty to use any colouring matter provided it was not prohibited by the Public Health (Preservatives etc. in Food) Regulations, 1925 to 1953 or contravened the provisions of sections 1 and 3 of the Food and Drugs Act, 1938. The new legislation restricts food manufacturers to a list of specified colours and thus imposes on Public Analysts and others the task of examining large numbers of samples of food containing single colours or mixtures of colours.

The general scheme of analysis proposed consists of extraction of the colour, separation of the colours if more than one is present, and finally, identification.

Although foods vary in nature it has been possible to divide them into four groups as far as the preliminary treatment to extract the colouring matter is concerned. A table containing the results of examining 368 foodstuffs shows that 49·7% contained one added colour, 42.7% two colours and 7·6% three or more colours. As the permitted water soluble colours are all acidic they are extracted on wool from acid solution. They are then stripped from the wool and finally separated by paper chromatography. Identification of the recovered colours is accomplished by chromatography, spectrophotometry, or chemical means. R_F values of the water soluble colours in a series of six solvents are given. Absorption curves of all the permitted colours are collected together at the end of the volume.

A separate section is devoted to the two oil-soluble colours: oil Yellow GG and oil Yellow XP.

This is a book which can be thoroughly recommended to all those concerned in the examination of colouring matter in food, and the methods outlined will no doubt rapidly become standard. The book is also likely to be of interest to a wider field of readers outside the food industry.

The standard of production is on the whole good, the illustrations and absorption curves are clear, but as the book will undoubtedly find its way to the laboratory bench it is unfortunate that the binding has not been made more robust to stand up to the hard wear it will receive.

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A. J. HOWARD

Automatic Titrators. J. P. PHILLIPS. Academic Press Inc., New York, 1959. Pp. viii + 225. $6.00.

AUTOMATIC analytical techniques for application in the laboratory and on the production plant, have made tremendous strides in the past 10 years. "Chemists of talent and originality can hardly fail to profit from the freedom from routine chores afforded by automatic instruments of all kinds." This quotation is from this excellent book on automatic titrators; it is a most readable review of their development up to 1958. The approach used is that of a chemist and the emphasis is on the performance and use of titrators and on instruments that are either simple or readily obtainable.

After a brief introduction, concerned mainly with the significance of automatic titration methods, the general considerations of titrator design are discussed in some detail. Backed by many references, this section of the book is factual and covers types of burette, instrumental indicators, recorders and controllers.

Sections then follow on potentiometric, amperometric, conductometric, photometric and coulometric titrators. Although the latter could have been placed in any of the other categories, according to which indication technique was used, the author has wisely treated them separately. Ideally suited to automation, coulometric titrators are now rapidly coming to the fore.

In dealing with fully automatic and continuous titrators the author is labouring under the disadvantage of the inadequacy of literature coverage. It is difficult to obtain practical evaluations of the majority of commercial titrators because they have not been in general use long enough. Thus, the Technican Auto-Analyser is dismissed in 9 lines of script. It is known in Great Britain that, particularly in biochemical laboratories, this instrument is proving a boon, saving both laboratory space and labour. This section, therefore, tends to be a recital of information published by the manufacturers, which the author rightly admits has obvious disadvantages.

A chapter describing commercially available titrators with a list of applications completes the survey.

The book provides a concise account of the subject and, being fully referenced, should find a ready market amongst forward-thinking analysts and those who employ them and have to "foot the bill." As the author points out, obsolescence in automatic titrators is exceedingly rapid at the present time, so that some parts of the book will soon be out-dated. Nevertheless, the book gives a worthwhile grounding on the subject.

R. M. PEARSON

Talanta, 1960, Vol. 4, pp. 218–219. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The following meetings have been arranged:

Wednesday 22 *June* 1960: **Society for Analytical Chemistry,** Microchemistry Group. London Discussion Meeting on *The Direct Determination of Oxygen.* "The Feathers", Tudor Street, London, E.C.4. 6.30 p.m. Discussion will be opened by Mr. D. W. Wilson, M.Sc., F.R.I.C.

Wednesday–Friday 12–14 *October* 1960: **Oak Ridge National Laboratory:** Fourth Conference on *Analytical Chemistry in Nuclear Reactor Technology* and First Conference on *Nuclear Reactor Chemistry.*

The Oak Ridge National Laboratory has announced that a combined meeting will be held at Gatlinburg, Tennessee, on October 12, 13 and 14, 1960, which will include the Fourth Conference on Analytical Chemistry in Nuclear Reactor Technology and the First Conference on Nuclear Reactor Chemistry.

The general theme of that portion of the meeting pertaining to analytical chemistry will be instrumentation and methods for the determination of minor and trace components in nuclear fuels, coolants, moderators or related materials. Specific sessions are planned on advances in methods for the analysis of UO_2-base fuels and on in-line instrumentation and methods for the analysis of gas and liquid streams in reactors and test devices.

The contribution of papers pertaining to these or closely related subjects is solicited. Improvements or new concepts in instrumentation or in methods of chemical analysis are especially sought. Theoretical or review papers on topics within the scope of the agenda may, however, be of equal interest and will be given careful consideration.

To facilitate the preparation and the distribution of the programme well in advance of the meeting and compilation of abstracts for use at the conference, authors are requested to submit abstracts of about 500 words not later than August 1, 1960, and to indicate the time, not to exceed 25 minutes, required for presentation of their paper.

The Proceedings of the Fourth Conference on Analytical Chemistry in Nuclear Reactor Technology will be published. Manuscripts must be submitted at the time of the conference in order to be included in the published Proceedings.

Enquiries concerning the meeting in general and communications relative to the analytical chemistry section, including the submission of abstracts, should be addressed to: C. D. Susano, Oak Ridge National Laboratory, P.O. Box Y, Oak Ridge, Tennessee.

For information concerning accommodation or for reservations, write to: Reservation Services, Chamber of Commerce, Gatlinburg, Tennessee.

The tentative programme for the analytical chemistry section of the conference is:

Wednesday 12 *October*
Morning—*Activation and Non-destructive Methods of Analysis*
Afternoon—*Radiochemical Analysis, including Applications of Tracers*

Thursday 13 *October*
Morning—*Continuous Analysis of Radioactive Liquid and Gas Streams*
Afternoon—*Non-radiochemical Methods for Trace Analysis of Reactor Materials*

Friday 14 *October*
Morning—*Analysis of Diverse Reactor Fuels and Fertile Materials*
Afternoon—*Application of Analytical Chemistry in Preparation, Evaluation and Use of* UO_2-*Base Fuels*

Monday-Saturday 24-29 *April* 1961: **Hungarian Chemical Society:** *Analytical Congress.*

The Analytical Section of the Hungarian Chemical Society, sponsored by the Hungarian Academy of Sciences, has arranged an Analytical Congress, with international participation, to be held from April 24 to 29, 1961, in Budapest.

The lectures will comprise the whole field of analytical chemistry. Plenary and section lectures will be delivered for 4 days. The sections will be organized according to papers received. Papers in any language will be accepted, although it is desirable to use English, Russian, German or Hungarian. Registration of plenary and short papers with the Organising Committee is requested not later than September 15, 1960.

In order to proceed with arrangements for the Congress, the Organising Committee requests registration of attendance—without any obligation—to be made not later than July 1, 1960.

A more detailed programme of the Congress will be available probably in October, together with details of accommodation, excursions, social events. After the Congress visitors will have the opportunity of touring Budapest and its surroundings and of visiting Lake Balaton.

All correspondence should be addressed to the Secretariat of the Hungarian Chemical Society, Budapest, V., Szabadsag ter 17, Hungary.

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

B.S. 1016: The analysis and testing of coal and coke: Part 14 (preliminary statement). The analysis of coal ash and coke ash. (Ref. PD 3714). Included in all copies of B.S. *1016: Part 15.* (Gratis)

B.S. 1016: The analysis and testing of coal and coke: Part 15: 1960. Fusibility of coal ash and coke ash. This deals with the determination of the deformation temperature, the hemisphere temperature and the flow temperature on samples of coal ash and coke ash. (Price 4s. 6d.)

B.S. 1428: Microchemical apparatus: Part D3: 1960. Micro-nitrometer (Pregl type). The micro-nitrometer specified is intended for use with the micro-Dumas nitrogen combustion train specified in *B.S. 1428: Part A2.* Full dimensions are specified, with tolerances given in some cases and "normal working tolerances" specified for the remainder. A porcelain stand and a potassium hydroxide levelling vessel with a porcelain support suitable for use with the nitrometer are described in one appendix: a stopcock leakage test procedure and notes on the method of use of the apparatus are given in other appendices. Detailed diagrams are provided for the nitrometer and ancillary equipment. (Price 4s.)

B.S. 1428: Microchemical apparatus: Part HI: 1960. Weighing vessels for microchemical analysis. This specifies five types of glass vessel: three sizes of weighing bottles with ground stopper, a weighing pig with ground cap, long-handled weighing tubes with and without ground cap, and a weighing tube with two ground caps. Details are given of construction (fully dimensioned drawings), finish and maximum weights. (Price 3s.)

B.S. 1728: Methods for the analysis of aluminium and aluminum alloys: Part II: 1960. Method for the determination of silicon (perchloric acid method). This specifies reagents required, recommended methods of samplings, and analytical procedure, for the determination of silicon in alloys having a silicon content from 0.1% to 24% or over. (Price 3s.)

Talanta, 1960, Vol. 4, p. 220. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

A critical review of methods of isolating and separating the six platinum metals. F. E. Beamish. (2 *April* 1960).

New redox systems—III: Indirect cerimetric determination of cobalt. František Vydra and Rudolf Přibil. (4 *April* 1960).

Analytical uses of bromine chloride: Determination of hydroxylamine: Contributions to the bromic acid-hydrochloric acid reaction. K. Burger, F. Gaizer and E. Schulek. (4 *April* 1960).

Cation-exchange studies of lead^{II} on Dowex 50W-X8: Separation from mixtures. Shripad M. Khopkar and Anil K. De. (5 *April* 1960).

Quantitative oxidations by potassium ferricyanide: F. Solymosi. (8 *April* 1960).

A specific spot test for isatin. F. Feigl and D. Goldstein. (11 *April* 1960).

Estimation of carbon disulphide by chloramine-T. V. R. Satyanarayana Rao and A. R. Vasudeva Murthy (12 *April* 1960).

Simply designed safety pipette. Tsutomu Momose. (19 *April* 1960).

Scintillation radioautography of tritium-labelled compounds on paper chromatograms. E. V. Parups, L. Hoffman and H. R. Jackson. (23 *April* 1960).

The sequential analysis of long-range fallout debris. George A. Welford, William R. Collins Jr, Robert S. Morse and Doris C. Sutton. (21 *April* 1960).

Die chelatometrische Titration des Titans in Gegenwart von Niob und Tantal. E. Lassner und R. Scharf. (23 *April* 1960).

Chlorite as an oxidising agent in titrimetric analysis. Jerzy Minczewski and Urszula Glabisz. (23 *April* 1960).

A new reducing agent: Reduction of vanadium^{IV} and uranium^{VI} with ferrous ion in catechol solution. John W. Miller. (25 *April* 1960).

Contributions au problème de la détermination du point d'équivalence—I: Une nouvelle méthode de calcul du point d'équivalence dans la titration linéaire. Candin Liteanu et Dumitru Cörmös. (30 *April* 1960).

Contributions au problème de la détermination du point d'équivalence—II: Une nouvelle méthode pour déterminer le coefficient réel d'asymmétrie dans la titration potentiométrique. Candin Liteanu et Dumitru Cörmös. (30 *April* 1960).

Contributions au problème de la détermination du point d'équivalence—III: Une nouvelle méthode pour le calcul du point d'équivalence dans la titration potentiométrique. Candin Liteanu et Dumitru Cörmös. (30 *April* 1960.)

PUBLICATIONS RECEIVED

The Radiochemistry of Cadmium. James R. DeVoe, U.S. Atomic Energy Commission, NAS-NS 3001, Jan. 1960. Pp. vi + 57. $0.75.

The Radiochemistry of Arsenic. Harold C. Beard. U.S. Atomic Energy Commission, NAS-NS 3002, Jan. 1960. Pp. vi + 27. $0.50.

The Radiochemistry of Francium. Earl K. Hyde. U.S. Atomic Energy Commission, NAS-NS 3003, Jan. 1960. Pp. vi + 34. $0.50.

Chromatographic Reviews, Vol. II. Editor M. Lederer. D. Van Nostrand Company, Ltd., London: Elsevier Publishing Company, Amsterdam, 1960. Pp. viii + 195. 46s.

Oxidation-Reduction Potentials of Organic Systems. W. Mansfield Clark. 1960.

Talanta, 1960, Vol. 4, pp. 221 to 226. Pergamon Press Ltd. Printed in Northern Ireland

THE DETERMINATION OF SULPHUR IN ORGANIC COMPOUNDS WITH METALLIC SILVER AS ABSORBENT

A CRITICAL EXAMINATION

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Summary—Interfering factors in the determination of microgram quantities of sulphur by the absorption on silver of the sulphur oxides produced during combustion of sulphur compounds have been isolated and eliminated. The method comprises "empty tube" oxidation, absorption of sulphur oxides on electrolytically prepared silver, and potentiometric titration of the silver ion equivalent to sulphur. The minimum limit of determination is 10–15 μg using a 25-mg sample, and the reproducibility about 3%.

INTRODUCTION

NUMEROUS methods have been reported in the literature for the determination of sulphur and chlorine, with metallic silver as the absorbing medium. The following recent references will provide an introduction to the literature on this subject. Stragend and Safford[1] describe procedures in which the sulphur is retained on silver gauze and determined gravimetrically. Kuck and Grim[2] extended the scope of the method by using a quartz-fibre balance to determine the small weight changes in the silver gauze when decimilligram samples were analysed. Removal of silver sulphate from the gauze by dissolving it in hot water, and subsequent titration of the silver ion with potassium iodide,[3] offered a more sensitive and rapid method of assay for low sulphur contents. Papers describing the titration technique were published by Vecera and Snobl[4], and Bladh, Karrman, and Andersson[5]. In both of these, experimental work led to the conclusion that the blank was too high and inconsistent to attempt the determination of sulphur in low concentrations. The method described by Kuck and Grim[2], however, does achieve determination in the sub-micro range (50–100 μg), although on a gravimetric basis. There seemed no reason, therefore, why the technique should not be capable of adaptation to the microgram range, using a titrimetric procedure, if the causes of the variable blank could be identified and eliminated. Mitsui and Sato[6] describe a special preparation of silver for the quantitative absorption of chlorine, and claim that it has an activity fifty times that of silver wool or silver gauze. Other workers, *e.g.* MacNevin[8], have reported that a similar preparation is necessary in the carbon and hydrogen determination to remove chlorine and sulphur. The information obtained from the literature is conflicting in that some workers report satisfactory results with silver gauze and others consider that specially prepared silver is necessary. With the exception of the method described by Kuck and Grim[2], the use of silver as an absorbent in the microgram range has not proved successful, because of the high and variable blanks obtained. The investigation was, therefore, based on isolating the causes of the blank, the reason for using specially prepared silver, and the sensitivity that could be obtained by the titrimetric potassium iodide procedure.

DEVELOPMENT OF METHOD

The first experimental work by the present author was carried out according to the publication by Zinneke[3], in which the sample is oxidised by passage over platinum gauze (650–700°) in a stream of oxygen, and the sulphur oxides are absorbed on silver gauze (450–500°). The silver sulphate was extracted with hot water and the silver ions titrated potentiometrically with $0{\cdot}01N$ potassium iodide solution, using a glass and silver electrode pair. Low results, of poor repeatability, were obtained on standard sulphur compounds, but the advantage of the extreme sensitivity of the potassium iodide titration procedure was realised. The low results could be attributed to one or more of the following factors, each of which will be treated separately:

(*a*) Incomplete removal of silver sulphate from the gauze.
(*b*) Incomplete oxidation of the sample.
(*c*) Inefficient absorption of sulphur oxides on the silver gauze.

(*a*) *Extraction of silver sulphate from silver gauze*

The possibility of errors due to incomplete extraction of silver sulphate was not suspected since frequent extraction of the silver with boiling water after a determination had been made yielded washings in which silver ions were not detected.

(*b*) *Oxidation*

Classical methods for oxidising organic compounds include the use of heated silica chips, porous silica plates, platinum contacts and platinum gauzes. In all cases combustion is carried out in a stream of oxygen. Some sulphur compounds are difficult to oxidise and instances have occurred in which the use of platinum has been inadequate. On the other hand, the oxidation efficiency of the "empty tube" combustion technique[7,9] is known to be good. In this procedure, the vapours of the sample are intimately mixed with oxygen in the turbulence caused by a series of quartz baffle plates inside the oxidation tube. The procedure is widely used in the determination of carbon, hydrogen, sulphur and halogens, and in practice it has been found that its reliability far exceeds that of other combustion-tube oxidation methods. Accordingly this technique was adopted, and its reliability for the oxidation of sulphur compounds merely checked by conventional titrimetric methods.

When the above technique was used in conjunction with silver gauze low results were again obtained. It was clear, therefore, that the silver gauze was not retaining sulphur oxides quantitatively.

(*c*) *Absorption of sulphur oxides by silver*

Literature references[6,8] already quoted emphasise the need to use specially prepared silver for the absorption of sulphur oxides and chlorine in microchemical combustion work. We have found in practice that this is most important in the case of sulphur. Commercially manufactured silver wool and silver gauze retained chlorine quantitatively, but under similar conditions silver sulphate recoveries were low.

Electrolytic silver was prepared according to the method of Mitsui and Sato[6]. Using this preparation, in which the large surface area provides much greater efficiency, theoretical recoveries of silver sulphate were obtained. The results of these analyses are recorded in Table I, and confirm the author's belief that the extraction technique is satisfactory.

In order to make this procedure applicable to the determination of microgram amounts of sulphur, the manipulation of the silver during and after analysis and its effect on the blank were investigated further.

Extraction of silver sulphate and blank control

The operating blank is dependent on the technique used to extract the silver sulphate, and includes the effects of the atmosphere on the silver and the quality of water used. Previous workers in this field[3–5] devised circulatory systems in which hot water flowed repeatedly over the gauze, and also made use of electric heating[5] during extraction. The same authors reported that heating the silver gauze in the absence of sulphur oxides gave rise to soluble silver ions. The possibility of the formation of soluble silver oxide led to experiments in which the gauze was blanketed with nitrogen. Similar blanks were obtained, and the authors concluded that the procedure was not applicable to accurate determination of microgram concentrations of sulphur.

Previous investigators make no mention of the quality of distilled water used in the determination, or the preparation of the silver for individual analyses. Distilled water may contain traces of impurity and although samples tested with $0{\cdot}1N$ potassium iodide may indicate a negligible blank (0·001 ml) this was found to be no criterion of suitability for the determination. The use of distilled water percolated over a mixed anion- and cation-exchange resin bed, and boiled before use, gave an immediate reduction in the blank. The only apparent explanation of this is that distilled water contains a small but variable amount of salts which react with silver to release soluble silver ion. Furthermore, if the silver was dried by heating directly after water washing, the blank increased. This again suggested the presence of traces of foreign ions left behind on the silver when the water evaporated, which would affect the next blank or determination.

Interference of this type was eliminated by using boiled percolated water, and by washing the silver with alcohol and ether between determinations.

Contrary to previous investigations we have found that the silver must be blanketed with nitrogen to prevent the formation of silver oxide during cooling from 450° to below 100°. This requirement in no way complicates the procedure, because the extraction technique uses nitrogen to agitate the wash water.

EXPERIMENTAL

Reagents

Ion-free water was obtained by percolating distilled water through a mixed-resin bed composed of Amberlite IR 120 and Amberlite IRA 400. *Electrolytic silver*[6] was prepared by electrolysis in 1 litre of 0·5% nitric acid containing 7 g of silver nitrate, the anode (silver plate 0·5 mm thick, 10 × 5 cm) and the cathode (silver wire 1 mm diam. × 15 cm long, twisted into a spiral) being connected to a 1·5 V dry cell. The electrolysis was continued for some time (overnight) and the crystalline product washed, dried and stored in nitrogen. Conventional reagents included oxygen, nitrogen (oxygen free), "Carbosorb" (soda-lime) 14–20 mesh, and standard $0{\cdot}1N$ solutions of silver nitrate and potassium iodide.

Apparatus

Fig. 1 shows the flow diagram of the apparatus.

Fill the preheater with wire-form copper oxide, and seal in the stopper. Connect the base of the rotameter to the oxygen line, and the top to one arm of the preheater. Insert the preheater in the back of the furnace. Fill the scavenging tube with "Carbosorb", seal the stopper with Kronig cement, and attach the tube to the free side of the preheater. Attach a stainless steel lead from the scavenger to the end of the combustion tube through a fitting rubber bung.

Insert the baffle tube in the front of the furnace and connect to the combustion tube via the B10 quartz joint. Raise the temperature of the large furnace to 900° and the other to 400–450°.

Preparation of the silver absorber: fill the end of the tube next to the tap with glass beads to a depth of 1½ in. Insert the silver loosely but evenly to provide a layer 2½ in. long. Attach the side arm to the nitrogen supply with rubber tubing. Mount the tube vertically in a clamp and wash the silver repeatedly with boiling percolated water. Admit nitrogen at such a rate that the liquid in the tube is agitated without overflowing. Drain off the final wash water, wash the silver with alcohol and ether and place it on top of the furnace to dry, maintaining the flow of nitrogen.

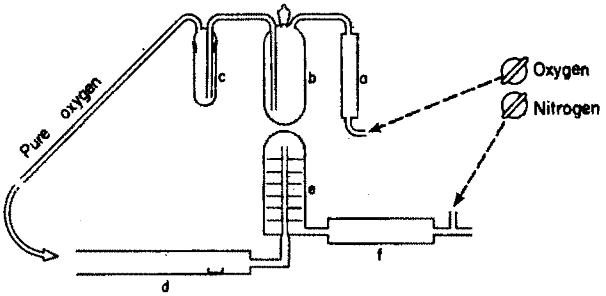

FIG. 1.—Flow diagram.
(a) Rotameter. (b) Preheater (900°). (c) Scavenger. (d) Combustion tube. (e) Baffle tube (900°).
(f) Absorption tube (400°–450°).

Insert the dry absorber in the small furnace, connect to the baffle furnace via the ground joint, and turn the tap to allow oxygen to pass through the tube. Adjust the oxygen flow to 50 ml/min.

Procedure

Weigh small samples (<10 mg) in platinum boats, and ignite in the normal way; for larger samples (10–25 mg) use a quartz sample tube. This consists of a small quartz test tube, 2 in. long and of such a diameter that it can be pushed into the combustion tube. Introduce the tube so that the open end faces the baffle furnace. Heat from the open end of the sample tube. Advance the burner towards the sample until decomposition begins. This will be indicated by deposition of carbon inside the sample tube. Do not advance the burner until the carbon begins to burn. Decompose the sample completely by moving the burner in this way until it reaches the closed end of the sample tube. Move the burner rapidly back along the combustion tube.

Two burners are used, one to ignite the sample and the other, which is attached to the furnace, to ignite the protruding end of the baffle tube. After the combustion, rotate the stationary burner to ignite the quartz between the baffle furnace and the silver absorber*.

Allow 5 minutes before detaching the absorber.

Turn the absorber tap to admit nitrogen, detach the absorber and mount it vertically in a small clamp. When the tube has cooled somewhat, cover the silver with boiling percolated water from the wash-bottle jet, using a pressure bulb, and allow the nitrogen to agitate the liquid. Drain into a 100-ml beaker. Repeat the washing until about 40 ml of water have been used.

Remove the beaker, cover the silver with alcohol and agitate, and repeat this operation with ether. Drain, and place on top of the furnace to dry. Maintain the flow of nitrogen.

Titrate the solution with $0{\cdot}1N$ potassium iodide, using a micro glass and silver electrode pair, a magnetic stirrer and a syringe burette.

$$0{\cdot}001\ \text{ml}\ 0{\cdot}1N\ \text{KI} \equiv 1{\cdot}6\ \mu\text{g of sulphur}$$

DISCUSSION

The results shown in Tables I and II are typical of many obtained with the proposed method during routine use for over a year. In Table II sample sizes are included

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* There is a tendency for SO_3 to condense.

with the results, which illustrate the reproducibility for low sulphur contents in small samples.

Interference from chlorine may be encountered in the microgram range, since the solubility of silver chloride in hot water may become significant. No effective method for overcoming this interference has been evolved.

TABLE I.—ANALYSIS OF STANDARD COMPOUNDS

Compound	Sulphur content	
	Theory %w	Found %w
Sulphonal	28·1	27·9
		28·1
Di-*p*-tolyl disulphide	26·6	26·2
		26·6
Thia*cyclo*hexane	31·4	31·2
		31·5
1 : 4-Dithia*cyclo*hexane	53·4	52·8
		53·6

TABLE II.—RESULTS OF ANALYSES SHOWING SAMPLE SIZE AND REPRODUCIBILITY

Material		Sample size, *mg*	Sulphur, %w
Oil	A	9·9	3·24
		13·2	3·22
	B	18·4	3·57
		14·1	3·63
	C	13·6	3·74
		16·2	3·76
Oil fraction	A	23·4	0·62
		15·3	0·68
	B	12·9	0·322
		18·7	0·316
Olefin	A	10·6	0·48
		12·2	0·45
	B	18·2	0·193
		15·3	0·188
	C	12·6	0·114
		20·2	0·111

The advantage of using the quartz sample-tube technique for larger samples is twofold. The combustion is much faster, and the danger of explosions when igniting volatile samples is eliminated. Moreover, the reproducibility of results for low sulphur contents is much better when this type of combustion is employed.

CONCLUSION

A procedure has been developed which overcomes the high and variable blanks previously reported when the silver absorption/potassium iodide method was applied to the microgram range of sulphur determinations. The blank is consistently low, and as little as 10–15 micrograms of sulphur can be determined. The use of boiled percolated water, and the drying of electrolytically prepared silver with organic solvents before use are recommended.

Acknowledgement—The author is indebted to the Directors of "Shell" Research Ltd. for permission to publish this article.

Zusammenfassung—Störungen bei der Bestimmung von Mikrogrammengen Schwefels nach der Silberabsorptionmethode wurden aufgezeigt und beseitigt. Die Methode verwendet Verbrennung im Leerrohr, Absorption des Schwefeldioxydes an elktrolytisch niedergeschlagenem Silber und potentiometrischer Titration de dem Schwefel äquivalenten Silbermenge. Die Mindestgrenze an bestimmbarem Schwefel liegt bei 10-15 Mikrogramm in einer Menge von 25 Milligramm Ausgangsmaterial.

Résumé—L'auteur a isolé et éliminé les facteurs gênants dans le dosage de microgrammes de soufre par la méthode d'absorption par l'argent. Cette méthode comprend une oxydation dans un tube sous vide, une absorption des oxydes de soufre sur de l'argent préparé électrolytiquement et un titrage potentiométrique de l'ion argent correspondant au soufre. La limite minimum du dosage est 10 à 15 µg en utilisant un échantillon de 25 mg.

REFERENCES

[1] G. L. Stragend and H. W. Safford, *Analyt. Chem.*, 1949, **21**, 625; 1951, **23**, 520.
[2] J. A. Kuck and E. C. Grim, *Mikrochim. Acta*, 1954, 201.
[3] F. Zinneke, *Z. analyt. Chem.*, 1951, **132**, 175.
[4] M. Večeřa and D. Šnobl, *Mikrochim. Acta* 1958, 28.
[5] E. Bladh, K. J. Karrman and O. Andersson, *ibid.*, 1958, 60.
[6] T. Mitsui and H. Sato, *ibid.*, 1956, 1603.
[7] R. Belcher and C. E. Spooner, *J. Chem. Soc.*, 1943, 313.
[8] W. MacNevin, *Ind. Eng. Chem. Anal.*, 1938, **10**, 341.
[9] G. Ingram, *Chem. and Ind.*, 1956, 276.

Talanta, 1960, Vol 4, pp. 227 to 235. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF ULTRAMICRO AMOUNTS OF SULPHATE AS METHYLENE BLUE—I

THE COLOUR REACTION

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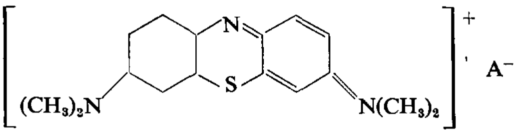
Summary—Sulphate may be determined spectrophotometrically as methylene blue after reduction to sulphide, which is allowed to react with *p*-aminodimethylaniline and ferric iron to form the dye. This paper deals with the colour reaction.

The standard method for the colour development proposed is founded on an investigation of the following variables: hydrogen sulphide losses, acidity at reaction and measurement, reagent concentrations, temperature at reaction and measurement, concentration of traces of heavy metals, time, and air-oxidation. Previously found deviations from Beer's law are confirmed and discussed. The yield of the reaction is determined.

THE difficulty of finding a method for the determination of ultramicro amounts of sulphate has led to attempts to reduce this substance to hydrogen sulphide, which can be determined by sensitive titrimetric or colorimetric methods. Among the latter, the methylene blue (MB) method seems to deserve special attention; it is entirely specific for hydrogen sulphide and the colour reaction is one of the most sensitive. The method, however, has not been sufficiently investigated to permit its immediate application. This paper will deal with the colour reaction; the reduction of sulphate to hydrogen sulphide will be considered in a later paper.[1]

Caro's MB reaction was recommended by Emil Fischer[2] for the identification of hydrogen sulphide. The solution containing hydrogen sulphide is mixed with an acidic solution of *p*-aminodimethylaniline, and ferric iron is added. The solution first becomes red from an intermediate compound but changes to blue as MB is formed. The formula of MB



where A^- represents an arbitrary anion, includes one atom of sulphur. The anion is chloride in commercial products of the dye.

This method was later used for quantitative determinations of sulphide by Mecklenburg and Rosenkränzer[3] and by Almy[4]. Lorant[5] developed a method for the reduction of microgram amounts of sulphate to hydrogen sulphide, which was determined colorimetrically as MB. Fogo and Popowsky[6] used modern spectrophotometric instruments in their investigation of the MB method and applied it to the determination of hydrogen sulphide in gases. Lorant's method was further developed by Roth[7] and by Johnson and Nishita.[8] The results of these investigations will be discussed in their appropriate places.

According to Bernthsen,[9] ferric iron together with *p*-aminodimethylaniline gives a red oxidation product, Wurster's red, which reacts in several ways with hydrogen sulphide. Among other products, sulphide green, leuco methylene blue and methylene red are said to be formed. The first two are easily transformed to MB, whereas methylene red is not. Lorant assumes that methylene red and MB are formed in the proportion 1:50. It is evident that hydrogen sulphide is not quantitatively transformed to methylene blue. In order to make full use of the reaction for quantitative purposes, a study of the effects of different factors on the yield and precision of the method is needed.

EXPERIMENTAL

Apparatus

In order to obtain accurate results, it is essential that all glassware used for the colour development should be kept free from traces of heavy metals. The glassware is washed with hydrochloric acid (1 + 1), then with water, and is finally rinsed with de-ionised, distilled water (see below).

The light absorption was determined with a Beckman DU spectrophotometer, the wavelength scale of which had been checked against Hg spectral lines. It proved necessary to use a water-cooled lamp-compartment to prevent temperature changes of the solutions during measurement; later on, a thermostated cell-compartment was used. Distilled water was used as a reference solution.

Reagents

Reagent-grade chemicals were used.

De-ionised water: distilled water was run through a 30-ml column of cation-exchange resin (Amberlite IR-120, H-form) at a rate not exceeding 0·5 litre/h.

Zinc acetate solution: 0·25*M* $ZnAc_2$; 0·10*M* NaAc. Remove traces of heavy metals by precipitating them as sulphides, with zinc sulphide as a carrier as follows: add drop by drop, with thorough shaking, 2 ml of freshly-prepared 0·05*M* sodium sulphide to 1 litre of the zinc acetate solution. Let stand overnight. Swirl up the precipitate, and filter through a quantitative paper of fine texture. Discard the first portion of the filtrate. A gradually developing turbidity is of no consequence.

"Amino" reagent: 0·005*M* $NH_2C_6H_4N(CH_3)_2 \cdot \frac{1}{2}H_2SO_4$; 3·50*M* H_2SO_4. Dissolve 0·93 g of the Eastman preparation No. 1333 in 750 ml of de-ionised water, add 3·50 moles of H_2SO_4, cool and dilute to 1 litre with de-ionised water. The reagent will keep at least 6 months.

Ferric solution: 0·25*M* $NH_4Fe(SO_4)_2$; 0·5*M* H_2SO_4. Use de-ionised water.

Preparation of the standard sulphide solution

Sulphide solutions are easily oxidised and must consequently be prepared and standardised immediately before use.

Standard solutions, 0·03–0·05*M* in sulphide, were prepared from large crystals of $Na_2S \cdot 9H_2O$. To remove traces of sulphite from the surface of the crystals, they were rapidly rinsed with water on a coarse glass filter before dissolution. Vacuum-boiled, de-ionised water was used for preparing the solutions.

Preliminary standardisations were made by iodimetric titration according to Bethge.[10] The final standardisation was made as follows. Depending on the concentration, 20–50 ml of the sulphide solution were pipetted into a 250-ml beaker followed by 5 ml of 1*M* NaOH and 5 ml of 30% H_2O_2. The beaker was covered, and heated on a hot-plate until evolution of oxygen had ceased, and the solution was evaporated to about half the original volume. After cooling, the solution was passed through a cation-exchanger (Dowex 50, H-form) and boiled to expel carbon dioxide. The sulphuric acid formed was titrated with 0·1*M* NaOH. Blanks were carried out, but no blank exceeded 0·1% of the titrated acid.

In those series of experiments where only relative values were required, standardisation was omitted, and the approximate concentration was determined according to the standard procedure (see below), using the results of Table III for calculating the amount of sulphide.

Appropriate dilutions of the standard solution were made immediately before each series of experiments using vacuum-boiled, de-ionised water.

The standard procedure for colour development

It is assumed that the hydrogen sulphide to be determined in actual analyses has been absorbed in zinc acetate solution.

Pipette 10 ml of zinc acetate solution into a 100-ml glass-stoppered volumetric flask and add de-ionised water to make 80 ml after the addition of sulphide solution to follow. Mix and add the sulphide solution from a pipette, immersing its tip. Mix by gentle swirling and place the flask, together with the bottles containing amino reagent and ferric solution, in a thermostat at 20° for at least 10 minutes. Use rapidly-running pipettes for the next two additions. Add 10 ml of amino reagent so that the solution flows down the wall of the flask and forms a layer on the bottom. Mix by swirling, and immediately add 2 ml of ferric solution. Stopper the flask, and shake vigorously for about half a minute. Dilute to the mark, mix, and place the flask in subdued light at 20°. Measure the extinction at 20° and 667 mμ the same day, after 15 minutes or more. Perform a blank and apply the correction.

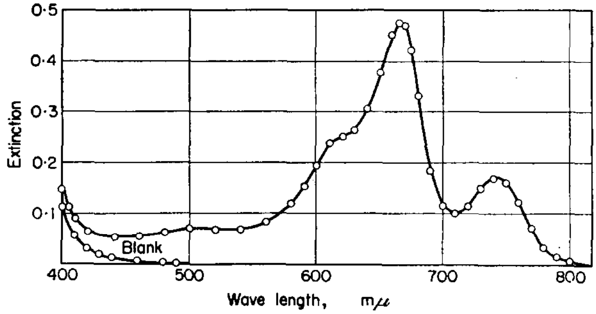


FIG. 1. Extinction-wavelength curve of a MB solution prepared from about 38 μg S according to the standard procedure. Cell length 1 cm.

THE ABSORPTION CURVE

Fig. 1 shows the extinction-wavelength curve of a MB solution prepared according to the standard procedure. The wavelengths of maximum absorption are 667 and 743 mμ. The higher peak, at 667 mμ, is rather sharp, so that the extinction should be determined at a constant and preferably small slit-width, and care should be taken to reach the maximum, the position of which may vary for instruments of poorer spectral quality. The relation of the two absorption maxima to each other is discussed in connection with the acidity effect.

For comparison, the absorption curve of a commercial preparation, "Methylenblau B extra, Merck," was determined. It was dissolved in a solution containing the same amount of reagents as in the standard procedure. This curve was essentially the same as the one just discussed, with the exception that the latter had a stronger absorption at about 500 mμ. This band is assumed to arise from methylene red formed during the colour development.

THE EFFECT OF VARIABLES

Hydrogen sulphide losses upon addition of reagents

The standard procedure for colour development proved to give the largest yield and the greatest precision. It seems that Roth[7] and others mix the solution rather gently before and after the addition of the ferric solution by inverting the flask a few times. Mixing before the addition of the acid ferric solution brings part of the hydrogen sulphide into the gas phase; this part has no opportunity to react quantitatively after the addition of the ferric solution if the flask is only gently shaken.

The yield is consequently decreased, a fact that was experimentally confirmed in this laboratory. Gentle mixing without shaking before the addition of the ferric solution decreases the transfer of hydrogen sulphide to the gas phase; vigorous shaking after the addition of ferric solution facilitates the reaction of the hydrogen sulphide in the gas phase. That such a reaction really occurs a short time after the additon of the ferric solution was experimentally shown. Sulphide solution added 30 seconds after the ferric solution reacted to 90% of the normal yield.

Insufficient mixing before the addition of the ferric solution causes low results.

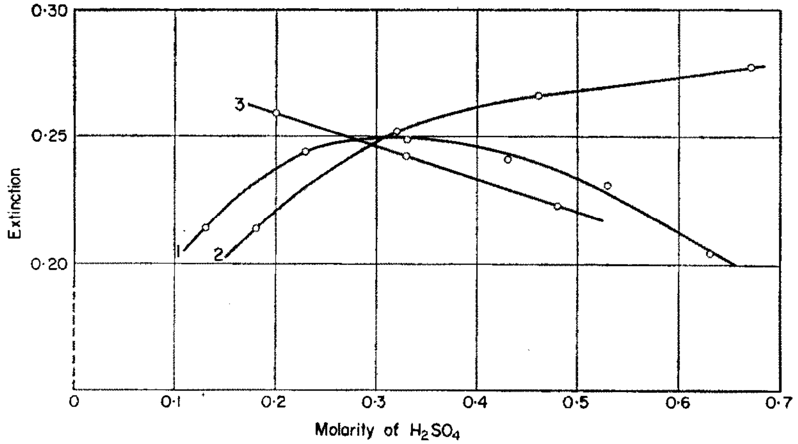


FIG. 2. Effect of acidity on light absorption and yield. Solutions prepared (see text) from about 18 μg S and extinction determined at 667 mμ in a 1-cm cell. Molarity of H_2SO_4 signifies concentration at

(1) reaction and measurement
(2) reaction; concentration at measurement 0·10*M*
(3) measurement; concentration at reaction 0·59*M*

The acidity effect

The acid concentration may affect both the yield of the reaction and the extinction of MB. To elucidate this the following experiments were performed:

1. The colour reaction was performed according to the standard procedure with the exception that "amino" reagents of different acidities were used.
2. The colour reaction was performed with amino reagents of different acidities, but before measurement the solutions were brought to the same acidity by addition of the appropriate amount of ammonia. Special experiments showed that the presence of ammonium sulphate had no significant influence on the results.
3. The colour reaction was performed at constant acidity. Before measurement different amounts of ammonia were added, causing variable acidity at the extinction measurement.

It was found (Fig. 2) that the yield of MB increases with increasing acidity, whereas its extinction at 667 mμ decreases. A combination of these two relations explains the maximum obtained in experiment 1. This result is opposed to the assumption made by Fogo and Popowsky[6] that variable acidity of the "amino" reagent influences the light absorption rather than the reaction yield.

The optimal sulphuric acid concentration in the final solution is about 0·30*M*.

There is a slight displacement of the extinction maximum towards longer wavelengths with increasing acidity. An increase in sulphuric acid concentration from 0·23*M* to 0·63*M* resulted in a displacement of the peak from 666 mμ to 668 mμ; the extinction found at those peaks differed from the values at 667 mμ by less than 1 %.

The absorption maximum at 743 mμ, which is absent in solutions of MB in distilled water, increases with the acidity, indicating the formation of another compound possibly produced by the addition of a proton to the MB cation. The decrease of the 667 mμ peak with increasing acidity is thus explained.

TABLE I. EFFECT OF TEMPERATURE ON THE EXTINCTION AT 667 mμ OF MB SOLUTIONS PREPARED AT 20° ACCORDING TO THE STANDARD PROCEDURE.

Temperature at measurement, °*C*	Extinction	Mean temp. coefficient in the interval, % *per* °*C*
	96 μ*g sulphide-S*, 1-*cm cell*	
15	1·049	0·45
20	1·073	0·33
25	1·091	0·25
30	1·105	
	19 μ*g sulphide-S*, 5-*cm cell*	
20	1·197	0·05
25	1·200	

In a series of experiments using hydrochloric acid instead of sulphuric acid for the "amino" reagent, a lower extinction was obtained even at the optimal concentration of this acid.

Effect of variable concentrations of zinc acetate, ferric ammonium sulphate and p-*aminodimethylaniline*

Varying the amounts of "amino" reagent as well as those of zinc acetate and ferric solutions will generally produce acidity effects. If, however, precautions are taken to keep the concentration of free sulphuric acid constant, only slight effects are produced by fairly large variations. Thus, varying the amount of ferric iron in the interval 0·1–1·0 millimoles of Fe (standard amount 0·5 millimole) gave deviations within 2 % of the extinction; lower amounts as well as complexing by phosphoric acid delayed the reaction considerably. The amount of *p*-aminodimethylaniline should not be much less than the standard amount, 0·05 millimole; the use of 0·10 millimole increased the yield by about 1 %.

Temperature effects

Mecklenburg and Rosenkränzer[3] and others report a larger light absorption when the reaction is performed at a lower temperature. Temperature variations may, however, affect both the yield and the extinction of MB. These effects seem not to have been studied separately.

The temperature effect on the extinction was determined on two solutions prepared according to the standard procedure from 96 μg and 19 μg of sulphide-S. The extinction was determined at various temperatures (Table I), beginning and ending at

20° as a control. The temperature coefficient around 20° was found to be about +0·4% per degree for the higher concentration and 0·05% per degree for the lower one. This result agrees qualitatively with the observations made by Rabinowitch and Epstein[11] on MB solutions in water at pH 3·4, which will be further discussed later on.

To study the temperature effect on the yield of MB, all reagent solutions were brought to the same temperature in a thermostat and the colour development performed at this temperature. The extinction was determined at 20°.

From the results of Table II obtained with 106 μg S, it is seen that the yield is steadily lowered with increasing temperature; the negative temperature coefficient decreases further with increasing temperature and at 20° is about −0·5% per degree. Similar results were obtained with 20 μg S.

TABLE II. EFFECT OF TEMPERATURE ON THE YIELD OF MB.

MB solutions prepared from 106 μg sulphide-S according to the standard procedure, but at varying temperatures. Extinction is determined at 667 mμ and 20° in a 1-cm cell.

Temperature at reaction, *°C*	Extinction	Mean temp. coefficient in the interval, *% per °C*
10·1	1·209	−0·36
15·0	1·188	−0·46
20·0	1·161	−0·65
24·7	1·126	−0·74
30·0	1·083	

Using hydrochloric acid solutions, Fogo and Popowsky[6] obtained a maximum yield of MB at 24°. They assume that the yield is decreased at higher temperatures because more hydrogen sulphide escapes from the acid solution into the gas phase; at lower temperatures little hydrogen sulphide escapes but the MB reaction becomes so slow that side reactions occur to a larger extent.

No such maximum was obtained in this investigation. The absorption coefficient for hydrogen sulphide in water decreases strongly with increasing temperature. Further, it was demonstrated that the capacity of the reaction mixture to react with further amounts of sulphide added after 10 or 30 seconds was strongly lowered with increasing temperature. These two facts combined will, at least qualitatively, explain the steadily decreasing negative temperature coefficient, though the influence of some side reaction cannot be excluded.

The opposite signs of the temperature coefficients of the yield and the extinction may, in isolated cases, cancel the errors. It is, however, obvious that the precision is much improved by keeping the temperature constant at both the reaction and the extinction measurement.

Colour stability

The colour was found to be fully developed after 15 minutes at 20°; the extinction was then constant for several hours if the solution was kept in subdued light. If kept overnight, a slight fading occurred (0·3% for a solution made from 100 μg S). It seems to be a commonly accepted fact that strong light will bleach the colour; no experiments to confirm this were performed.

Effects of traces of heavy metals

Water from a metal still often contains about 30–50 μg of Cu per litre. Preliminary experiments indicated that these traces in the water used for diluting the zinc acetate solution were responsible for certain anomalies in the yield of MB. In order to eliminate this source of error, the water had to be re-distilled in a glass apparatus or passed through a H^+-saturated cation-exchanger. Also, the zinc acetate solution had to be purified as previously described.

Experiments where traces of copper sulphate were added to the diluted zinc acetate solution showed a nearly linear decrease of the extinction with increasing amounts of copper. As expected, addition of copper after the colour development had no effect. Addition of a constant amount of copper (3·0 μg Cu as sulphate) to the diluted zinc acetate solution produced the same losses (1·5–1·7 μg S) in the determination of 5–33 μg S. The molar ratio (copper added)/(loss of sulphur) is approximately 1:1. This supports the assumption that formation of copper sulphide is the cause of the interference. Addition of copper to the ferric solution had no effect, thus excluding the assumption that copper may serve as a catalyst for some harmful side-reaction appearing at the colour development.

While this work was being done, a short communication by Johnson and Arkley[12] appeared. They state that traces of copper in the water precipitate sulphide quantitatively, resulting in low yields of MB. This observation as to the low yields is confirmed in this laboratory; the formation of any precipitate was, however, never observed. It may be assumed that, at such small concentrations, copper sulphide remains in solution as a mononuclear complex.

Interference from lead and mercury was also studied. As expected from the ionic solubility of PbS, addition of 10–20 μg of Pb as nitrate had no effect. The interference from Hg was, however, serious. The molar ratio (Hg added)/(loss of S) was found to be about 1:2, indicating the formation of the complex $Hg(SH)_2$. The interference was almost as large when Hg was present in the ferric solution as in the zinc acetate solution. This difference in behaviour from Cu^{II} may be explained by the fact that Hg^{II} forms complexes of greater stability with S^{2-} and SH^-.

Susceptibility of sulphide to air oxidation in zinc acetate solution

Two diluted zinc acetate solutions containing about 22 μg sulphide-S were treated with a stream of air, 50–100 ml per minute, for 1 hour before colour development. Losses of 1·1 and 1·8% were indicated. The sulphide in the zinc acetate solution is consequently unexpectedly stable.

THE RELATION TO BEER'S LAW

Different amounts of sulphide were treated according to the standard procedure (Table III). There is a noticeable decrease in specific extinction at 667 mμ at concentrations larger than about 25 μg S per 100 ml. This lack of linearity of the calibration curve has been observed by Johnson and Nishita[8] and others. By diluting more concentrated solutions (50–100 μg S) with a blank solution and determining the extinction, Johnson and Nishita proved that this lack of linearity is caused by deviation from Beer's law and not by a decrease in the yield of MB; this has also been confirmed in this laboratory.

Rabinowitch and Epstein[11] have found that solutions of MB in water (pH 3·4) do not follow Beer's law even at very low concentrations ($<10^{-6}$ *M*). They have proved that this deviation is quantitatively explained by the formation of dimeric ions $(MB)_2^{2+}$. The absorption spectrum of methylene blue consists of two overlapping absorption bands with maxima at 600 mμ and 656 mμ. The former is more pronounced in more concentrated solutions, and is due to the dimeric ion; the latter, due to the monomeric ion, predominates in very dilute solutions. The dissociation of $(MB)_2^{2+}$ is increased by an increase in temperature as well as by diluting the solution. This explains the increase of the extinction at 667 mμ with increasing temperature illustrated in Table I.

TABLE III. THE RELATION OF EXTINCTION TO SULPHIDE-SULPHUR TREATED ACCORDING TO THE STANDARD PROCEDURE

The extinction, E, is determined at 667 mμ in a 1-cm cell. Cf also Table IV.

Sulphide-S, μg	Extinction	$E \times 10^2$ per μg sulphide-S	Yield of MB calcd. from Table IV, %
0	0·003	—	—
10·42	0·137	1·290	64·5
20·56	0·269	1·293	65·1
23·62	0·309	1·294	65·4
30·90	0·394	1·265	64·9
41·17	0·517	1·248	65·5
51·55	0·635	1·226	65·3
61·98	0·746	1·199	—
103·1	1·160	1·122	—

THE YIELD OF THE METHYLENE BLUE REACTION

According to Lorant,[5] exactly 68·7% of the added sulphide is transformed to MB. The method used for standardising the sulphide solution is not stated, and the colorimetric determination, made by means of a Duboscq colorimeter, is performed with a solution of MB and methyl red (not methylene red) as a reference solution; Lorant seems to have mistaken methyl red for methylene red, the by-product reported by Bernthsen. The reported value for the yield of MB is, therefore, uncertain; however, it is evident that sulphide is not quantitatively transformed to MB. This is also assumed by several other authors, although no quantitative results are published.

The reaction yield can be determined by comparing the extinction of a MB solution made from a known amount of sulphide with the extinction of a solution containing a known amount of MB. The latter solution was prepared from "Methylenblau B extra, Merck" which was dissolved in a solution of the same composition as is obtained by performing a blank. The purity of the preparation used as calculated from nitrogen determinations was 97·5%, ash content 1·2%. Using the values given in Tables III and IV, and correcting for the purity, the reaction yield is calculated to 66·7% ± 0·5% throughout the investigated interval.

No computation of the standard error has been made at this point in the investigation, but it will be found in a following paper[1] which also includes the reduction of sulphate to sulphide.

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TABLE IV. THE EXTINCTION OF "METHYLENBLAU B EXTRA" AS A FUNCTION OF ITS CONCENTRATION

The preparation is dissolved in blank solutions prepared according to the standard procedure. The extinction, E, is determined at 667 mμ in a 1-cm cell. Cf also Table III.

MB sulphur, μg	Extinction	$E \times 10^2$ per μg MB sulphur
0	0·002	—
3·94	0·082	2·03
7·78	0·158	2·01
11·70	0·233	1·974
15·60	0·310	1·974
19·52	0·385	1·962
27·30	0·522	1·905
39·10	0·728	1·857

Zusammenfassung—Es existiert eine photometrische Bestimmung von Sulfat die auf folgender Reaktion beruht: Sulfat wird zu Sulfid reduziert und dieses in Gegenwart von Ferriionen mit p-Aminodimethylanilin zu Reaktion gebracht vobei Methylenblau gebildet wird. Die vorliegende Abhandlung befasst sich mit der Farbreaktion. Die zur Bestimmung führende Farbreaktion ist abhängig von folgenden Faktoren: Schwefelwasserstofferluste, Säuregehalt der Lösung während Reaktion und Messung, Temperatur während Reaktion und Messung, Spuren von Schwermetallen, Zeit, Oxydation durch Luftsauerstoff. Geeignete Berücksichtigung aller Faktoren führte zu einer vorgeschlagenen Standardmethode. Früher schon festgestellte Abweichungen vom Beer'schen Gesetz wurden bestätigt und diskutiert. Die Ausbeute der Reaktion wurde bestimmt.

Résumé—Les sulfates peuvent être dosés par spectrophotométrie à l'état de bleu de méthylène après réduction en sulfures, ce qui permet la réaction avec la p-aminodiméthylaniline et le fer ferrique pour former le colorant. Cet article est relatif à la réaction colorée.

La méthode étalon pour le développement de la couleur proposée ici est basée sur l'étude des paramètres suivants: pertes en H_2S, acidité pour la réaction et la mesure, concentration de traces de métaux lourds, oxydation par l'air et en fonction du temps. Les déviations à la loi de Beer, déjà signalées, sont confirmées et discutées. On détermine le rendement de la réaction.

REFERENCES

[1] L. Gustafsson, *Talanta*, 1960, **4**, 236.
[2] E. Fischer, *Ber.*, 1883, **16**, 2234.
[3] W. Mecklenburg and F. Rosenkränzer, *Z. anorg. Chem.*, 1914, **86**, 143.
[4] L. H. Almy, *J. Amer. Chem. Soc.*, 1925, **47**, 1381.
[5] I. St. Lorant, *Z. physiol. Chem.*, 1929, **185**, 245.
[6] J. K. Fogo and M. Popowsky, *Analyt. Chem.*, 1949, **21**, 732.
[7] H. Roth, *Mikrochem. Mikrochim. Acta*, 1951, **36/37**, 379.
[8] C. M. Johnson and H. Nishita, *Analyt. Chem.*, 1952, **24**, 736.
[9] A. Bernthsen, *Ann.*, 1885, **230**, 73; 1889, **251**, 1.
[10] P. O. Bethge, *Analyt. Chim. Acta*, 1953, **9**, 129.
[11] E. Rabinowitch and L. F. Epstein, *J. Amer. Chem. Soc.*, 1941, **63**, 69.
[12] C. M. Johnson and T. H. Arkley, *Analyt. Chem.*, 1954, **26**, 1525.

Talanta, 1960, Vol. 4, pp. 236 to 243. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF ULTRAMICRO AMOUNTS OF SULPHATE AS METHYLENE BLUE—II

THE REDUCTION

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Summary—Sulphate may be determined spectrophotometrically as methylene blue after reduction to sulphide, which is allowed to react with *p*-aminodimethylaniline and ferric iron to form the dye. A previous paper[1] dealt with the colour reaction; this paper deals with the reduction.

A method for the reduction of sulphate to sulphide by hydriodic and hypophosphorous acids in acetic acid solution is proposed. It is founded on an investigation of the following variables: composition of the reducing reagent, composition of the carrier gas and gas-washing liquid, temperature at reduction, and time. The yield of the reduction is found to be 100% within the experimental errors. The standard deviation of a single determination of 100 μg S or 2 μg S is found to be 0·14 μg S or 0·05 μg S, respectively. Some interferences in connection with the application of the method for certain purposes are discussed.

In a previous paper[1] the reaction of sulphide with *p*-aminodimethylaniline and ferric iron to form methylene blue (MB) was investigated as part of an attempt to determine, spectrophotometrically, ultramicro quantities of sulphate after reduction to sulphide. The present paper deals with the reduction and the final method.

Lorant[2] seems to have been the first to employ the reducing properties of hydriodic acid for the quantitative determination of sulphate. The sulphate is reduced to sulphide by boiling with a mixture of hydriodic acid, formic acid and red phosphorus. More recently, some variants of this reduction method have been published. Thus Luke[3] performs the reduction with hydriodic acid, hydrochloric acid and hypophosphorous acid, Roth[4] with hydriodic acid, formic acid and hypophosphite, and Johnson and Nishita[5] with a mixture similar to the one used by Lorant. Lorant states that sulphate is quantitatively reduced to sulphide. The basis for this statement is, however, not quite free from objections. Using a reducing agent of the same type as that employed by Luke, Bethge[6] reports a quantitative yield in the reduction of centigram amounts of potassium sulphate.

In these methods, generally, the optimum range of several analytically important variables seems not to have been established, precluding their immediate application at least for ultramicro determinations.

EXPERIMENTAL

Apparatus

The apparatus (Fig. 1) used for the reduction is chiefly according to Johnson and Nishita.[5] The sample, together with the reducing mixture, is boiled in the round-bottomed flask (*a*). Nitrogen, purified with permanganate solution, is introduced through the side-tube (*b*). This gas carries the hydrogen sulphide formed through the water-jacketed condenser (*c*) to the gas-washing column (*d*) where the gases are freed from hydriodic and acetic acid by washing with water. The gases are carried further through the delivery tube (*e*) dipping into a solution of zinc acetate which absorbs the hydrogen sulphide; the solution is kept in a 100-ml volumetric flask with a ground-glass stopper. A small burner with a steady flame is used for the heating. The round-bottomed flask rests on an asbestos board fitted with a round hole to prevent overheating of the walls. The side tube (*b*) ends 1–2 mm from the bottom of the flask. The delivery tube (*e*) is constricted to an opening 1–2 mm in diameter at its lower end, and connected to the apparatus, glass-to-glass, with a short piece of latex tubing. The rate of the nitrogen flow is checked with a flowmeter (measuring the fall of gas pressure across a capillary tube). The ground-joints are greased with sulphur-free silicone lubricant.

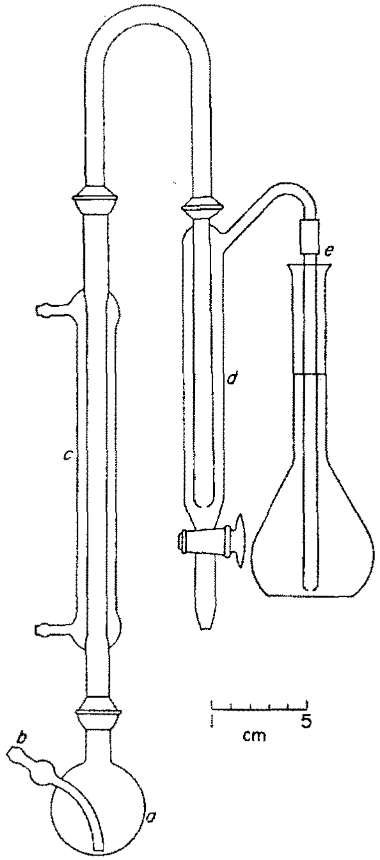

FIG. 1. Apparatus for the reduction of sulphate.

Concerning the importance of keeping the apparatus and other glassware free from traces of heavy metals as well as the spectrophotometer and thermostatic arrangements, *cf* Gustafsson.[1]

Reagents

All reagents, except sodium hypophosphite, were of reagent-grade quality.

Concerning *de-ionised water, zinc acetate solution, "amino" reagent* and *ferric solution, cf* Gustafsson.[1]

Reducing reagent: Dissolve 2·5 g $NaH_2PO_2{\cdot}H_2O$ in 25 ml of glacial acetic acid and 100 ml of hydriodic acid (sp. gr. 1·7) in a 150–250-ml round-bottomed flask with a ground-in condenser and a gas delivery tube. The hydriodic acid should be taken from a newly-opened flask. Boil under reflux for 1 hour, bubbling a stream of nitrogen (about 50 ml per minute) through the solution; traces of sulphur are removed in this way, and iodine is reduced to iodide. Allow to cool in the nitrogen stream, close the flask with a glass stopper, and store in subdued light.

Sulphate-free water: If necessary, purify distilled water by passing it through a 20-ml column of an anion-exchange resin (Dowex 1, Cl-form) at a rate not exceeding 250 ml per hour.

Sulphate standard solution: Dissolve 5·435 g K_2SO_4, dried at 105° for 2 hours, in distilled water to make 1 litre. This solution contains 1 mg of S per ml, and is used as a stock solution in preparing standard solutions of lower concentrations by diluting with sulphate-free water.

Nitrogen wash solution: 2% potassium permanganate solution, saturated with mercuric chloride.

Sulphur-free silicone lubricant: This is prepared according to Johnson and Nishita as follows: In a 100-ml beaker, mix about 5 g of Dow-Corning silicone lubricant with 10 ml of a solution consisting of equal volumes of hydriodic acid and hypophosphorous acid (30%). Boil for 45 minutes with occasional stirring. Use a round-bottomed flask filled with cold water as a condenser. Pour off the acid solution and wash the lubricant thoroughly with sulphate-free water.

Recommended procedure

The sample should not contain much more than 100 μg S. If the sample is a solid, introduce it to the bottom of the reduction flask. If the sample is a solution, *e.g.* standard sulphate solution, add it with a pipette to the reduction flask and evaporate to dryness, preferably in a drying oven at 130°. The solution should contain bases equal to or in excess of sulphuric and other high-boiling acids in the sample. The evaporation can be accelerated by blowing a stream of air, washed with 4*M* potassium hydroxide, into the upper part of the flask. Allow the flask to cool to room temperature.

Lubricate all ground-joints of the apparatus with sulphur-free silicone lubricant. Add 10–15 ml of de-ionised water to the gas-washing column (*d*). Add 10 ml of zinc acetate solution and 68 ml of de-ionised water to the 100-ml volumetric flask and connect it to the apparatus with the delivery tube (*e*) reaching to the bottom of the flask.

Start the nitrogen flow through the gas-washing bottle containing nitrogen wash solution at a rate of 150–200 ml per minute. Pipette 3 ml of reducing reagent into the flask containing the sample, and connect it to the condenser and the nitrogen source. Heat to boiling in about 60 seconds with a small flame ending a few mm below the flask. Interrupt the heating after boiling for 10 minutes. Detach the delivery tube from the apparatus, but keep it in the volumetric flask.

The apparatus is now ready for another reduction. If there is more than a few minutes' delay between the reductions, iodine is formed in the apparatus, and this should be rinsed out with water before use. After 6–8 reductions, the water in the gas-washing column should be replaced.

Place the volumetric flask, together with the "amino" reagent and ferric solution bottles, in a thermostat at 20° for at least 10 minutes. Use rapid-running pipettes for the addition of the reagents to follow. Pipette 10 ml of "amino" reagent through the delivery tube so that the tube is rinsed and the reagent forms a layer on the bottom of the flask. Rinse the tube with 2 ml of de-ionised water, and remove it from the flask. Mix by gently swirling the flask, and immediately add 2 ml of ferric solution. Stopper the flask and shake it vigorously for half a minute. Dilute to 100 ml with water, mix, and place the flask in subdued light at 20°. Determine the extinction at the peak maximum, 667 mμ, at 20° the same day, after 15 minutes or more. Perform a blank and apply the correction. Determine the relation of extinction to amount of sulphur by performing the procedure on different amounts of sulphate standard solution (*cf.* Tables II and III).

EFFECTS OF VARIABLES

The composition of the reducing reagent

In the search for a reducing reagent able to give quantitative reduction of sulphate to sulphide and, moreover, one which was stable and easy to prepare, a systematic investigation was made of reducing mixtures of various compositions. The following mixtures were studied: (1) HI + P; (2) HI + P + HCOOH; (3) HI + P + HAc; (4) HI + P + H_3PO_2; (5) HI + H_3PO_2; (6) HI + H_3PO_2 + HCOOH; (7) HI + NaH_2PO_2 + HAc. The proportions of the constituents were also varied. Before use, the mixtures were refluxed for 1 hour with a stream of nitrogen bubbling through the solution to remove traces of sulphur.

As a result of these experiments, it was found that reagents made up of HI + NaH_2PO_2 + HAc gave the best precision and the lowest blanks. Varying the volume ratio HI:HAc from 10 to 1 did not affect the yield of the reduction. Using formic instead of acetic acid, Roth[4] obtained a constant yield only for reagents containing 43–53% of formic acid; he consequently recommends these proportions in spite of the fact that he had obtained as much as 20% higher yield with reagents containing less formic acid.

Reducing mixtures containing red phosphorus gave rather large and varying blanks (up to 0·3 μg S per ml). It seems probable that remaining sulphur compounds are slowly extracted from the solid particles.

Attempts to reduce the concentration of water in the reagent resulted in severe losses of gaseous hydrogen iodide during boiling.

With reagents composed of $HI + P$ or $HI + H_3PO_2$, the evolution of white fumes was sometimes observed to occur in a seemingly random way. These fumes were not wholly absorbed in the washing column and caused very large negative errors. As it seemed probable that this phenomenon was caused by overheating, a number of reductions were performed with the reaction vessel immersed in boiling water; but the errors remained. It is of great interest that such low and erratic results are not obtained if formic or acetic acid is added to the reaction mixture.

As a consequence of these results, the recommended reagent was finally chosen. It is of great advantage that interfering sulphur compounds can easily be removed by refluxing in a stream of nitrogen; at the same time free iodine is converted to iodide. Experiments showed that boiling for 10 minutes removed 99% of the sulphur contamination. After preparation, the reagent should not be transferred to another vessel, but should be stored in the same flask. Under these conditions, the reagent blank is found to have a low and constant value for at least several weeks; it is unnecessary to boil the solution each day before use as prescribed by Roth. If carefully prepared and handled, *e.g.* protected from contamination and undue exposure to light and air, the reducing solution is found to be stable for months. When the initially colourless or faintly yellow solution has turned brown from iodine formed by air-oxidation, it should be refluxed again before use.

Effect of temperature at reduction

According to Lorant[2], sulphate is reduced even at room temperature, though slowly. With a reducing mixture similar to that used by Lorant, the influence of temperature was studied. It was found that the reaction performed under boiling gave the highest yield, whereas no reduction could be observed at room temperature. At 50° reduction was slow; of 20 μg S added, only 4 μg was recovered in the first 20 minutes and 6μg in the next 40 minutes. At 80° no more hydrogen sulphide was produced after 20 minutes, but the yield was considerably lower than at boiling. It seems probable that at lower temperatures part of the added sulphur escapes the reaction, presumably as sulphur dioxide. With regard to these losses at lower temperatures, the reducing mixture should be heated to boiling fairly rapidly.

The composition of the washing liquid

In order to prevent traces of iodine and hydriodic acid from being transferred to the zinc acetate solution, Lorant and others wash the gases with a solution of pyrogallol and sodium dihydrogen phosphate. Experiments proved, however, that deionised water could, with advantage, be substituted for this washing solution. This was usually replaced after about 6 reductions in succession, and then was found to contain about 2 milliequivalents of acetic acid and very little hydriodic acid. No yellow colour from iodine was ever observed in the washing column.

The carrier gas

According to Lorant, not only hydrogen, nitrogen or carbon dioxide but also air may be used as carrier gas. This seems objectionable, as there may be losses of hydrogen sulphide by air oxidation. When performing a series of reductions with air instead of nitrogen as a carrier gas, the first reduction gave the same extinction as when nitrogen was used; the next reduction, made immediately after, gave an extinction that was 3–4% too low. The loss of hydrogen sulphide was evidently caused by iodine formed in the condenser. In consequence air should not be used as carrier gas. It is, however, not necessary to remove traces of oxygen from the nitrogen as many authors prescribe.

The time variable

Experiments showed that the reduction of sulphate is complete after a few minutes. The time necessary for the transfer of the hydrogen sulphide to the zinc acetate solution is obviously dependent on the rate of the nitrogen flow and the amount of the water in the washing column. When working according to the recommended procedure, the transfer is complete in 10 minutes.

Effect of diluting the reducing reagent with water

For practical reasons it would be of great advantage if the reduction method could be directly applied to sample solutions. Experiments proved, however, that addition of only 0·5 ml of water to the evaporated sulphate sample decreased the yield by 6%; when 2 ml of water was added the error amounted to −35%. This effect is not only obtained with the recommended reagent. Several other reducing mixtures prepared from HI + P or from HI + P + HAc were investigated in this respect. In all cases, diluting with water caused considerable losses, and boiling for a longer time did not increase the yield; the losses are therefore not due to a slower reduction. It seems as if part of the sulphur escapes the reaction, probably as sulphur dioxide.

It might be possible to reduce these losses to some extent by using a larger amount of reagent. Using a more concentrated reagent might also be considered, but then this reagent cannot be boiled to remove traces of sulphur without serious losses of gaseous hydrogen iodide. Dissolving the sample in acetic or formic acid might be possible in some cases. The safest way is, however, to evaporate the sample to dryness.

Conditioning the apparatus

When reducing 5 μg and smaller amounts of sulphate, it was observed that the first reduction of a series often gave a result too low by 0·1 — 0·2 μg S. This loss was presumably caused by absorption of hydrogen sulphide in the apparatus in spite of the precautions taken to keep the glass walls and the water in the washing column free from traces of metals. This error was eliminated by running the procedure on a small amount of sulphate before the actual series.

Magnitude of blanks

To indicate the magnitude of blanks to be expected, the following results are reported. The reducing reagent prepared on 4 different occasions in blank experiments gave the extinctions 0·008, 0·008, 0·010 and 0·011 (5-cm cell); blank experiments on the colour development alone gave 0·007. Sulphate-free water (10 ml) made alkaline with a few drops of 0·001*M* $NaHCO_3$ and evaporated to dryness gave no larger blank after reduction than the reagents alone.

THE YIELD OF THE REDUCTION

The yield of the reduction was determined by comparing the amounts of methylene blue obtained from known quantities of sulphate with those obtained by applying the colour development to known quantities of sulphide. The latter determinations were performed on freshly prepared and standardised solutions of sodium sulphide, *cf* Gustafsson[1]. The uncertainty of the amount of sulphide is estimated to be less than 0·3%. Both the colour development and the photometric determination were performed at 20°. The results of Table I show that the yield of the reduction is quantitative well within the experimental errors.

RELATION TO BEER'S LAW AND PRECISION

It was confirmed in a previous paper[1] that the light absorption of methylene blue solutions does not follow Beer's law and that above 20 μg of S per 100 ml the deviations begin to be larger than the experimental errors. As the percentage yield of methylene blue from sulphide is constant and the yield of the reduction of sulphate is quantitative, the same deviations are obtained in the relation of amount of sulphate to extinction. (Table II. These values can only be compared approximately with those given in Table III of the previous paper[1] because the temperature constancy in the experiments of the latter table was not quite satisfactory.)

The serious deviations from linearity of the relationships of extinction to amount of sulphate make it advantageous to use a curve of specific extinction as a function of extinction for the calculations.

The precision in determining 100 μg of sulphate-S is obtained from the results of Table I; the standard deviation of a single determination is 0·14 μg of S.

Quantities of sulphate in the range 0–20 μg of S were determined using 5-cm cells for the absorption measurements (Table III). Assuming the extinction to be a linear function of the amount of sulphate, the method of least squares was applied to the results giving the curve

$$\text{Extinction} = -0{\cdot}00019 + 0{\cdot}06336\ (\mu\text{g S}).$$

The constant term, corresponding to 0·003 μg of S, may be omitted as insignificant and the relation

$$\mu\text{g S} = 15{\cdot}78 \times \text{Extinction}$$

was used for calculation of sulphur found.

It is apparent that Beer's law is valid up to 20 μg of S within the errors of the method. The standard deviation is calculated to be 0·12 μg of S, assuming it to be independent of the amount of S. This assumption is certainly not true, but the number will give an approximate conception of its magnitude.

TABLE I. THE YIELD OF THE REDUCTION OF SULPHATE TO SULPHIDE
As a mean of 7 determinations in each series, the following extinctions (667 mμ, 1-cm cell, 100 ml, 20°) were obtained.

Starting from	Extinction	Standard deviation of single result	Standard deviation of mean
101·1 μg sulphide-S	1·120	0·0037	0·0014
101·1 μg sulphate-S	1·121	0·0016	0·0006

TABLE II. THE RELATION OF EXTINCTION TO AMOUNT OF SULPHATE, 0–100 μg S
Extinction, 667 mμ, 1-cm cell, 100ml, 20°, corrected for blank.

Sulphate taken, *μg S*	Extinction	Extinction × 100 *per μg S*
6·00	0·077	1·28
11·84	0·153	1·29
17·80	0·225	1·26
20·05	0·253	1·26
23·71	0·302	1·274
39·56	0·494	1·249
59·46	0·715	1·202
101·1	1·121	1·109

TABLE III. THE RELATION OF EXTINCTION TO AMOUNT OF SULPHATE, 0–20 μg S
Extinction, 667 mμ, 5-cm cell, 100 ml, 20°, corrected for blank (0·008; 0·010). Sulphur found is calculated as 15·78 × Extinction.

Sulphate taken, *μg S*	Extinction	Sulphur found, *μg S*	Deviation, *μg S*
0·59	0·039	0·62	−0·03
1·20	0·081	1·28	+0·08
1·57	0·089	1·40	−0·17
2·36	0·143	2·26	−0·10
2·37	0·155	2·45	+0·08
3·94	0·246	3·88	−0·06
7·90	0·510	8·05	+0·15
11·87	0·751	11·85	−0·02
15·82	1·011	15·95	+0·13
18·98	1·196	18·87	−0·11
19·72	1·257	19·84	+0·12
19·72	1·239	19·55	−0·17

The standard deviation of a single result in the determination of 2 μg of S was found to be 0·05 μg of S from 9 determinations in 5-cm cells. The precision may possibly be improved by using apparatus and solutions of smaller volume.

APPLICATIONS AND INTERFERENCES

The method proposed has been used occasionally in this laboratory for a few years. The objects of analysis have essentially been fresh water samples and biochemical preparations. For water samples, 1–10-ml portions have been evaporated and analysed. In cases where there is a very small sulphate content, such as glacial stream waters which may contain less than 1 ppm, a sample size of 10 ml has been used. Milligram samples of biochemical preparations with low percentages of sulphur ($<1\%$) were burnt in oxygen according to Mikl and Pech[7] (*cf* Schöniger[8]), the sulphur dioxide and trioxide formed was absorbed in 5–10 ml of dilute sodium hydroxide containing hydrogen peroxide, and an aliquot was then evaporated for analysis. This method worked well on standard samples. However, a limiting factor for its use on low-percentage samples is the varying sulphur content of the paper used for wrapping up the sample; the total blank amounted to about 2 μg of S.

Some interferences were studied in connection with these analyses. Oxidising agents as a rule interfere. Thus 3 mg of NO_3^- reduced the yield by 3%. Johnson and Nishita ascribe these losses to some volatile reduction product which is absorbed in the zinc solution and interferes with the colour reaction; our own results confirm this hypothesis. Iron^{III} in amounts up to at least 20 mg did not interfere.

Certain nitrogenous organic substances interfere, giving low results. The determination of sulphate in the presence of organic material by this method, without further investigation, is not recommended. Sulphur-containing organic material will give off varying amounts of its sulphur content.

Moderate amounts of alkalies or alkaline earths do not interfere; barium sulphate is rapidly reduced. Reduction of elementary sulphur, if newly formed, is quite rapid; reduction of flowers of sulphur, for example, proceeds slowly.

Acknowledgement—This work was suggested by Professor Folke Nydahl. The author wishes to thank him for his valuable discussions and the facilities placed at her disposal.

Zusammenfassung—Im vorhergehenden Beitrag wurde die Farbreaktion bei der Bestimmung von Sulfat nach Reduktion zu Sulfid und Bestimmung dessen nach der Methylenblaumethode behandelt. Hier wird der Reduktionsschritt diskutiert. Es wird die Reduktion mittels Jodwasserstoffsäure und hypophosphoriger Säure in essigsaurer Lösung vorgeschlagen. Die Reduktion hängt von folgenden Faktoren ab: Zusammensetzung des Reduktionsreagenses, Zusammensetzung des Trägergases und der Gaswaschflüssigkeit, Temperatur bei der Reduziert wird und schliesslich Zeit. Die Ausbeute der Reduktionsreaktion wurde zu 100% innerhalb der experimentellen Schwankungen gefunden. Die Standardabweichung einer Einzelbestimmung von 100 μg Schwefel wurde zu 0·14 μg und die von 2 μg Schwefel zu 0·05 μg S gefunden. Einige Störmöglichkeiten in Zusammenhang mit der Anwendung der Methode für bestimmte Zwecke werden diskutiert.

Résumé—Les sulfates peuvent être dosés par spectrophotométrie à l'état de bleu de méthylène après réduction en sulfures ce qui permet la réaction avec la p-aminodiméthylaniline et le fer ferrique pour former le colorant. Un précédent article traitait de la réaction colorée, celui-ci est relatif à la réduction.

On propose une méthode pour la réduction des sulfates en sulfures par les acides iodhydrique et hypophosphoreux en solution dans l'acide acétique. Elle est basée sur l'étude des paramètres suivants: composition du réactif réducteur, composition du gaz entraîneur et du liquide lavant le gaz, température de réduction et temps. Le rendement de la réduction est égal à 100% aux erreurs expérimentales près. L'écart type pour une seule détermination de 100 μg de S est de 0.14 μg S et pour 2 μg de S, elle est de 0,05 μg S. On discute l'influence de quelques interférences relatives à l'application de la méthode à certains objectifs.

REFERENCES

[1] L. Gustafsson, *Talanta*, 1960, **4**, 227.
[2] I. St. Lorant, *Z. physiol. Chem.*, 1929, **185**, 245.
[3] C. L. Luke, *Analyt. Chem.*, 1949, **21**, 1369.
[4] H. Roth, *Mikrochem. Mikrochim. Acta*, 1951, **36/37**, 379.
[5] C. M. Johnson and H. Nishita, *Analyt. Chem.*, 1952, **24**, 736.
[6] P. O. Bethge, *Analyt. Chim. Acta*, 1953, **9**, 129.
[7] O. Mikl and J. Pech, *Chem. Listy*, 1952, **46**, 382; 1953, **47**, 904.
[8] W. Schöniger, *Mikrochim. Acta*, 1956, 869.

Talanta 1960, Vol. 4, pp. 244 to 249. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHATE USING LANTHANUM CHLORANILATE

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Summary—The spectrophotometric determination of phosphate using lanthanum chloranilate has been investigated. It is possible to determine 3–300 ppm of phosphate with an accuracy of ±2%, if suitable conditions are chosen. Chloride or nitrate ions do not interfere up to 400 ppm. Interference from sulphate ion can be compensated for by adding a large amount of sulphate both to the sample and to the standard solutions. This method is simpler, has less critical reaction conditions, and develops a much more stable coloration than the conventional heteropolyacid methods.

INTRODUCTION

PHOTOMETRIC determinations of phosphate are based usually on the colour reaction of phosphate with molybdate or vanadomolybdate to form heteropolyacids or heteropoly blue. In all of these procedures, it is necessary, however, to carry out the colour reaction under critically controlled conditions to obtain reproducible results.

In a previous paper[1] the use of the lanthanum salt of chloranilic acid (2:5-dichloro-3:6-dihydroxy-*p*-benzoquinone) was proposed for the photometric determination of fluoride, the metathesis reaction between lanthanum chloranilate and fluoride ion to form insoluble lanthanum fluoride being utilised. As it was known that phosphate may be precipitated quantitatively by lanthanum or thorium ion, the uses of lanthanum chloranilate and thorium chloranilate were investigated in an analogous manner to the fluoride determination.

The reactions between phosphate and lanthanum or thorium chloranilate may be shown schematically as follows:

$$2PO_4^{3-} + La_2(C_6Cl_2O_4)_3 + 3H^+ \rightarrow 3HC_6Cl_2O_4^- + 2LaPO_4$$

$$4PO_4^{3-} + 3Th(C_6Cl_2O_4)_2 + 6H^+ \rightarrow 6HC_6Cl_2O_4^- + Th_3(PO_4)_4$$

Insoluble lanthanum phosphate or thorium phosphate is precipitated, with the liberation of acid chloranilate ion, which is proportional to the amount of phosphate in the sample. After filtering excess reagent and metal phosphate, the liberated acid chloranilate ion in the filtrate is determined spectrophotometrically.

As reported earlier,[1] the spectrophotometric determination of acid chloranilate ion can be carried out either in the visible region (520–550 mμ) or in the ultraviolet region (280–350 mμ) of the spectrum. In the case of visible spectrophotometry, the instrument is less expensive and the determination will be less influenced by foreign materials, although the sensitivity is slightly lower.

This paper reports on the visible spectrophotometric determination of phosphate using lanthanum or thorium chloranilate, which is simpler in procedure, has less

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critical reaction conditions, and develops a much more stable coloration than the conventional heteropoly acid methods. With this procedure, it is possible to determine 3–300 ppm of phosphate with an accuracy of ±2%.

EXPERIMENTAL

Reagents

Lanthanum chloranilate: Prepared as described previously.[1]

Thorium chloranilate: Prepared in an analogous manner to lanthanum chloranilate from chloranilic acid and thorium nitrate. These reagents can be kept for an indefinite period without appreciable deterioration.

Standard phosphate solution (approximately 5,000 ppm as PO_4^{3-}): Prepared by dissolving 19 g of disodium hydrogen phosphate in 1 litre of distilled water. The phosphate ion concentration was determined by precipitating phosphate as $MgNH_4PO_4$, followed by the EDTA titration of excess magnesium in the supernate.[2]

Buffer solutions: Acetate buffer pH 4 (sodium acetate and acetic acid) and succinate buffer pH 7 (sodium succinate), prepared according to standard practice. All other chemicals were reagent grade.

Apparatus

A Beckman Model DU spectrophotometer, equipped with a tungsten lamp and 1-cm Corex cells, was used for the spectrophotometric determinations. A glass electrode pH-meter (Horiba Model T) was used for all pH measurements, and a mechanical shaking apparatus with a time switch device was employed to ensure a constant reaction condition.

General procedure

The following general procedure was employed to investigate the influences of reaction conditions and of various interfering ions:

> Pipette the standard phosphate solution, containing 0·15–5 mg of phosphate, into a 50-ml volumetric flask. Add 5 ml of buffer solution, 25 ml of water-miscible organic solvent and 0·1 g of lanthanum chloranilate (or thorium chloranilate) crystalline powder, and dilute the mixture to the mark with distilled water. After shaking the flask on a shaking machine for a given period, filter the solution through a filter paper. Discard the first portion of filtrate, then collect the middle portion into a Corex cell. Determine the absorbance of this solution at 530 mμ against a reagent blank.

RESULTS AND DISCUSSION

Comparison of lanthanum chloranilate and thorium chloranilate

Both lanthanum chloranilate and thorium chloranilate were tried as reagents for the photometric determination of phosphate. When thorium chloranilate reacted with phosphate, however, thorium phosphate precipitated in a colloidal form which could not be removed by simple filtration; further, the colour intensity of the resulting solution was weaker than in the case of lanthanum chloranilate. On the other hand, the precipitate of lanthanum phosphate could be easily filtered, and lanthanum chloranilate was found to be a more suitable reagent for the photometric determination of phosphate. In the following investigations, only lanthanum chloranilate was employed.

Effect of organic solvents

As described previously[1], the use of a water-miscible organic solvent increased the sensitivity of the colour reaction. In the general procedure described above, ethanol, methanol, methylcellosolve, dioxan or acetone was added to the sample solution to give a final solvent concentration of 50%, and the results are shown in Fig. 1 and

Table I. With the same pH value and buffer solution, the order of decreasing sensitivity was 50% dioxan > 50% acetone, 50% methylcellosolve > 50% ethanol, 50% methanol > water. The absorbance of the reagent blank was, however, higher in 50% dioxan and in 50% methylcellosolve than in 50% ethanol and in water. The solvent system of 50% ethanol was therefore the most suitable, because it showed a fairly high sensitivity with a relatively low reagent blank.

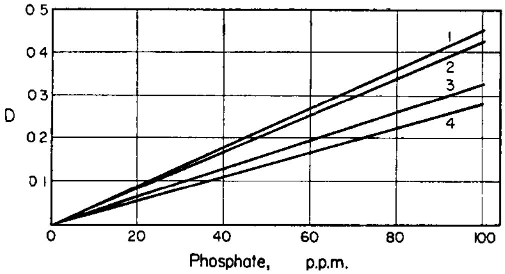

FIG. 1.—Effect of buffer and solvent on the absorption at 530 mμ. (10 min shaking)
1: Acetate buffer, pH 4 and ethanol
2: Acetate buffer, pH 4 and methylcellosolve
3: Succinate buffer, pH 7 and methylcellosolve
4: Succinate buffer, pH 7 and ethanol.

TABLE I.–EFFECT OF ORGANIC SOLVENT ON SENSITIVITY AND ON REAGENT BLANK

Solvent	Absorbance		Absorbance difference
	Sample*	Reagent blank	
Water	0·227	0·026	0·201
50% Methanol	0·266	0·039	0·227
50% Ethanol	0·250	0·024	0·226
50% Methylcellosolve	0·319	0·059	0·260
50% Acetone	0·299	0·039	0·260
50% Dioxan	0·415	0·073	0·342

*Absorbance was determined on the sample containing 80 ppm of phosphate in the final solution at pH 7 (succinate buffer) after 10 min shaking.

Effect of pH and buffer solutions

The absorption spectrum of acid chloranilate ion in aqueous solution is greatly influenced by the pH of solution. The absorbance is at its maximum between pH 1 and 2, and it is progressively decreased with increasing pH value of the solution. The change in absorbance is less marked in the pH range of 5 to 12.[3]

If the colour reaction is carried out in the lower pH region, higher sensitivity will therefore be attained. At the same time, reproducible results will, however, hardly be obtained, and the interferences from anions are more marked in this pH region. The most suitable pH for the colour reaction was chosen as 7, where the absorbance was not appreciably influenced by pH and was less interfered by anions.

The composition of the buffer solution also affected the absorbance of acid chloranilate ion, as previously reported, and acetate and succinate buffers were found to be preferable for this procedure.

Reaction time

The condition of shaking was not so critical as in the case of fluoride determination. With the use of the shaking apparatus (350 strokes per min), the absorbance reached an almost constant value after 5 min, and no appreciable change in absorbance was observed by further shaking. The spectrophotometric determinations were therefore carried out after 10 min shaking.

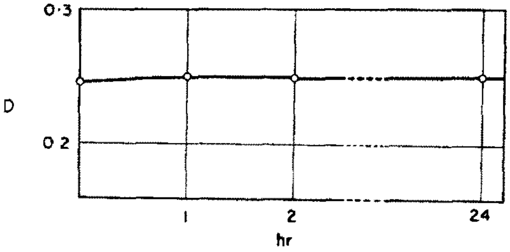

FIG. 2.—Stability of coloration. Determined on the sample containing 80 ppm of phosphate in the final solution, at pH 7 (succinate buffer) with 50% ethanol after 10 min shaking.

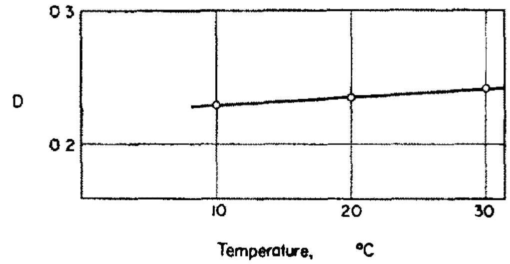

FIG. 3.—Effect of temperature. Determined on the sample containing 80 ppm of phosphate in the final solution, at pH 7 (succinate buffer) with 50% ethanol after 10 min shaking.

Stability of coloration and effect of temperature

The colour of the solution, once developed, was quite stable for many hours, and the absorbance after 24 h standing was almost the same as after 1 h, as shown in Fig 2. Hence, the absorbance can be measured at any time after the reaction.

The temperature during the reaction slightly affected the absorbance of the resulting solution, as shown in Fig. 3. The absorbance increased with increasing reaction temperature from 10° to 30°, but reproducible results could be obtained without taking any particular care for maintaining the reaction temperature constant.

Range of phosphate concentration

As Beer's law was obeyed for acid chloranilate ion up to 100 mg/100 ml, phosphate could be determined over a wide concentration range. The consumption of lanthanum chloranilate increased with increasing phosphate concentration in the sample solution, so that it was necessary to use an additional 0·1 g of the reagent for each 5 mg of phosphate present. With this procedure, it was possible to determine 0·15 to 15 mg of phosphate, or 3 to 300 ppm of phosphate in the final solution.

Interfering ions

Since almost all cations interfered in the determination, as in the case of fluoride

TABLE II.—INTERFERENCES BY ANIONS

(*a*) SULPHATE

Buffer	Solvent	Absorbance				
		Without sulphate	With sulphate			
			200 ppm	Error (%)	400 ppm	Error (%)
Succinate pH 7	Ethanol	0·226	0·248	+9·7	0·256	+13·3
Succinate pH 7	Methyl-cellosolve	0·260	0·293	+12·7	0·306	+17·7
Acetate pH 4	Ethanol	0·359	0·413	+15·0	0·423	+17·8

(*b*) CHLORIDE

Buffer	Solvent	Absorbance				
		Without chloride	With chloride			
			200 ppm	Error (%)	400 ppm	Error (%)
Succinate pH7	Ethanol	0·226	0·226	0	0·223	−1·3
Succinate pH 7	Methyl-cellosolve	0·260	0·259	−0·4	0·260	0
Acetate pH 4	Ethanol	0·359	0·339	−5·6	0·326	−9·2

(*c*) NITRATE

Buffer	Solvent	Absorbance				
		Without nitrate	With nitrate			
			200 ppm	Error (%)	400 ppm	Error (%)
Succinate pH 7	Ethanol	0·226	0·223	−1·3	0·221	−2·2
Succinate pH 7	Methyl-cellosolve	0·260	0·261	+0·4	0·263	+1·2
Acetate pH 4	Ethanol	0·359	0·333	−7·2	0·326	−9·2

The absorbances in the tables are the average of at least five determinations on a sample containing 80 ppm of phosphate in the final solution after shaking 10 min.

TABLE III.—COMPENSATION FOR SULPHATE INTERFERENCE

Sample composition	PO_4^{3-}, *ppm*	80	80	80
	SO_4^{2-}, *ppm*	800	1000	1200
Absorbance		0·274	0·272 (−0·7%*)	0·280 (+2·2%*)

* The difference from the value in the first column, %.

determination, it was necessary to remove previously all cations from the sample solution by means of ion-exchange. The only exception was ammonium ion which did not interfere, even in large amounts.

Interferences from anions such as sulphate, nitrate and chloride are summarised in Table II. With regard to nitrate and chloride, when the reaction was carried out at pH 7 with succinate buffer, no appreciable interference was observed up to 400 ppm of these anions.

The interference from sulphate was not negligible, even with small amounts. However, in the presence of amounts of sulphate greater than 800 ppm, the difference in absorbance due to the additional 200 ppm or 400 ppm of sulphate was found to be not more than ±2%, as shown in Table III. Therefore, the interference due to sulphate could be compensated for by adding 800 ppm of sulphate both to the sample solution and to the standard phosphate solution.

Fluoride interfered seriously, even in small amounts, because it reacted with the reagent to form insoluble lanthanum fluoride.

Recommended procedure

After considering the results of the foregoing investigations, the following procedure is recommended for the determination of phosphate:

Place the sample solution, containing 0·15–5 mg of phosphate, in a 50-ml volumetric flask. To this, add 5 ml of 0·03*M* sodium succinate solution (pH 7), 25 ml of 95% ethanol and 0·1 g of lanthanum chloranilate crystalline powder, and dilute the solution to 50 ml with distilled water. Shake the flask for 10 min on a shaking machine (350 strokes per min), then filter the solution through a filter paper. Discard the first portion of the filtrate, and collect the middle portion in a cell for spectrophotometric measurement. Determine the absorbance at 530 mμ against a reagent blank. Obtain the phosphate concentration from a calibration curve which has been prepared from the standard phosphate solution by the same procedure.

Further study of this procedure and the practical applications is now being made, and the results will be published elsewhere.

Zusammenfassung—Die spectrophotometrische Bestimmung von Phosphat unter Verwendung von Lanthanchloranilat wurde untersucht. Es ist möglich 3–300 ppm Phosphat auf ±2% genau zu bestimmen, wenn geeignete Bedingungen gewählt werden. Chlorid- und Nitration stören nicht bis hinauf zu 400 ppm. Störungen durch Sulfat werden durch Zugabe einer grossen Menge Sulfats sowohl zu Probe als auch Vergleichslösung kompensiert. Die Methode ist einfacher, gestattet weinger strickte Reaktionsbedingungen und erzaugt eine stabilere Färbung als die conventionelle Heteropolysäuremethode.

Résumé—Les auteurs ont étudié le dosage spectrophotométrique du phosphate en utilisant le chloranilate de lanthane. Il est possible de doser 3 à 300 p.p.m. de phosphate avec une précision de ±2% en choisissant des conditions convenables. Les ions chlorure ou nitrate ne gênent pas jusqu'à 400 p.p.m. On peut compenser l'interférence du sulfate en ajoutant une grande quantité de sulfate aux deux solutions: solution standard et celle contenant l'échantillon. La méthode est plus simple, tient mieux compte des conditions de la réaction et donne une coloration plus stable que les méthodes conventionnelles mettant en jeu un hétéropolyacide.

REFERENCES

[1] K. Hayashi, T. Danzuka and K. Ueno, *Talanta*, 1960, **4**, 126.
[2] S. Wakamatsu, *Japan Analyst*, 1957, **6**, 579.
[3] P. V. Ferro and A. B. Ham, *Amer. J. Clin. Pathol.*, 1957, **28**, 208.

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ANALYTICAL CHEMISTRY OF α-BENZOINOXIME COMPLEXES OF MOLYBDENUM, TUNGSTEN AND VANADIUM

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Summary—Molybdenum^{VI} is precipitated by α-benzoinoxime as $MoO_2(C_{14}H_{12}O_2N)_2$ from acid solutions from pH 2 to 5% by volume sulphuric acid. The procedure of Knowles for molybdenum in steel is modified to yield precipitates which can be weighed without ignition to the oxide. In extraction of this molybdenum complex into chloroform the interference of tungsten and vanadium is eliminated by adding dihydrogen phosphate ion and ferrous ion. Tungsten^{VI} forms $WO_2(C_{14}H_{12}O_2N)_2$ on addition of α-benzoinoxime to tungstate solutions freshly acidified with sulphuric acid. Precipitation of tungsten as this complex is not complete even in the presence of fluoride or phosphate ions. Extraction of the tungsten complex into chloroform is not feasible because of its limited solubility. Vanadium^{V} with α-benzoinoxime forms a yellow precipitate at pH 3, and on long standing at pH 1.5 a white precipitate. The yellow precipitate changes to the white precipitate with time. The white precipitate has the composition $VO_2(C_{14}H_{12}O_2N)$ but is always contaminated with excess reagent. Using the α-benzoinoxime complex, vanadium^{V} can be extracted at pH 2.2 into chloroform and converted into the 8-quinolinol complex for measurement. Bismuth, antimony^{III} and uranyl ions interfere slightly. Chromium^{VI} in acid solution oxidises α-benzoinoxime so rapidly that studies were not possible.

INTRODUCTION

FEIGL[1] first used α-benzoinoxime as a reagent for the precipitation of copper. Knowles[2] found that α-benzoinoxime precipitates molybdenum^{VI} from acid solution. In this procedure tantalum, niobium, and silicon contaminate the precipitate by formation of insoluble hydrated oxides; tungsten^{VI} and palladium^{II} appear to be quantitatively precipitated; and the possible interference of chromium^{VI} and vanadium^{V} is prevented by reduction. Yagoda and Fales[3] reported that molybdenum and tungsten are quantitatively precipitated together, provided that both are present. Variations of these procedures have been summarised by Flagg[4], Blanco[5], and Jensen and Weaver[6]. Recently Jeffrey[7] and Goldstein, Manning, and Menis[8] have used α-benzoinoxime as a reagent for the extraction of molybdenum into chloroform.

In all of these procedures molybdenum^{VI}, tungsten^{VI}, vanadium^{V} and chromium^{VI} are said to form complexes of some stability in acid solution or to interfere in the use of α-benzoinoxime as a precipitating reagent. With the exception of the palladium complex, the characterisation of the metal complexes formed from acid solution is incomplete. In addition, the nature of the metal ions in acid solution has been the subject of investigations for many years.

This paper presents an account of the composition of the complexes from extraction or precipitation studies; the effects of solvent composition, pH, and excess reagent on the precipitation of molybdenum^{VI}; the extraction of molybdenum and

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vanadium, and the effect of tungsten; and correlation of this work with the literature on the nature of molybdenum^{VI}, tungsten^{VI}, and vanadium^{V} in solution.

EXPERIMENTAL

All chemicals used were C. P. or reagent-grade with the following exceptions. The α-benzoinoxime used was obtained from Paragon Testing Laboratories, and was recrystallised from ethanol where high purity was required. The quercetin, m.p. 195°, was a special student preparation. The pH measurements were made with a Beckman model H2 pH meter with glass and calomel electrodes. Spectra and single wavelength measurements were taken with a Beckman model DK2 automatic recording spectrophotometer or a Beckman model DU spectrophotometer.

The following general methods were used. Where specific details are important, these will be provided in the discussion. Any variations will be noted also.

Precipitation studies were done as follows. Solution containing the desired amount of the element being studied was pipetted using a calibrated pipette into a 150- or 250-ml beaker. The acidity was adjusted and any additional materials were added. The desired amount of α-benzoinoxime dissolved in 50% acetone, or in some cases in ethanol, was then added from a burette equipped with a Teflon stopcock. The solution was stirred during the addition of the reagent. After the precipitates had stood for the required time, they were collected on weighed, 30-ml, medium porosity, sintered-glass crucibles. They were then washed, care being taken to wash down the sides of the crucibles, and were dried to constant weight at 105°.

To determine the amount of metal in the complex, some of the previously dried complex was ignited at 500–550° in silica crucibles, and the metal content was calculated from the weight of oxide obtained.

All extractions were done batchwise. The solution to be extracted was placed in a 60-ml separatory funnel and additional materials in solution were added. Acidity was controlled by adding acid to the separatory funnel, except that where close pH control was required, the pH was adjusted before adding the solution to the funnel. Extractions were carried out by adding controlled amounts of α-benzoinoxime in chloroform solution from a burette equipped with a Teflon stopcock and shaking the separatory funnels in a mechanical shaker. The chloroform layer was drawn off into a volumetric flask, the aqueous layer was extracted with chloroform which was added to the previous extract, and the chloroform was made to volume. Metals were determined in aliquots of this solution or in the whole solution by adding the reagents and measuring the colour intensity.

The method of continuous variations could not be used to establish the metal:reagent ratio in the complexes because no difference in absorption between the reagent and the complex was found. The metal:reagent ratio was derived from extraction or precipitation results.

RESULTS AND DISCUSSION

1. *Molybdenum complex with α-benzoinoxime*

The exact nature of the molybdenum^{VI} species in acid solution is not clear. In the review of the literature by Huckel[9] it is stated that at pH 0.9 polymerised molybdenum trioxide precipitates, but in more acid solution molybdenum trioxide is depolymerised and redissolves. Other workers[10,11,12,13] have reported that MoO_2^{2+} ion appears to be the major species in hydrochloric and sulphuric acid solution. Molybdenum^{VI} is precipitated by 8-quinolinol from slightly acid solution as bis(8-quinolinolo)dioxomolybdenum[14].

When α-benzoinoxime in 50% aqueous acetone is added to solutions of molybdenum^{VI}, no precipitation occurs in the range pH 2.5–7. At pH 1.5 and 2.5 a slight cloudiness is observed, and in solutions more acid than pH 1 a heavy, white, flocculent precipitate is formed. This behaviour suggests that the complex is formed from the MoO_2^{2+} ion. Since α-benzoinoxime is not soluble in water, the solubilities had to be determined for various alcohol-water and acetone-water compositions and are summarised in Table I. The solubility of the molybdenum-α-benzoinoxime complex in the same media is included here for conciseness.

As mentioned previously, when the method of continuous variations was tried in 50% ethanol containing 5% hydrochloric acid, solutions containing α-benzoinoxime or the molybdenum complex in equivalent concentration gave the same spectra. In order to establish the ratio of molybdenum to α-benzoinoxime in the complex, a variation of the extraction method of Goldstein, Manning, and Menis[8] was used.

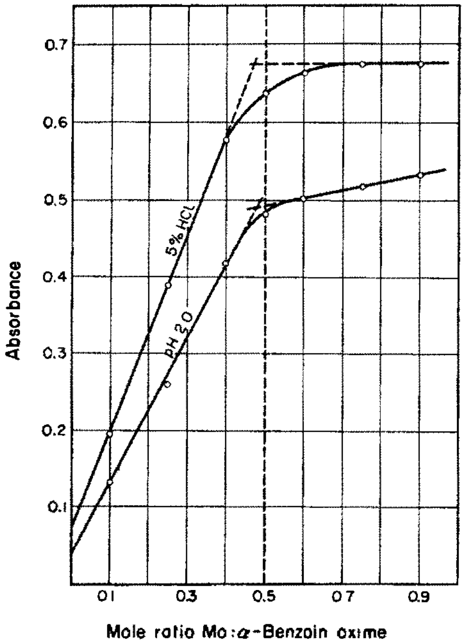

FIG. 1. Determination of molybdenum: α-benzoin oxime ratio by extraction procedure.

A series of 10-ml portions of 5% hydrochloric acid solutions containing 0.2—1.8 × $10^{-3}M$ molybdenum^{VI} were extracted with 20 ml of 1 × $10^{-3}M$ α-benzoinoxime in chloroform, and the aqueous layer was washed with 10 ml of chloroform using a 15-min shaking time in both cases. The combined chloroform extracts were diluted to 50 ml. A 2-ml aliquot plus 3 ml of 0.1% quercetin in ethanol was diluted to 25 ml with ethanol and measured at 420 mμ against a quercetin blank. The results are shown in Fig. 1. There is a break in the curve where the ratio of Mo to α-benzoinoxime is slightly less than 1:2, which indicates that the precipitate in the absence of chloroform should have this composition. The extractions were repeated with the water layer adjusted to pH 2. The results are also shown in Fig. 1. It is clear that 1:2 composition is still present, but that the extraction is incomplete. This is in agreement with the suggestion that formation of the MoO_2^{2+} species is not complete until the acidity is greater than pH 0.9.

Preliminary experiments to determine the composition of the molybdenum^{VI}-α-benzoinoxime complex indicated that the blue colour noted by previous workers[4] was caused by reduction of molybdenum by excess α-benzoinoxime in the precipitate. To prepare a sample of pure complex, 20 ml of 0.0156M α-benzoinoxime in ethanol was added dropwise to 40 ml of ice-cold 0.0052M molybdenum^{VI} in 5% sulphuric acid. After 15 minutes standing the precipitate was filtered, washed twice with 5 ml of ethanol to remove excess reagent, and dried at 105°. The white precipitate did not turn blue, and in a separate test it melted sharply at 158–9°. Three more samples were prepared in the same way. These were dried at 105° and weighed, and on ignition to MoO_3 they gave 16.40, 16.52, and 16.45% Mo in the dried precipitate.

Since molybdenum^{VI} exists in acid solution as MoO_2^{2+} and the complex contains molybdenum:α-benzoinoxime in a 1:2 ratio, it appears that the molybdenum^{VI}-α-benzoinoxime complex should be described as bis(α-benzoinoximato)dioxomolybdenum^{VI}, $MoO_2(C_{14}H_{12}O_2N)_2$. This complex contains 16.51% Mo, is based on MoO_2^{2+}, and has the correct ratio of molybdenum to α-benzoinoxime.

TABLE I. SOLUBILITY OF α-BENZOINOXIME (ABH) AND MOLYBDENUM COMPLEX OF α-BENZOINOXIME (Mo-ABH)

Solvent, *Volume %*	ABH, *g*/100 *ml*	Mo-ABH, *g*/100 *ml*
Water-Ethanol		
25	0.20	
50	0.30	
75	1.25	
Water-Acetone		
25	0.20	0.004
50	1.90	0.006
100	13.50	0.014

TABLE II. EFFECT OF ACETONE CONCENTRATION

% Acetone at end	Mo taken, *mg*	Mo found, *mg*	Error, *mg*
33	12.5	12.1	−0.4
25	12.5	12.3	−0.2
20	12.5	12.4	−0.1
20	12.5	12.5	—
15	12.5	12.5	—
15	12.5	12.6	+0.1

Quantitative precipitation of molybdenum

Quantitative precipitation of the complex was attempted. Based on the results in Table I, acetone was used as the solvent for the reagent. From preliminary experiments it was clear that the acetone concentration was critical and that the precipitate matted on the crucible if it was not covered with wash liquid. The results in Table II show that up to 20% acetone can be present in the final solution without affecting the results. With some acetone present, precipitation of excess reagent is not a factor. Since it is very difficult to tell when enough reagent has been added, another series of experiments was run to check the effect of excess reagent. In all cases the final acetone concentration was held to 15–20% by addition of water. The results are summarised in Table III. Further experiments using 25, 50, and 100 mg of Mo showed that up to 100 mg of Mo could be precipitated. However, 25 mg is the largest convenient amount because above this the washing and handling of the precipitate becomes difficult. With 50 mg the precipitate mats together, and washing becomes extremely slow.

In previous work[15] niobium, silicon, tantalum, palladium, tungsten^{VI}, vanadium^{V}, and chromium^{VI} interfered in the precipitation of molybdenum^{VI}. The precipitation of palladium by the reagent cannot be avoided and palladium must be absent.

TABLE III. EFFECT OF EXCESS REAGENT

% Excess of Oxime	Mo taken, *mg*	Mo found, *mg*	Error, *mg*
10	12.5	12.4	−0.1
25	12.5	12.5	—
50	12.5	12.4	−0.1
100	12.5	12.4	−0.1

Niobium, silicon, and tantalum are precipitated as hydrated oxides by the acid and can be separated, provided that no molybdenum is carried down by the hydrated oxide. Tungsten^{VI} is precipitated by the reagent and must be absent.[3] The interference of vanadium^{V} and chromium^{VI} is avoided[15] by reduction with sulphur dioxide or ferrous ammonium sulphate. In the regular procedure for determining molybdenum in steel,[2] vanadium and chromium do not interfere. It was necessary to check the interference of Fe^{III}, Cr^{III}, and V^{IV} in precipitation of the complex. When the precipitate from a sulphuric acid solution containing both Mo^{VI} and Fe^{III} was washed with aqueous acetone to remove reagent, the precipitate turned brown showing hydrolysis of the iron. This difficulty is eliminated by using 1% sulphuric acid to transfer the precipitate to the crucible and to wash the precipitate before the 50% acetone wash. Cr^{VI} and V^{V} were added to Mo^{VI} solutions and then excess ferrous ammonium sulphate was added to form Cr^{III} and V^{IV}. The precipitation of Mo^{VI} was then carried out as described using the sulphuric acid wash. Typical results of all these experiments are summarised in Table IV. It is apparent that Fe^{III}, Fe^{II}, Cr^{III}, and V^{IV} do not interfere in the determination of Mo^{VI} by the following recommended procedure.

TABLE IV. EFFECT OF Fe, Cr, AND V ON Mo^{VI} PRECIPITATION

Added			Mo taken, *mg*	Mo found, *mg*	Error, *mg*
$Fe_2(SO_4)_3 \cdot XH_2O$, *g*	CrO_3, *g*	V_2O_5, *g*			
2.5			25.0	25.0	—
2.5			25.0	24.9	−0.1
	0.02		25.0	24.8	−0.2
	0.02		25.0	25.1	+0.1
		0.04	25.0	25.1	+0.1
		0.04	25.0	25.1	+0.1
2.5	0.02	0.04	25.0	25.0	—
2.5	0.02	0.04	25.0	24.9	−0.1

Procedure: To 25 ml of 5% sulphuric acid containing 8–20 mg. of Mo^{VI} add excess ferrous ammonium sulphate to reduce chromium and vanadium, and then dropwise, with stirring, 10 ml 0.05*M* α-benzoinoxime in 1:1 aqueous acetone. After 10 min decant into weighed sintered-glass crucibles. Wash by decantation with 5 ml of 1% sulphuric acid and transfer the precipitate using water. Do not allow all the solution to be drawn out of the crucible or the precipitate will mat. Wash the walls of the crucible and the precipitate with two 5-ml portions of 1:1 aqueous acetone. Dry at 105° for 1 h and then for 0.5-h periods to constant weight. The precipitate contains 16.51% Mo.

TABLE V. DETERMINATION OF Mo IN NBS STEELS

NBS No.	Mo, %	Sample, *g*	Complex, *g*	Mo found, %
106	0.164	5.0620	0.0497	0.162
		5.0063	0.0493	0.163
		4.9964	0.0492	0.163
139	0.178	5.0135	0.0547	0.180
		5.0685	0.0565	0.182
		5.1698	0.0549	0.175
159	0.414	3.9952	0.1007	0.416
		3.9921	0.0996	0.412
		4.1141	0.1049	0.420
36	1.01	2.1918	0.1335	1.014
		2.1219	0.1290	1.004
		1.9974	0.1217	1.006

This procedure was then used to determine Mo in some NBS steels which contained no tungsten. The procedure of Knowles[2] was used to dissolve the samples, oxidise the carbon, and remove insolubles. Since the volume was large, acetone was added to give 15–20% acetone by volume after the reagent was added. These results are summarised in Table V.

Extraction of molybdenum

Goldstein, Manning, and Menis[8] determined small amounts of molybdenum by extraction with α-benzoinoxime followed by determination with quercetin. Both vanadium and tungsten were found to interfere in the determination. Since the interference of $vanadium^{V}$ in the precipitation of molybdenum was prevented by reduction with ferrous ion, the reduction of $vanadium^{V}$ was tried in the extraction. In a later section it will be shown that phosphate ion prevents the precipitation of $tungsten^{VI}$ by α-benzoinoxime. This was tried in the extraction. The solubility of the molybdenum complex in the extracts was improved by dilution with ethanol rather than chloroform as previously suggested.

Revised procedure: 1. Add 5 ml of KH_2PO_4 solution (1 ml = 1 mg KH_2PO_4) and 100 mg of ferrous ammonium sulphate hexahydrate to the 5% hydrochloric acid solution containing the molybdenum before extraction. Up to 4 mg of W^{VI} and 2 mg of V^{V} may be present when determining 1 mg of Mo^{VI}.

2. Dilute the washed chloroform extracts to 100 ml with 95% ethanol rather than with chloroform. The molybdenum complex dissolves in the ethanol.

3. Use 2 ml of the diluted extract to measure 1 mg of Mo^{VI}.

The results of the procedure using these changes are summarised in Table VI. It is seen that V^{V} requires a higher concentration of Fe^{II} for reduction in the absence of phosphate ion than in the presence of phosphate ion. Also there is a slight negative error caused by V^{V} plus phosphate ion in the absence of W^{VI}. It appears that our knowledge of the chemistry of complex ions is inadequate to explain these cases.

2. *Tungsten complex with α-benzoinoxime*

The nature of the tungsten^{VI} species in solution has been summarised by Huckel[9] and by Bettinger and Tyree[16]. All workers agree that either H_2WO_4 or $H_2WO_4 \cdot 2H_2O$ is precipitated from acid solutions. Phosphoric acid forms phosphotungstic acid with tungsten^{VI} but the exact nature and molecular weight of this compound in aqueous solution are unknown.[17] The limiting composition in the solid state is 12W:1P.[9] A complex ion, $WO_2F_4^{2-}$, keeps tungsten^{VI} in solution in the presence of fluoride ion.[18,19] From this point of view it is interesting that tungsten^{VI} is precipitated by 8-quinolinol from acid solution as $WO_2(C_9H_6ON)_2$.[20]

TABLE VI. ELIMINATION OF INTERFERENCE OF VANADIUM AND TUNGSTEN IN THE EXTRACTION OF MOLYBDENUM

Interference, *mg*		Inhibitor, *mg*		Molybdenum, *mg*		
W^{VI}	V^{V}	KH_2PO_4	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	Present	Found	Error
				1.00	0.98	−0.02
					1.00	—
					0.99	−0.01
1.0					1.45	+0.45
	1.0				1.15	+0.15
1.0		2.5			0.99	−0.01
1.0		2.5			0.99	−0.01
2.0		2.5			0.99	−0.01
	1.0		50		1.05	+0.05
	2.0		100		1.04	+0.04
	1.0		100		1.00	—
	1.0	2.5	100		0.95	−0.05
1.0	1.0	2.5	50		1.00	—
1.0	1.0	2.5	50		0.99	−0.01
2.0	2.0	5.0	100		1.01	+0.01

To determine the ratio of tungsten to α-benzoinoxime in the complex the extraction procedure used for the molybdenum complex appeared to be applicable. Since tungsten was an interference in the quercetin method for molybdenum[8] but no further work was done, the spectrum of the tungsten-quercetin complex was studied. Some tungsten-α-benzoinoxime complex was prepared by adding α-benzoinoxime in acetone to freshly acidified tungstate solution and washing out excess reagent from the precipitate with acetone. The precipitated complex was dissolved in ethanol and 0.1% quercetin in chloroform was added. The absorption spectrum is shown in Fig. 2. In addition to the peak at 425 mμ a second broad absorption (370–380 mμ) was found for tungsten. Molybdenum gave only a peak at 420 mμ so that tungsten could be measured at 375 mμ even in the presence of molybdenum. When the extraction of the tungsten-α-benzoinoxime was attempted, it was found that almost no tungsten was extracted in spite of the appearance of a white precipitate at the water-chloroform interface. The addition of sodium dihydrogen phosphate decreased the amount of tungsten extracted. Since the tungsten-α-benzoinoxime complex appeared to be soluble in chloroform, the solubility was determined by evaporating a saturated solution to dryness and weighing the residue. The solubility was 0.12 mg of complex per ml of chloroform at room temperature. This solubility is too low to be of practical use for quantitative extraction, so the extraction experiments were abandoned.

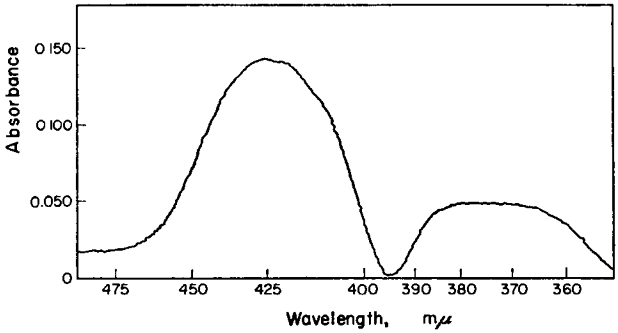

FIG. 2. Absorption spectrum of tungsten-quercetin complex versus quercetin.

Next, a series of solutions containing 0.1 millimole of tungstate ion in 10 ml of 4% sulphuric acid and 0.001*M* sodium dihydrogen phosphate were precipitated with α-benzoinoxime in 50% acetone as described for molybdenum. The samples using 0.04–0.4 millimole of α-benzoinoxime gave precipitates weighing from 1.4 up to 4.7 mg. These results suggest that phosphoric acid prevents the precipitation of the tungsten-α-benzoinoxime complex. The experiments were repeated omitting the phosphate addition but making the solution 0.1*M* in potassium fluoride to prevent precipitation of the tungsten. As the amount of α-benzoinoxime was increased, the weight of precipitate increased up to the mole ratio of tungsten to α-benzoinoxime of 0.5 as shown in Fig. 3. Thus it is seen that the precipitated complex contains one mole of tungsten to two moles of α-benzoinoxime.

Portions of a tungsten solution were made 15% in acetone and slightly more than 2 moles of α-benzoinoxime in 50% acetone per mole of tungsten were added. The precipitates were filtered, washed with small portions of 50% acetone to remove excess reagent and with water, and dried at 110°. The dried material was ignited at 500° and weighed as tungstic oxide. The results are listed in Table VII. Since the precipitate was expected to be $WO_2(C_{14}H_{12}O_2N)_2$, which contains 27.51% tungsten, the average of 27.58% tungsten found combined with the proper ratio supports the formula expected from analogy with the molybdenum complex as well as the 8-quinolinol-tungsten precipitate.

Attempted precipitation of tungsten

Since it was found that tungsten gave an α-benzoinoxime precipitate of definite composition, the gravimetric determination of tungsten by a procedure analagous to that for molybdenum was tried. The solubility of the complex in acetone solutions was checked by evaporating 150-ml portions of solutions saturated at 25° and weighing the residues. From the results in Table VIII it is seen that the tungsten complex is only sparingly soluble in dilute acetone and that no great losses will result using 15% acetone as the solvent, as was done with the molybdenum.

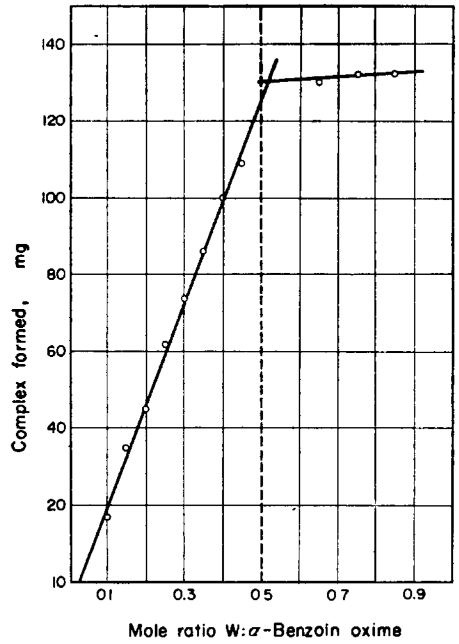

FIG. 3. Precipitation of tungsten complex with varying amounts of α-benzoin oxime.

TABLE VII. TUNGSTEN IN THE α-BENZOINOXIME COMPLEX

Complex, *g*	0.1848	0.1949	0.2073	0.1987	0.1720
WO_3, *g*	0.0645	0.0681	0.0715	0.0689	0.0691
% W in Complex	27.68	27.70	27.42	27.50	27.59
Average	27.58				

TABLE VIII. SOLUBILITY OF TUNGSTEN-α-BENZOINOXIME COMPLEX

Acetone, *Volume %*	Complex *mg/ml*
50	0.30
25	0.19
15	0.02

The original precipitation was made by acidifying a tungstate solution with sulphuric acid and adding α-benzoinoxime in 50% acetone. The precipitate obtained weighed only half as much as expected and by visual inspection contained tungstic oxide. When the tungstate solution was acidified with hydrochloric acid, and potassium fluoride was added to keep the tungsten in solution, again only half the expected weight of α-benzoinoxime precipitate was found. On acidification of the tungstate solution with sulphuric acid and adding a 20% excess of potassium fluoride based on the $WO_2F_4^{2-}$ ion, the α-benzoinoxime precipitates obtained were always slightly less than expected. In addition, anything which consumed fluoride ion, such as ferric ion, caused low precipitate weights. It appears that the fluoride:tungsten ratio is quite important.

A series of equal samples of tungstate solution were mixed with varying amounts of potassium fluoride, acidified with sulphuric acid, and precipitated with α-benzoinoxime, and the precipitates were weighed and calculated as $WO_2(C_{14}H_{12}O_2N)_2$.

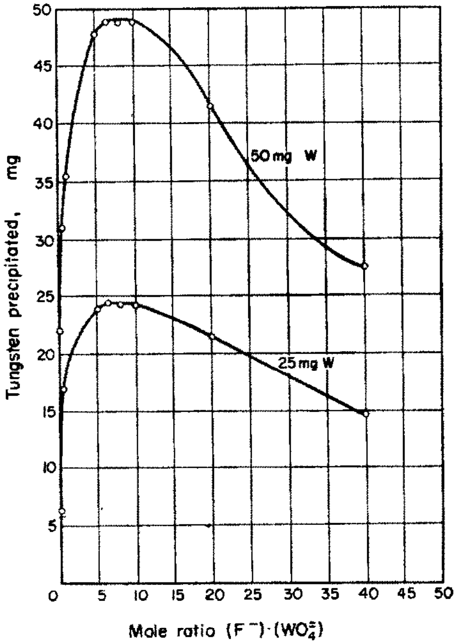

FIG. 4. Effect of fluoride ion concentration on tungsten precipitation.

From the results in Fig. 4 it is seen that the ratio of fluoride ion to tungsten must be controlled more closely than is reasonable for unknown samples. Therefore further investigations were abandoned.

Yagoda and Fales[3] reported the simultaneous precipitation of molybdenum and tungsten by α-benzoinoxime. Based on the preceding experiments it is clear that Yagoda and Fales were successful because the mixture was ignited to oxides and that the precipitate probably contained molybdenum-α-benzoinoxime complex, tungsten-α-benzoinoxime complex, and tungstic oxide.

3. *Vanadium complexes with α-benzoinoxime*

The literature on the vanadium^{V} species in acid solution has been thoroughly reviewed by Rossotti and Rossotti[21]. Using spectrophotometric and potentiometric measurements VO_2^+ ion was found to be the sole species in the pH range ±0.5 to 1.3. In the pH range 2.5–3.5, $H_2V_{10}O_{28}^{4-}$ ion was the predominant species. From pH 1.3 to 2.5 both ions were present in varying proportions. When an acetone solution of α-benzoinoxime was added to vanadium^{V} solutions, the following results were found. Above pH 4 no precipitate formed. At pH 2.8 and 2.0 a yellow precipitate formed, with much more at pH 2.0. At pH 1.5 a white precipitate formed only after long standing.

In an attempt to characterise the yellow precipitate, portions were washed with 1:1 aqueous acetone, dried under various conditions and ignited to vanadium pentoxide. The vanadium content was found to vary widely; the yellow precipitate changed colour from 115–130°, and the crystals did not melt sharply. It was concluded that the yellow precipitate was not a pure compound. Quite accidentally it was discovered that when the yellow precipitate stood in the mother liquor for several hours, it was converted to a flocculent white precipitate which was not α-benzoinoxime. When portions of this were washed with acetone to remove excess reagent, dried at 105°, and ignited to vanadium pentoxide, successive samples of white precipitate were found to contain 16.43, 16.53, 16.40, and 16.56% vanadium. The expected precipitate, $VO_2(C_{14}H_{12}O_2N)$, contains 16.47% vanadium. Additional experiments were conducted at different pH values. All of the experiments are summarised in Table IX. Qualitatively these results follow the experiments of Rossotti and Rossotti. At pH 3 the yellow precipitate would be based on a complex decavanadate which would not change. At pH 1.5 the white precipitate would be based on the VO_2^+ ion. At pH 2 the yellow precipitate changing to a white precipitate implies that the yellow precipitate dissolves to change to the less soluble, less complex white precipitate. A qualitative test showed that the yellow form was much more soluble in 1:1 aqueous acetone than the white form.

TABLE IX. pH EFFECTS ON VANADIUM-α-BENZOINOXIME PRECIPITATION

pH	Precipitate	
	Immediate	After 2 days
3	yellow	yellow
2	yellow	white
1.5	none	white

In an attempt to determine vanadium gravimetrically precipitations were made at pH 3 and allowed to stand, to change to the white precipitate, or precipitations were made by long standing at 1.5. In all cases the white precipitates were contaminated with excess reagent. If sufficient acetone was included to hold the excess reagent in solution, then the precipitation of vanadium was not quantitative. As a result, gravimetric studies were discontinued.

Extraction of the vanadium-α-benzoinoxime complex

Since the extraction of molybdenum^{VI} using α-benzoinoxime had been successful, the same process for vanadium^{V} was investigated. Preliminary experiments showed that the yellow complex was easily extracted into chloroform. Several difficulties soon became apparent. The extraction is dependent on the pH, with best results obtained at pH 2.2. The extraction is time dependent, with the best results found by 10-min shaking on an automatic shaker. The yellow complex is not stable, but fades with time. The last two difficulties may be attributed to the conversion of the yellow form to the white form which is less soluble in chloroform and colourless in solution. With larger amounts of vanadium the colour change was from yellow to greenish-blue, indicating reduction of the vanadium. One way to minimise these difficulties would be to transform the vanadium to a more tightly bound complex following extraction into chloroform.

A survey of the literature on vanadium complexes suggested that the vanadium 8-quinolinol complex[22] was stable and had the advantage that the red colour (550 mμ) was in a region where molybdenum and tungsten did not absorb. It was found that the complex formed readily on adding the chloroform solution of the vanadium-α-benzoinoxime complex to an ethanol solution of 8-quinolinol. To check this method the following procedure was used.

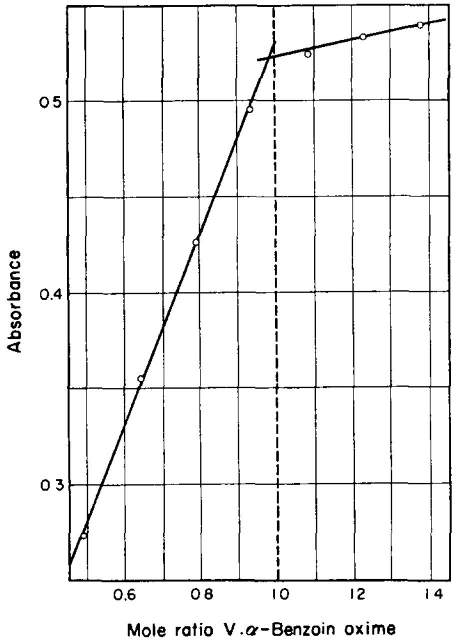

FIG. 5. Determination of vanadium: α-benzoin oxime ratio by extraction.

Procedure: A 10-ml portion of vanadium^{V} solution was adjusted to pH 2.2 with hydrochloric or sulphuric acid and extracted for 1 min with 10 ml of 0.1% α-benzoinoxime in chloroform. The chloroform extract was drawn off into a 100-ml volumetric flask containing 10 ml of 0.1% 8-quinolinol in 95% ethanol. The aqueous layer was extracted with two more 10-ml portions of α-benzoinoxime solution and finally with one 10-ml portion of chloroform. Twenty ml of 95% ethanol were added and the flask was filled to the mark with chloroform. After mixing, the absorption was measured at 550 mμ against a blank containing everything except the vanadium. It was found that Beer's law was followed for 5–80 μg of vanadium per ml of the starting aqueous solution. The extraction of the vanadium was complete as shown by a negative Feigl test.[23]

This extraction method was used to establish the ratio of vanadium^{V} to α-benzoinoxime in the complex extracted. Solutions containing 0.01–0.0275 millimole of vanadium^{V} were extracted with two 10-ml portions of $1 \times 10^{-3}M$ α-benzoinoxime in chloroform (total 0.02 millimole) and the colour was developed and measured as before. The results are shown in Fig. 5. It is seen that the complex has a 1:1 composition and that excess reagent is needed to get quantitative extraction.

Determination of vanadium

The determination of vanadium^{V} by extraction with 8-quinolinol proposed by Talvitii[22] requires the removal of iron^{III} before extraction. Using α-benzoinoxime as previously described eliminates the effect of iron^{III} and does not introduce any other difficulties. The vanadium in 10 ml of solution containing 0.049 mg per ml was determined as previously described. A variety of possible interfering ions was added. The results are summarised in Table X. The interference by antimony was caused by precipitation of a white substance which turned yellow with time, suggesting the adsorption of vanadium. This is supported by the decrease in vanadium found when the acid solution stands 24 h before extraction. The other low results are found with ions which form heteropoly acids with vanadium^{V}.

TABLE X. EFFECT OF IONS ON THE DETERMINATION OF VANADIUM

Ion, *mg*	Vanadium, *mg*		
	Present	Found	Difference
Mo^{VI} 2.50	0.49	0.48	−0.01
W^{VI} 2.50	0.49	0.47	−0.02
Cr^{VI} 2.50	0.49	0.49	—
Mn^{VII} 2.50	0.49	0.49	—
Cu^{II} 2.50	0.49	0.49	—
Si^{IV} 2.50	0.49	0.47	−0.02
Bi^{III} 2.50	0.49	0.45	−0.04
U^{VI} 2.50	0.49	0.46	−0.03
Sb^{III} 2.50	0.49	0.43	−0.06
after 24 h		0.35	−0.14
H_3PO_4 1.25	0.49	0.49	—
Fe^{III} 2.50	0.49	0.49	—
Al^{III} 2.50	0.49	0.49	—

4. *Chromium^{VI} complex with α-benzoinoxime*

Since there is some evidence for the existence of CrO_2^{2+} in acid dichromate solution,[9] experiments were run to determine if an α-benzoinoxime complex was formed. When α-benzoinoxime in 1:1 aqueous acetone was added to potassium dichromate in 5% by volume hydrochloric acid, a bright orange precipitate formed. Within minutes, however, the precipitate changed to a greenish-brown gummy mass. It appears that the reagent is oxidised by the chromium^{VI} so that no useful precipitations are possible. An attempt was made to extract chromium^{VI} from 5% hydrochloric acid using the procedure as described for vanadium. To test for chromium, diphenylcarbazide[6] was used. The largest amount of chromium found was only 1% of that put into the solution to be extracted. It was therefore concluded that further work at this time was not worth while.

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Zusammenfassung—Molybdän(VI) wird durch α-benzoinoxim als $MoO_2(C_{14}H_{12}O_2N)_2$ aus Lösungen von pH2 bis hinauf zu 5 Volumpercent Schwefelsäure gefällt. Die Methode von Knowles zur Bestimmung von Molybdän in Stahl wird modifiziert, sodass der Niederschlag gewogen werden kann ohne erst zum Oxyd verglühen worden zu sein. Die bei der Extraktion des Komplexes mit Chloroform auftretende Störung durch Wolfram und Vanadin wird durch Zusatz von Dihydrogenphosphat und Eisen(II)-Lösung ausgeschaltet. Wolfram bildet eine analoge Komplex und fällt auf Zusatz des Reagenses zu einer frisch mit Schwefelsäure angesäuerten Wolframsalzlösung aus. Die Fällung des Wolframs ist jedoch nicht komplett, selbst nicht in Anwesenheit von Fluorid- oder Phosphationen. Die Extraktion des Wolframkomplexes ist nicht anzuraten, da seine Löslichkeit zu gering ist. Vanadin(V) formt mit Benzoinoxim bei pH3 einen gelben Niederschlag und bei

pH1.5 nach langem Stehen einen weissen Niederschlag. Der gelbe Niederschlag geht bei längerem Stehen in die weisse Form über. Der weisse Niederschlag nat die Zusammensetzung $VO_2(C_{14}H_{12}O_2N)$ enthält aber stets erhebliche Mengen von Fällungsmittel. Der Vanadinkomplex kann bei pH 2.2 mit Chloroform extrahiert werden und wird zur Messung in den Oxinkomplex übergeführt. Wismut, Antimon(III) und Uranyl verursachen leichte Störung. Chrom(VI) oxydiert das Reagens so rasch, dass keine Studien möglich waren.

Résumé—Le molybdèneVI est précipité par l'α benzoïne oxime sous forme de $MoO_2(C_{14}H_{12}O_2N)_2$ dans des solutions acides de pH2 contenant jusqu'à cinq pour cent en volume d'acide sulfurique.

Le procédé de Knowles pour le dosage du molybdène dans les aciers est modifié afin d'obtenir des précipités qui peuvent être pesés sans calcination à l'état d'oxyde. Dans l'extraction de ce complexe du molybdène par le chloroforme, l'interférence du tungstène et du vanadium est éliminée par addition d'ion $H_2PO_4^-$ et d'ion ferreux. Le tungstèneVI forme $WO_2(C_{14}H_{12}O_2N)_2$ par addition d'α benzoine oxime à des solutions de tungstate fraîchement acidifiées par l'acide sulfurique. La précipitation du tungstène sous forme de ce complexe n'est pas complète même en présence d'ions fluorure ou phosphate. L'extraction du complexe du tungstène par le chloroforme n'est pas faisable à cause de sa solubilité limitée. Le vanadiumV forme avec l'α benzoïne oxime un précipité jaune à pH3 et, après un temps assez long, un précipité blanc à pH1,5. Le précipité jaune se transforme à la longue en précipité blanc.

Le précipité blanc a la composition suivante: $VO_2(C_{14}H_{12}O_2N)$ mais il est toujours contaminé par un excès de réactif. En utilisant le complexe avec l'α benzoïne oxime, le vanadiumV peut être extrait à pH 2,2 par le chloroforme et transformé en un complexe avec le 8-quinolinol pour permettre des mesures. Le bismuth, l'antimoineIII et les ions uranyl gênent légèrement. Le chromeVI en solution acide oxyde l'α benzoïne oxime si rapidement qu'aucune étude n'a été possible.

REFERENCES

[1] F. Feigl, *Ber.*, 1923, **B56**, 2083.
[2] H. B. Knowles, *J. Res. Nat. Bur. Stand.*, 1932, **9**, 1.
[3] H. Yagoda and H. A. Fales, *J. Amer. Chem. Soc.*, 1938, **60**, 1938.
[4] J. F. Flagg, *Organic Reagents Used in Gravimetric and Volumetric Analysis*, Interscience Publishers, Inc., New York, 1948, pp. 121–32.
[5] A. Blanco, *Quimica (Mexico)*, 1948, **6**, 52.
[6] K. J. Jensen and B. Weaver, Natl. Nuclear Energy Ser., Div. VIII, *Analytical Chemistry of the Manhattan Project*, 1950, **1**, 445–58.
[7] P. G. Jeffrey, *Analyst*, 1956, **81**, 104–9.
[8] G. Goldstein, D. L. Manning and O. Menis, *Analyt. Chem.*, 1958, **30**, 539–42.
[9] W. Huckel, *Structural Chemistry of Inorganic Compounds*, Elsevier, New York, 1950, p. 1794.
[10] F. Chaveau, *Compt. rend.*, 1956, **242**, 2154–7.
[11] I. Lindquist, *Acta Chem. Scand.*, 1950, **4**, 650.
[12] H. M. Neumann and N. Cook, *J. Amer. Chem. Soc.*, 1957, **79**, 3355.
[13] F. H. Nicholls, H. Saenger and W. Wardlaw, *J. Chem. Soc.*, 1931, 1443.
[14] R. Berg, *Z. analyt. Chem.*, 1927, **71**, 369.
[15] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, *Applied Inorganic Analysis*, 2nd ed., John Wiley and Sons, New York, 1953, p. 310.
[16] D. J. Bettinger and S. Y. Tyree, *J. Amer. Chem. Soc.*, 1957, **79**, 3355.
[17] M. Kerker, D. Lee and A. Chou, *ibid.*, 1958, **80**, 1539.
[18] J. C. Bailar, *Chemistry of the Coordination Compounds*, Reinhold Publishing Corp., New York, 1956, Chapter 14.
[19] F. Feigl, *Analyt. Chim. Acta*, 1948, **2**, 397.
[20] R. Niericker and W. D. Treadwell, *Helv. Chim. Acta*, 1946, **29**, 1472.
[21] F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.*, 1956, **10**, 957.
[22] N. A. Talvitii, *Analyt. Chem.*, 1953, **25**, 604.
[23] F. Feigl, *Qualitative Analysis by Spot Tests*, Nordemann Publishing Co., New York, 1939, p. 70.

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THE ESTIMATION OF THE STABILITIES OF BIVALENT TRANSITION METAL COMPLEXES AND DEVIATIONS FROM THE IRVING-WILLIAMS ORDER

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Summary—The free energies of formation of a range of ligands with Mn^{II} Fe^{II}, Co^{II} and Zn^{II} have been related to ligand field stabilisations, and it has been found possible to predict on theoretical grounds deviations from the Irving-Williams order.

THE ligand field stabilisations in complexes of a given ligand with Fe^{II}, Co^{II} and Ni^{II} have been shown[1,2] to be approximately proportional to the difference, Δ, in the free energies of formation of the complexes of Mn^{II} and Zn^{II} with the ligand. The free energies are corrected for the hydration energies of the metal ions. Thus, the course of the formation constants in the series Mn^{II} to Zn^{II} (with the possible exception of Cu^{II}) can be represented by such simple expressions that it is possible to calculate the constants for unknown members of the series if any two are known. With the aid of additional data taken from a recent compilation[3] and results obtained in our laboratories[4] it is possible to present more exact relationships covering a wider range of Δ values.

As before, the monotonic function which describes the increase in stabilities through the series Mn^{II} to Zn^{II} in the absence of any ligand field stabilisation is assumed to be linear. Some justification for this is given by the results of Holmes and McClure[5] who show a linear increase in the resulting hydration energies of the bivalent transition metals after corrections are made for the spectroscopic ligand field stabilisation energies. Then from this assumption and definition of Δ the following equations can be set up:

$$\Delta = \Delta F_{Zn} + \Delta H_{h_{Zn}} - \Delta F_{Mn} - \Delta H_{h_{Mn}}$$

$$\Delta F_{Ni} = \tfrac{3}{5}\Delta + \Delta F_{Mn} + \Delta H_{h_{Mn}} - \Delta H_{h_{Ni}} + E_{lf_{Ni}}$$

$$\Delta F_{Co} = \tfrac{2}{5}\Delta + \Delta F_{Mn} + \Delta H_{h_{Mn}} - \Delta H_{h_{Co}} + E_{lf_{Co}}$$

$$\Delta F_{Fe} = \tfrac{1}{5}\Delta + \Delta F_{Mn} + \Delta H_{h_{Mn}} - \Delta H_{h_{Fe}} + E_{lf_{Fe}}$$

where ΔF_M is the free energy of formation of a complex from the aquo ion, M^{2+}, ΔH_{h_M} is the hydration energy of M^{2+} and E_{lf_M} is the ligand field stabilisation energy of the complex.

Using the Benjamin and Gold hydration energies[6] the equations became

$$\Delta = \Delta F_{Zn} - \Delta F_{Mn} - 47.6 \text{ kcals}$$

$$\Delta F_{Ni} = \tfrac{3}{5}\Delta + \Delta F_{Mn} + 62.3 + E_{lf_{Ni}} \text{ kcals}$$

$$\Delta F_{Co} = \tfrac{2}{5}\Delta + \Delta F_{Mn} + 50.0 + E_{lf_{Co}} \text{ kcals}$$

$$\Delta F_{Fe} = \tfrac{1}{5}\Delta + \Delta F_{Mn} + 17.9 + E_{lf_{Fe}} \text{ kcals.}$$

These equations can be used to obtain the E_{lf} if the free energies are known or can be used to calculate unknown ΔF_M using two known values and the equations given below.

Simple proportionalities do not exist as first given,[1,2] but the relationships between the E_{lf} and Δ can be described by linear equations, the parameters of which depend on the metal ion and the type of complex. For the Ni^{II} complexes three equations are sufficient. These represent straight lines which intersect at the point for the aquo ion. The octahedrally symmetrical complexes ($Ni[H_2O]_6^{2+}$, $Nien_3^{2+}$ and $Ni[1:10\text{-phen}]_3^{2+}$) give the relationship

$$E_{lf} = 1.13\Delta + 20.3.$$

Those complexes with ligands that co-ordinate only through oxygen (oxalate, malonate and salicylaldehyde) also obey this relationship. It is thus indicated that not much difference exists in the behaviour of oxygen as a charged or uncharged donor, in this respect. Values of E_{lf} for the pyridine and 8-hydroxyquinoline-5-sulphonate complexes are also given by this equation.

For those mixed complexes in which both amino nitrogen and oxygen are co-ordinated, lower values of $E_{lf_{Ni}}$ are given by

$$E_{lf_{Ni}} = 0.88\Delta + 8.1.$$

These complexes are represented by $Ni(glycinate)(H_2O)_4^{+}$, $Ni(glycinate)_2(H_2O)_2$, $Ni(EDTA)^{2-}$, $Nien(H_2O)_4^{2+}$, $Nien_2(H_2O)_2^{2+}$, $Ni(nitrilotriacetate)(H_2O)_2^{-}$, $Ni(2{:}2\text{-diaminodiethylamine})(H_2O)_3^{2+}$, $Ni(ethylenediamine\text{-}N{:}N\text{-}diacetate)(H_2O)_2$ and $Ni(2\text{-methylthioethyliminodiacetate})(H_2O)_x$. The complex Ni[N:N:N′:N′-tetrakis (2-aminoethyl) ethylenediamine] also obeys this relationship. This may be an indication that all of the nitrogen atoms are not co-ordinated with this latter ligand. The lower stabilisation in this series probably results from the lower symmetry of the ligand field about the nickel ion.

The lowest values of $E_{lf_{Ni}}$ are obtained with the complexes Ni(mercaptoacetate)$_2^{2-}$[1] and Ni(2:3-dimercapto-1-propanolate)$_2^{2-}$.* [7] Here the relationship is

$$E_{lf_{Ni}} = 0.35\Delta - 17.3.$$

The octahedral cobalt^{II} complexes give the result

$$E_{lf_{Co}} = 0.84\Delta + 8.7$$

while in the mixed complexes (oxygen, nitrogen, sulphur) the relationship simply is

$$E_{lf_{Co}} = 0.66\Delta.$$

The values of E_{el} for Fe^{II} are relatively small and for both octahedral and mixed complexes one equation suffices. This is

$$E_{lf_{Fe}} = 0.27\Delta + 4.2.$$

A departure from this occurs with the well known 1:10-phenanthroline. The observed value of $E_{lf_{Fe}}$ for the tris-(1:10-phenanthroline) iron^{II} ion is much greater than

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* The value of Δ was calculated using the formation constants of $Mn(DMP)_2^{2-}$ and $Zn(DMP)_2^{2-}$ which have been found to be $3 \times 10^{+10}$ and $1.8 \times 10^{+23}$ at 30° (ref. 4). These give the largest value of Δ so far observed.

would appear likely from the stabilities of the Mn^{II}, Ni^{II} and Zn^{II} complexes. This is a consequence of the fact that in the diamagnetic Fe^{II} complex all the electrons are in the t_{2g} orbitals and enter into π bonding with the ligand molecules.

In the absence of steric or other abnormal factors these equations give an uncertainty in ΔF of about ± 1 kcal for the larger Δ values. The uncertainty is less for small values of Δ. If a more accurate value of a constant is needed, it is, of course, better to measure it under the prescribed set of conditions to be met in practice.

In addition to the case of tris-(1:10 phenanthroline) iron^{II} mentioned above, other deviations from the Irving-Williams order of complex stabilities are observed.

TABLE I.—THE FREE ENERGIES FOR THE REACTION
$M_{aq}^{2+} + SO_{4aq}^{2-} \rightarrow MSO_{4aq}$
$T = 25°$

M	ΔF_{298}[a] obs, *kilocalories*	ΔF_{298} calc, *kilocalories*
Mn^{2+}	−3.07	(−3.07)
Fe^{2+}	—	−3.5
Co^{2+}	−3.21	−3.6
Ni^{2+}	−3.16	−3.2
Zn^{2+}	−3.25	(−3.25)

[a] From Reference 9.

One deviation is found with the mercaptides where the Ni^{II} complexes are appreciably less stable than those of Zn^{II}. It appears that this is the result of abnormalities in the Ni^{II} complexes rather than in the Δ values as given by the Mn^{II} and Zn^{II} complexes. The Ni^{II} complexes are diamagnetic and the lower values of $E_{lf_{Ni}}$ can be attributed to the electron repulsion energy which is lost in pairing up the electrons. If no delocalisation of electrons occurs through π bonding this energy is not regained and net lower stability results.

Another deviation from the Irving-Williams order occurs with the weak complexes. In the sulphates, for example, the Ni^{II} complex has been found[9] to be less stable than even that of Co^{II}. The effect can be attributed primarily to the hydration energies, which are the largest in this series for the Ni^{II} ion. An analogy, in this respect, exists with the solubilities of the transition metal salts where an inversion of nickel also sometimes occurs[10].

Calculated values of the free energies of formation of the sulphate complexes are given in Table I, together with those observed. It is seen that the relationships presented in this paper, which were obtained from systems in which the Irving-Williams order is obeyed, correctly predict the inversion with the Ni^{II} sulphate complex. The calculated free energies of formation compare favourably with those observed and the order of stability of the Ni^{II} complex is correctly placed.

Another deviation of this type must also occur with the chloride complexes. Here it is found that nickel^{II} is not extractable from solutions as an anionic chloro complex with ion-exchange resins even though media up to $10M$-$11M$ in hydrochloric acid have been used. The other metal ions in this series are, on the other hand, easily extractable.

Zusammenfassung—Die freie Energie der Komplexbildung einer Reihe von Liganden mit Mn(II), Fe(II), Co(II) und Zn(II) wurde zur Stabilisierung des Lignadfeldes in Bezugvgesetzt. Es wurde gefunden dass es derart möglich ist auf Grund theoretischer Gründe Abweichungen von der Irving-Williams-Reihe vorauszusagen.

Résumé—Les énergies libres de formation d'une série de composés de Mn(II) Fe(II), Co(II) et Zn(II) ont été reliées aux "stabilisations du champ du composé" et l'auteur a trouvé qu'il était possible de prédire sur des bases théoriques, les écarts à l'ordre de Irving-Williams.

REFERENCES

[1] D. L. Leussing, *J. Amer. Chem. Soc.*, 1958, **80**, 4180.
[2] P. George, *Rec. trav. Chim.*, 1956, **75**, 671.
[3] J. Bjerrum, G. Schwarzenbach and L. G. Sillen, *Stability constants* Part 1, The Chemical Society, London, 1957.
[4] D. L. Leussing and T. N. Tischer, to be published.
[5] O. G. Holmes and D. S. McClure, *J. Chem. Phys,*. 1957, **26**, 1686.
[6] L. Benjamin and V. Gold, *Trans. Faraday Soc.*, 1954, **50**, 797.
[7] D. L. Leussing, *J. Amer. Chem. Soc.*, 1959, **81**, 4208.
[8] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192.
[9] V. S. K. Nair and G. H. Nancollas, *ibid.*, 1959, 3934.
[10] D. L. Leussing, in *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving, eds. Interscience, New York, N.Y., 1959, Chapter 17.

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A NEW METHOD FOR "FERROUS IRON" AND "EXCESS OXYGEN" IN ROCKS, MINERALS, AND OXIDES*

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Summary—A new method is given whereby oxygen excess or deficiency in many minerals and oxides may be simply determined. The method depends on the stability in phosphoric acid-pyrophosphate mixtures of both Mn^{III} and Mn^{II}. The sample is dissolved in a phosphoric acid mixture containing excess Mn^{II}, with or without the addition of standard oxidant, and Mn^{III} remaining in solution or produced by reaction with the sample is titrated with ferrous ammonium sulphate, using barium diphenylamine sulphate as indicator. The method is useful in many cases where existing methods are inapplicable or unsatisfactory. Accurate results can be obtained using relatively small samples.

IN presenting the results of silicate rock and mineral analyses, it is standard practice to report both ferrous and ferric oxides. "Ferrous iron" is determined by solution of the sample in acid and titration with standard oxidant: the titration is assumed to be proportional to the ferrous iron content (after making certain corrections, *e.g.* for sulphides and insoluble material such as chromite), and it is calculated to FeO and reported as such. Ferric oxide is obtained by subtracting the equivalent of the FeO from the total Fe_2O_3. Ferrous iron determination is discussed at length by Hillebrand *et al.*[4]

Although in most instances the volume of oxidant consumed by its acid solution is indeed a measure of the ferrous iron content of the sample, this is not always the case. The amount of ferrous iron in solution does not necessarily bear any relation to the number of Fe^{II} atoms in the sample itself. For instance, an equimolecular mixture of Fe_3O_4 and CeO_2 would show no ferrous iron by the usual procedures; neither would the oxide $Fe^{II}Fe^{III}Mn^{III}O_4$, though in each case Fe^{II} is an essential constituent.

It would thus seem that there are occasions when FeO should not be reported as such but, instead, a figure for "oxygen deficiency" should be given, just as "oxygen excess" is reported, for example, in the analyses of certain manganese ores. In interpreting such results, it should be understood that the figure reported represents the oxygen loss or gain necessary to bring all the elements in the sample to specified valency states. These valences need not be the maximum stable valences; for example, though manganese exists naturally in both the ter- and quadrivalent condition, it will invariably finish bivalent in the ferrous iron determination.

In certain mixed oxides, in particular Fe_2MnO_4, there may be either an excess or deficiency of oxygen, and it would be highly desirable to have a method whereby either could be determined with accuracy: such a method is presented here.

The method depends on the stability, over a wide temperature range, of both bi- and tervalent manganese in a phosphoric acid-pyrophosphate mixture. Many

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oxides and silicates are soluble in this mixture and, if these contain excess oxygen in the sense indicated above, they have only to be dissolved in the presence of a large excess of bivalent manganese; the resulting Mn^{III} may then be quite simply titrated with standard ferrous solution, using barium diphenylamine sulphonate as indicator. For "ferrous iron" or oxygen deficiency, a measured excess of oxidant, either permanganate or dichromate, is added to the acid mixture before dissolving the sample. The excess is then titrated as before with standard ferrous solution. The addition of either Mn^{VII} or Cr^{VI} to a phosphoric acid-pyrophosphate solution of Mn^{II} results in immediate oxidation of the latter to Mn^{III}.

The procedure is similar in its essentials to one described earlier[5] for the determination of manganese. It resembles, in some respects, certain modifications of the Seil method[6] for the determination of ferrous iron in chromite, particularly those of Shein[7] and Goswami,[2] who used V^{V} and Ce^{IV} respectively as intermediate oxidants. These procedures have been discussed and evaluated by Dinnin.[1] In the author's experience, Mn^{III}, produced when dichromate or permanganate is added to phosphoric acid-pyrophosphate solutions of bivalent manganese, is more satisfactory than either V^{V} or Ce^{IV} for this purpose, provided that certain precautions are taken in the preparation of the reagents.

The new method is not universally applicable, being limited to samples which dissolve directly in phosphoric acid-pyrophosphate, do not contain elements (notably sulphur and organic carbon) which oxidise variably, and do not yield peroxides on solution in acid. Peroxide reduces Mn^{III} immediately. Among materials which do not dissolve readily under the conditions of the procedure must be listed silicates low in iron and some oxides containing Mn^{IV}.

Despite its limitations, the method has proved very useful, particularly in cases where other methods are inapplicable or unsatisfactory. It has been used successfully with chromite, various silicate minerals, and rocks, and for the determination of excess oxygen in various oxides. A good determination of either excess oxygen or ferrous iron can be made on a relatively small sample: 100 mg or less is often sufficient. This is of importance when only a small amount of material is available.

In most cases where both have been used, the new and older methods agree quite satisfactorily; however, with some silicates (samples 5, 8, Table I) results for ferrous iron by the new method appear low. Further, the excess oxygen in some oxides is not completely recovered (Table II). Thus its indiscriminate application is inadvisable.

EXPERIMENTAL

Reagents

Ferrous ammonium sulphate: 0·01*N* in 0·5% (V/V) sulphuric acid.

Manganous sulphate: Dissolve 100 g of $MnSO_4.H_2O$ in 100 ml of water. Filter through glass-fibre paper to remove small particles of organic material.

Sodium dihydrogen phosphate: Dissolve 200 g of $NaH_2PO_4.H_2O$ in 200 ml of water. Filter through glass-fibre paper.

Phosphoric acid: Reagent-grade, 85% H_3PO_4.

Potassium permanganate: 0·1*N*, accurately standardised.

Potassium dichromate: 0·1*N*.

Barium diphenylamine sulphonate: 0·2% aqueous solution.

Prepare a reagent solution for each sample as follows: add 20 ml of phosphoric acid, 5 ml of sodium dihydrogen phosphate solution, and about 0·5 ml (more if necessary to oxidise organic impurities in the reagents) of 0·1*N* potassium dichromate to a 250-ml wide mouth conical flask. Mix,

TABLE I.—COMPARISON OF RESULTS FOR FERROUS IRON

Sample	Description	Weight, *mg*	$KMnO_4$, *ml* 0.1*N*	FeO found	
				New method	Other methods
1	Shonkinite	250	5	12·94	13·19*
2	Chromite	150	5	21·23	21·32† 21·25‡
3	Garnet	200	2	6·09 6·10	5·71*
4	Grunerite	250	10	27·86	27·16*
5	Amphibole	100	3	17·86 17·85	18·48*
6	Pyroxene	200	5	17·29	17·27*
7	Biotite	200	10	29·53	29·22
8	Olivine	100	10	59·72	60·36* 60·44*
9	Ilvaite	200	10	31·14	31·16*
10	Granite G-1	500	1	0·94	0·97§
11	Diabase W-1	200	1	8·75	8·71§
12	Olivine	200	3	7·51	7·21*‖

* Solution in $HF-H_2SO_4$, titration with $KMnO_4$ in presence of H_3BO_3.
† Closed tube method.
‡ Method of Seil[6].
§ Value reported by Goldich and Oslund[3].
‖ Result uncorrected for about 1% of chromite which remained largely unattacked.

TABLE II.—COMPARISON OF RESULTS FOR EXCESS OXYGEN

Sample	Description	Weight, *mg*	Excess oxygen, %	
			New method	Other methods
1	Iron-manganese oxide, Fe_2MnO_4	500	0·202 0·202	
2	Iron-manganese oxide, Fe_2MnO_4	500	0·340 0·341	
3	Manganese oxide, Mn_3O_4	100	6·91 6·92	6·94* 6·97* 6·99†
4	Manganese oxide, Mn_3O_4	100	6·94	6·93* 6·96* 6·99†
5	Manganese oxide, MnO	500	0·00	0·00
6	Manganese oxide	100	1·54	1·54†
7	Manganese oxide	100	3·06	3·04†
8	Ceric oxide	100	4·64	4·65†
9	Praseodymium oxide	173	2·76 2·65	3·13‡
10	Terbium oxide	100	1·84	2·14‡
11	Red lead	260	1·98	2·33‡
12	Cobalt oxide	120	4·02	6·64‡

* Solution in H_2SO_4-Fe^{II}, back titration with $KMnO_4$.
† Well-established calculated value.
‡ Calculated value, composition not certain.

and heat slowly, without boiling, gradually increasing the temperature until water is expelled and the excess chromate is destroyed. A final temperature exceeding 250° is required to remove excess chromate completely, but heating must not be continued to the point where insoluble polyphosphates separate. The solution should not be allowed to boil because of an extreme tendency to spatter.

Cool until the flask can be handled, then add about 2 ml of cold water. Mix, and cool to room temperature.

Add 1·0 ml of manganous sulphate solution, rinse down the sides of the flask with a very small volume of water, mix thoroughly, and add a measured excess of standard (0·1*N*) permanganate, sufficient to oxidise the ferrous iron expected and provide a small excess. It is essential that the manganous sulphate solution be thoroughly mixed with the acid before the permanganate addition. Dichromate may be used instead of permanganate if desired: in either case the effect is to add Mn^{III}. Dichromate has the disadvantage of imparting a green colour to the final solution which obscures the end-point somewhat.

Again evaporate the solution to remove most of the extra water added with the standard oxidant. This step may be omitted if water additions were kept to a minimum, and no more than 2·00 ml of the standard oxidant were used. If the sample is dissolved in a mixture containing much water, the pyrophosphate is depleted during solution to the point where Mn^{III} is no longer stable, and air oxidation of ferrous iron may occur.

If the sample contains excess oxygen, no addition of standard oxidant is required.

Sample

The sample weight should be chosen so that no more than 10 ml of standard (0·1*N*) oxidant need be used. If excess oxygen is to be determined, not more than 0·5 to 1·0 milliequivalents should be present.

Most samples require grinding to −115 mesh or finer. Chromite should be −325 mesh.

Procedure

To the prepared mixture, add the sample and shake or swirl until it is uniformly distributed. Rinse down the sides of the flask with a very small volume of water, and heat on the hot plate, without boiling, gradually increasing the temperature until attack is complete. Some materials dissolve rapidly even before water is expelled: others, chromite for example, do not react until the temperature of the mixture approaches or exceeds 300°. Some leave an insoluble fraction which may be ignored. With silicates, it is important that the sample be well dispersed, for particles which clump together and become coated with silicic acid may escape attack. Not more than 0·2 to 0·5 g of silicate mineral should be used under the conditions described, but with silicious rocks, up to 1 g will usually give no trouble.

When solution is complete, cool until the flask can be handled, add 5 ml of cold water, mix thoroughly, and cool in running water. Dilute to about 20% in phosphoric acid, cool to room temperature, and titrate with 0·01*N* ferrous ammonium sulphate solution, adding 1–2 drops of barium diphenylamine sulphonate indicator just before the end-point. It is best to delay the indicator addition until the pink colour of Mn^{III} is nearly discharged.

A blank determination should be made using a small volume of standard oxidant (say 0·100 ml of 0·1*N* permanganate). A small negative blank (about 0·2 ml of 0·01*N* solution) is always obtained. For example, 0·100 and 1·994 ml of 0·1001*N* permanganate gave titrations of 0·81 and 19·93 ml of 0·00993*N* ferrous ammonium sulphate solution when carried through the procedure, and 0·99 and 20·13 ml when titrated directly. The actual indicator blank is very small : about 0·02 ml of 0·01*N* solution.

If the reagents are not subjected to a preliminary treatment to remove oxidising and reducing impurities, the blank is very large and non-reproducible.

DISCUSSION

The procedure described for the preliminary treatment of the reagents to remove oxidising and reducing impurities is more effective than several others tried. Preparation of the reagent in bulk is possible, but has serious disadvantages: a high temperature is necessary to decompose chromate completely, and the resulting mixture tends to freeze into a glass on standing.

Because of the relative ease with which Mn^{II} is oxidised in phosphoric acid solution, the possibility of air oxidation was investigated, and it is certain that no such oxidation takes place under the conditions of the procedure. Likewise the stability of Mn^{III} has been established, though there is a possibility of slight loss of oxygen when heating is continued for several hours above 360°.

When determining ferrous iron, especially in samples which dissolve readily, it is essential that most of the water be evaporated from the reagent mixture before adding the sample. Failure to do this often leads to low results (presumably because the pyrophosphate formed in the early stages of reagent preparation becomes depleted, leaving the sample liable to air oxidation). With a ferrous olivine (sample 8, Table I) 57·18, 57·23, and 56·54% FeO were found when this step was omitted, as compared to 59·72% when the reagent was evaporated as directed. With chromite, which is unattacked below about 250°, the removal of excess water before addition of the sample makes very little difference to the results.

In the course of the titration, vanadium is reduced to V^{IV}; when this element is present, a correction must be made if results are to be compared with those obtained by methods in which vanadium finishes in the quinquevalent condition.

The behaviour of sulphur and sulphides is not stoichiometric. Most metallic sulphides are completely attacked by the phosphate mixture containing excess Mn^{III}: some of the sulphur is volatilised in the elemental state; some is presumably oxidised to sulphate. The possibility of using an empirical correction based on the sulphide content of the sample was investigated, but results were not very satisfactory. If minor amounts of sulphide are present, a correction based on the relation

$$S^{--} + 2Mn^{+++} \rightarrow S + 2Mn^{++}$$

may be applied with fairly good results.

Most silicate minerals to which the method can be applied dissolve readily if passed through a 115-mesh screen, though amphiboles and pyroxenes must usually be −200 mesh. Chromite should be −325 mesh. Grinding is best done by hand in an agate mortar, with frequent screening to remove fines so that air oxidation is minimised. The samples should always be passed through the appropriate screen, then thoroughly mixed before the determination is attempted. Grinding without screening is certain to be unsatisfactory.

The heating period necessary for solution of the sample varies greatly. It does no harm to heat for 2 h or more at 200-250° if attack is slow. At higher temperatures, Pyrex is attacked rapidly, and much silica is thereby introduced. Polyphosphates may separate on prolonged heating at elevated temperatures. It is best to heat at the lowest effective temperature, for if polyphosphates separate because of too rapid heating, these tend to coat particles of sample, greatly slowing the rate of solution. The use of Vycor flasks may be desirable with chromites.

During solution of some oxide samples, the Mn^{III} colour may fade after a preliminary development, sometimes with the deposition of dark-coloured oxides. This is presumably due to depletion of the pyrophosphate in solution. On further heating to remove water, the colour reappears, and the determination proceeds normally.

The behaviour of the rare earth oxides is of interest. Ignited ceric oxide dissolves readily in the hot phosphoric acid mixture, and the excess oxgyen is quantitatively retained and titrated. Praseodymium oxide dissolves with the evolution of gases: whether this is due to peroxide formation or liberation of oxygen from solid solution is in doubt. Terbium oxide dissolves without perceptible gas evolution, but the values obtained for excess oxygen are less than indicated by the formula Tb_4O_7.

Higher oxides of cobalt and lead (Co_3O_4 and Pb_3O_4) dissolve with the evolution of oxygen, and results for excess oxygen are low.

Acknowledgment—Thanks are due to A. I. Muan for supplying oxide samples of known composition, to R. O'Neil for helpful criticism, and to Marilyn Grender, who carried out many of the determinations during the development of the method.

Zusammenfassung—Eine neue Methode wird beschrieben, um Überschuss oder Mangel an Sauerstoff in Mineralen oder Oxyden einfach zu bestimmen. Die Methode beruht darauf, dass sowohl Mn(III) als auch Mn(II) in einer Mischung von Phosphorsäure und Pyrophosphate beständig sind. Die Probe wird in gegenwart oder Abwesenheit von Standard-Oxydans in einer Phosphorsäuremischung gelöst, die überschüssigess Mn(II) enthält. Das in Lösung vergleibende oder durch Reaktion mit der Probe gebildete Mn(III) wird mit Ferro-ammonsulfat gegen Diphenylamin als indicator titriert. Die Methode kann in vielen Fällen angewendet werden, in denen übliche Methoden versagen oder unbefriedigende Resultate liefern. Genaue Ergebnisse werden mit relativ kleinen Probemengen erhalten.

Résumé—L'auteur donne une nouvelle méthode par laquelle l'excès ou le manque d'oxygène peut être dosé simplement dans de nombreux minerais et oxydes. La méthode dépend de la stabilité de Mn(III) et Mn(II) dans les mélanges acide phosphorique-pyrophosphate. L'échantillon est dissous dans un mélange d'acide phosphorique contenant un excès de Mn(II), avec ou sans addition d'un oxydant standard; Mn(III) restant en solution ou produit par réaction avec l'échantillon est titré avec du sulphate d'ammonium et de fer ferreux, en utilisant la diphénylamine sulfonée comme indicateur. La méthode est utile dans de nombreux cas où les méthodes existantes sont inapplicables ou ne sont pas satisfaisantes. Des résultats précis peuvent être obtenus en utilisant des échantillons relativement petits.

REFERENCES

[1] J. I. Dinnin, *U.S. Geological Survey Bulletin*, 1959, 1084-B.
[2] H. Goswami, *Science and Culture*, 1957, **22**, 398–400.
[3] S. S. Goldich and E. H. Oslund, *Bull. Geol. Soc.*, 1956 **67**, 811–815.
[4] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, *Applied Inorganic Analysis*, John Wiley and Sons, New York, 2nd Ed., 1953.
[5] C. O. Ingamells, *Talanta*, 1959, **2**, 171–175.
[6] G. Seil, *Ind. Eng. Chem. Anal.*, 1943, **15**, 189–192.
[7] A. V. Shein, *Zavodskaya Lab.*, 1937 **6**, 1199–1205: *Chem. Abs.*, **32**, 1211.

Talanta, 1960, Vol. 4, pp. 274 to 291. Pergamon Press Ltd. Printed in Northern Ireland

RADIO-FREQUENCY METHODS IN ANALYTICAL CHEMISTRY

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Summary—The theory of radio-frequency measurements of chemical importance is outlined, and suitable apparatus is discussed. The applications, especially to analytical chemistry, are reviewed.

INTRODUCTION

The first applications of radio-frequency (RF) measurements were concerned with dielectric constant determination. For example, the moisture content of powdered materials has been measured by packing them between the plates of a capacitor in an oscillatory circuit and observing the change in frequency by a heterodyne-beat method.[1,2] The separation of organic mixtures by fractional distillation may be controlled by such dielectric measurements.[2] The classical work of Debye and Falkenhagen showed that ionic-atmosphere effects decreased with increase in frequency; a considerable change in equivalent conductance was observed[3] above 30 Mc/sec. The absorption of higher frequencies (300–500 Mc/sec) by electrolyte solutions shows that the product of the wavelength for maximum absorption and the concentration of the solution in g-equiv/litre is a constant.[4]

Radio-frequency measurements were first used for the determination of titrimetric end-points in 1946,[5,6] and since that time over one hundred and fifty publications have appeared on this subject. The apparatus used in these determinations has been of two main types: standard electronic measuring equipment adapted for this purpose; and specifically designed instruments (generally much simpler). Some commercial apparatus is now available. Operating frequencies have varied within the range 0.1–415 Mc/sec.

The conductivity cells in general use are distinguished from those employed in low-frequency conductivity work by having the electrodes on the outer wall of the cell or even dispensing with them altogether. The electrodes cannot, therefore, become polarised or contaminated by precipitation occurring within the cell; this is one of the principal advantages of the radio-frequency technique. Furthermore, changes which affect mainly the dielectric constant of the cell contents rather than its electrical conductance may be followed just as easily. To gain these advantages, however, it is necessary to operate at frequencies within the above mentioned range instead of at audio-frequencies.

Many attempts have been made to formulate a theory of the observed changes in terms of parameters of the oscillatory circuit, and to produce an electrical "equivalent circuit" for the cell used. The effects of change of frequency and concentration upon the shape of titration curves have been predicted from "transfer-plots."[7]

Applications of the radio-frequency technique fall conveniently into two classes: those which follow conductance changes within the cell as in conductimetric titrations, and those recording changes in dielectric constant of non-conducting solutions. The technique has been applied also to flame-detection and measurement of flame speeds.[8]

A number of short reviews of this subject have appeared;[9–15] accounts have been given in standard texts on instrumental chemical analysis;[16–19] and monographs dealing specifically with the radio-frequency technique have been published.[20–22]

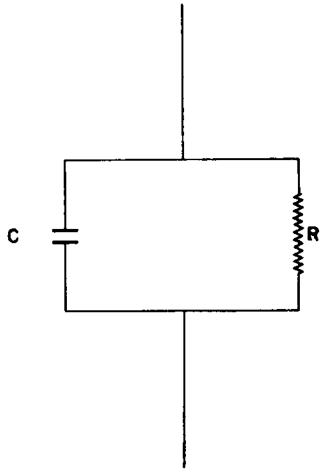

FIG. 1. Equivalent electrical circuit of LF conductivity cell.

THEORY

The conventional low-frequency conductivity cells with internal electrodes may be represented electrically by the circuit of Fig. 1. The resistance R is the parameter measured and C represents the capacity between the plates with the cell solution as dielectric together with the stray capacities between the bridge components and earth. In practice, C is balanced-out by a variable capacitor across the appropriate arm of the bridge.

The usual radio-frequency conductivity cell, a glass tube with band-electrodes on the outer wall, may be represented electrically [23,24,7] by Fig. 2. C_2 is the capacity from the electrodes to the solution; the dielectric of this capacitor is the glass or ceramic cell-wall. C_1 and R_1 are respectively the capacitance and resistance of that part of the path between the electrodes through the cell-solution; this solution is, therefore, the dielectric of C_1. The resistance through the cell-wall which shunts C_2 is normally so large that its effect is negligible. Typical values for the components in Fig. 2 relating to a cell of volume 100 ml and having band-electrodes of width $\frac{1}{4}$ in. spaced 1 in. apart are: $C_1 = 100$ pf, $C_2 = 30$ pf. If the cell be filled with 0·1N KCl solution, then R_1 is approximately 5 ohm.

Changes occurring within the cell affect C_1 and/or R_1; so that these fluctuations may influence the supply or detector circuits connected across AB, the reactance of C_2 must be relatively small. This is why it is necessary to make measurements with this type of cell at radio-frequencies; the reactance of C_2 at 1000 c/sec is about 5×10^6 ohm but at 10 Mc/sec this is reduced to 500 ohm. Again, increasing the capacity of C_2 by decreasing the cell wall-thickness or by using high-permittivity ceramic in place of glass improves the sensitivity by reducing the reactance of C_2.[25] The impedance of the cell depends upon the frequency, which must therefore be maintained constant during an experiment.

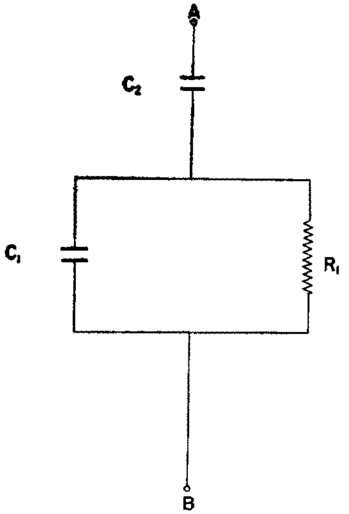

FIG. 2. Equivalent electrical circuit of RF conductivity cell.

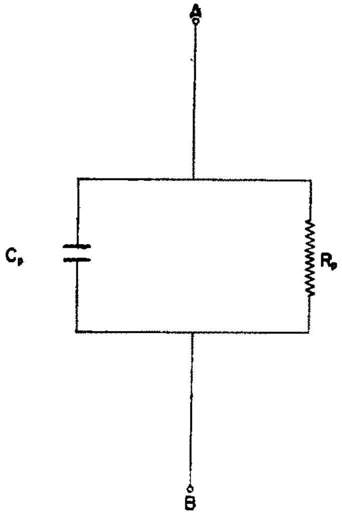

FIG. 3. Reduced equivalent circuit of RF conductivity cell.

The circuit of Fig. 2 may be simplified to that of Fig. 3 by equating the real and imaginary components of the reactance of each circuit; at a frequency of ω radian/sec these circuits are equivalent if

$$R_p = \frac{\kappa^2 + \omega^2(C_1 + C_2)^2}{\kappa^2\omega^2C_2^{\,2}} \tag{1}$$

and

$$C_p = \frac{\kappa^2 C_2 + \omega^2 C_1 C_2 (C_1 + C_2)}{\kappa^2 + \omega^2(C_1 + C_2)^2} \tag{2}$$

where $\kappa = 1/R_1$, *i.e.* the conductivity of the cell contents in ohm^{-1}.

The apparatus connected across AB responds to the parallel combination of Fig. 3; changes in C_1 and/or R_1 affect both C_p and R_p. Electronic impedance bridges (for example, the Twin-T Test Bridge[26] or the Wayne-Kerr Impedance Bridge[27]) enable the components C_p and R_p to be separately determined; actually C_p and G_p $(=1/R_p)$ are the quantities directly measured. Such test equipment can be used to follow the course of reactions within the cell, but it has been used mainly in fundamental investigations attempting to relate the measurements to the absolute specific conductance κ_0 and to the dielectric constant ε.

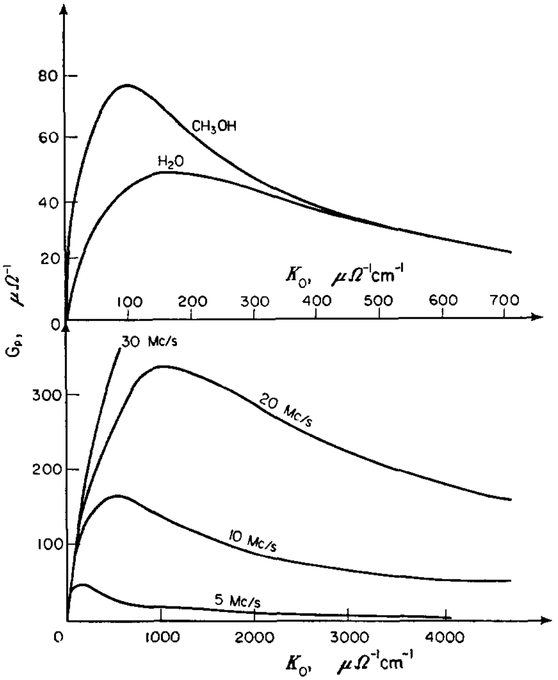

FIG. 4. Variation of G_p with κ_0 for change in dielectric constant and frequency (after ref. 7).

The variations of G_p and C_p with the low-frequency specific conductance κ_0 depend on frequency, Fig. 4, and upon the dielectric constant of the medium,[7] Fig. 5. To determine κ from the equation,

$$G_p = \frac{\kappa\omega^2 C_2{}^2}{\kappa^2 + \omega^2(C_1 + C_2)^2} \tag{3}$$

i.e. from the inverse of equation (1), or from equation (2), we require C_1 and C_2 for the cell. If the cell is filled with mercury, then $R_1 = 0$, $\kappa = \infty$ and from equation (2) C_p (Hg) $= C_2$. Replacing the mercury with conductivity water, $\kappa = 0$, and C_p (H_2O) $= C_1C_2/(C_1 + C_2)$. With the cell previously considered, C_p (Hg) $= 30$ pf, $C_p(H_2O) = 23$ pf. C_1 and C_2 may then be determined and used in equation (2) or (3) to obtain κ at a known frequency, ω radian/sec.

For a cell in which the electrode area and spacing are effectively A and d respectively, the conductivity is related to the specific conductance of the solution in the cell by:

$$\kappa = \kappa_0 A/d.$$

The capacitance of the same cell filled with a liquid of dielectric constant ε is:

$$C_1 \risingdotseq \frac{\varepsilon \,.\, A}{4{\cdot}4\pi d}\,\text{pf.}$$

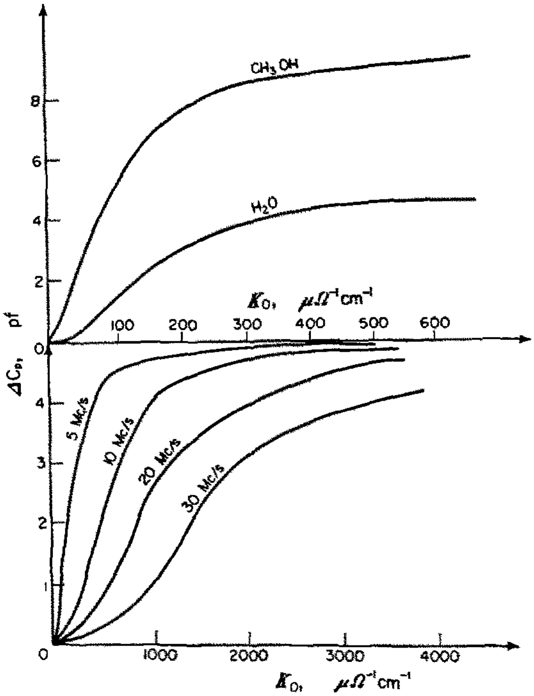

FIG. 5. Variation of ΔC_p with κ_0 for change in dielectric constant and frequency (after ref. 7).

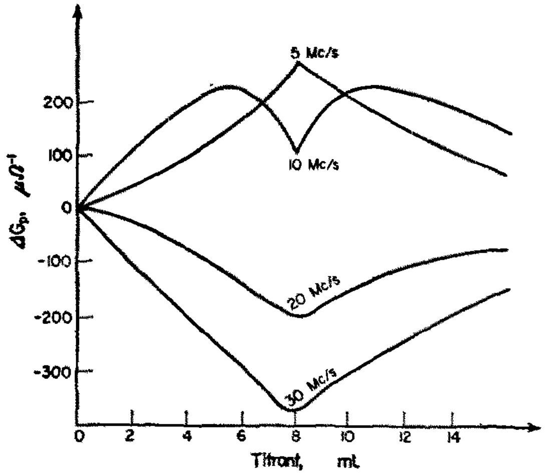

FIG. 6. Effect of change of frequency upon titration curves. HCl v NaOH (after ref. 28).

Hence, A/d, the cell-constant, $= \dfrac{4{\cdot}4\pi C_1}{\varepsilon}$

and $$\kappa = \kappa_0 . \frac{4.4\pi C_1}{\varepsilon}$$

so that κ_0 may be determined from κ. For a given electrolyte, solvent and temperature, κ_0 is a function of concentration; thus, from Fig. 4 or 5, the corresponding variations of G_p or C_p with concentration may be derived for a given electrolyte.

The widely varying shapes of the curves representing G_p and C_p during the course of a titration are characteristic of the high-frequency method; typical response curves of G_p and C_p, at various frequencies, are shown in Fig. 6 and 7 for the titration of HCl with NaOH. The usual V-shaped conductimetric titration curves may, with change in frequency or concentration, become S- or M-shaped. These have been explained by "transfer-plots",[7] which relate low-frequency conductances over a range of concentration to the corresponding high-frequency conductances. By differentiation of G_p with respect to κ, it is found that, for a given cell, the concentration for maximum sensitivity (maximum $dG_p/d\kappa$) varies directly as the frequency, ω radian/sec. The highest frequencies used in this procedure have been adopted in order to extend the concentration range.[29,30]

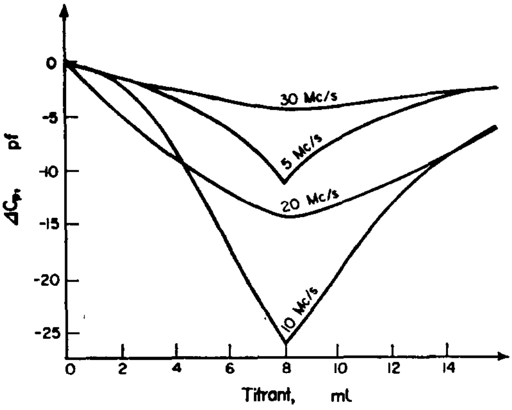

FIG. 7. Effect of change of frequency upon titration curves. HCl v NaOH (after ref. 28).

With regard to C_p, maximum sensitivity $dC_p/d\kappa$ is obtained for $C_2 \gg C_1$. This may be achieved as already indicated by decrease in cell-wall, increase in electrode area, or by use of a high permittivity ceramic cell. Reduction in ε (*e.g.* by the addition of EtOH to the aqueous solution) reduces C_1, and this increases its reactance; the sensitivity of both G_p and C_p measurements is thus increased.

In following the course of titrations or precipitations it is unnecessary to derive κ_0 from the measurements or even to obtain G_p and C_p separately. An oscillator connected across *AB* will experience some change in loading upon its oscillatory circuit because of changes within the cell and this may be followed as a variation in anode or grid current or in the oscillator frequency. A frequency change is easily measured by mixing the cell oscillator output with that of a second oscillator of constant frequency and observing the beat-frequency audibly or upon the screen of a cathode-ray oscilloscope. Alternatively, if the oscillator is restricted to operation within a few hundred cycles of its nominal frequency, *e.g.* by piezo-electric crystal control, changes within the cell may cause oscillations to die away. The variation of a tuning capacitor necessary to restore oscillation may then be followed.

Changes in grid-current may be measured directly by a micro-ammeter, or a lamp-and-scale galvanometer connected in series with the grid resistor. It might be thought that the changes in anode current would be less sensitive than those in grid current, since they are of the order of 10–100 microamps in a steady anode current of 5–10 milliamps. However, the changes may be recorded on a micro-ammeter by "backing-off" the steady current with a reverse-connected variable voltage source. The "zero-shunt" circuit was described in this connection by Blake[20] and we have adopted it in a satisfactory instrument of our design. Under these conditions the anode current variations afford the greater sensitivity.[31]

The magnification factor, or "Q"-factor, of the oscillatory circuit *i.e.* the ratio of its impedance at resonant frequency to its resistance, evidently depends upon external resistance connected in parallel with it. If this resistance is supplied by the cell, changes in it are reflected in the "Q" of the circuit, and these may be measured directly on a commercial "Q"-meter.[32]

Advantages are claimed for differential measurements in RF titrimetry.[33]

APPARATUS

Considering firstly apparatus specifically designed for RF titrimetry, the principles of stable oscillator construction have been followed.[34–37] The earliest apparatus for analytical purposes[5] appeared in 1946 and used a tuned-anode tuned-grid (TATG) oscillator with the cell inside the anode-circuit inductance ("tank coil") working at frequencies between 15 and 20 Mc/sec; variations in anode current were followed. Simple feed-back oscillators have also been used.[6]

The TATG oscillator has frequently been used;[38–41] improved sensitivity is claimed for a modification which encloses the cell by a capacitor in the oscillatory circuit,[42] and for the inclusion of a metal plate in the coil.[43] The cell has been used to couple the anode and grid coils[44] and a similar circuit has been adapted for battery operation in a portable instrument.[45,46] The course of titrations has been followed by changes in grid voltage,[47] in screen current[48] and in the resistance in the anode circuit necessary to maintain constant anode current.[49]

The Clapp oscillator[50] has been used in a number of titrimeter circuits covering the frequency range 5 to 30 Mc/sec. Anode current,[51,31] grid current[31] and oscillatory voltage[52] have been followed. The Clapp oscillator has been incorporated in a heterodyne-beat circuit, the beat-frequency being measured by a frequency meter,[29,53,54] or by an oscilloscope.[55] The Colpitts circuit has been used at 14 Mc/sec with the cell in the capacitor between anode and cathode.[56] It has also been used as a blocking oscillator at 100 Mc/sec.[57]

A tuned transmission-line oscillator at 350 Mc/sec uses the heterodyne-beat method of measurement.[58] Advantages are claimed for modulation of the oscillator frequency (2·5 or 6 Mc/sec) at 1000 c/sec, the audio-frequency being detected.[59,60] Crystal-controlled oscillators may be tuned by a variable capacitor for maximum amplitude of oscillation.[61,62] The "grid dip" or sudden decrease in grid current has been followed[63] in a Clapp oscillator at 8, 22 and 35 Mc/sec; the circuit was later modified.[64] A crystal oscillator of frequency 2 Mc/sec indicates the position of oscillation by means of a "magic-eye" tube, conductance changes being followed by a valve-voltmeter.[65–67,162] A Pierce crystal oscillator employs frequency doubling up to 14 Mc/sec.[68] The differential method of measurement[33,69] follows the rate of change of beat-frequency with the volume of titrant added. Oscillators of higher frequency have been designed for use with more concentrated electrolyte solutions.[30,37,58,70–72] The Franklin two-valve oscillator has been used, and the rectified oscillatory voltage measured.[73] Other stable-oscillator instruments have been described.[74–78]

Commercially available electronic test equipment which has been adapted for radio-frequency titrimetry and for the determination of specific conductances includes the Twin-T Impedance Measuring Bridge,[7,26,28] and the Magnification ("Q") Meter.[32,79] The use of any available stable oscillator with diode detector and "backed-off" meter has been discussed.[80,81]

It should be noted that the Twin-T Bridge requires auxiliary equipment in the form of a stable, variable-frequency oscillator and a "communications" radio-frequency receiver as detector. The complete apparatus is thus bulky and expensive.

Some commercial titrimeters are available. The Model V Oscillometer[22] operates at 5 Mc/sec and employs a frequency discriminator circuit to follow the heterodyne beat-frequency. Special conductivity cells are normally used but adaptors for the band-electrode type of cell have been described.[82,83] The Fischer titrimeter[84] is a modification of the apparatus of Hall.[65] The HFT30C titrimeter[85] operates at 30 Mc/sec and incorporates a precision variable capacitor tuning for maximum response; the apparatus and some applications have been described.[86]

The heterodyne-beat apparatus would appear to be the most sensitive; it may be combined with a null indicator if a tuned frequency discriminator is incorporated, as in the Model V Oscillometer. However, the circuit is relatively complicated and very careful screening is required. Crystal-controlled oscillators in which oscillations are maintained at maximum amplitude by adjustment of a tuning capacitor may be very simple and reliable. However, we have found that the type of circuit in which changes in the loading of the oscillator are followed by changes in grid or anode current is generally more sensitive. It should be pointed out that in a steady anode current of 5 milliamps, for a variation of 1 microamp to be significant, very careful mains and HT voltage stabilisation is required. The "reliable-series" valves are sometimes found to improve the stability.[87] There seems little advantage in operating at frequencies higher than about 30 Mc/sec except in the study of very concentrated electrolyte solutions.

Cell design

The first cells used in this work were of the pipette type.[81,88-90,91] Aluminium sleeve electrodes[51] and a central wire[80] or spigot[22] electrode were subsequently introduced. The cell may be designed to minimise changes due to dielectric constant variations;[92] on the other hand, disc-shaped cells are sensitive towards such variations.[82]

Recent workers have preferred cells with external bands to the "electrodeless" cell placed inside the tank coil. Band-electrodes of silver or gold fired on to a glass or ceramic cell avoid having a layer of air between the electrodes and the cell wall. They may be protected by embedding in a thermosetting resin and terminated in plugs for direct connection to the oscillatory circuit.[31] Thermostatted cells have been described.[79,93,94]

PRACTICAL APPLICATIONS

Several investigators have given the range of concentration over which their apparatus is sensitive; some of these concentrations are listed in Table I.

The radio-frequency technique has been extensively employed in acid-base titrations; these are summarised in Table II.

The RF method is thus applicable to acid-base titrations over a wide range of concentrations. Except in the case of weak acid-weak base titrations,[63] the technique appears to offer no advantage over potentiometric titrations, which may now be made fully automatic.

TABLE I.—REPRESENTATIVE CONCENTRATION RANGES FOR ADEQUATE SENSITIVITY

Electrolyte	Concn. range, *g-equiv/litre*	Freq. range, *Mc/sec*	Refs.
HCl	1·0 × 10^{-4} to 5·0	1 to 40	43, 59, 77, 79, 92
H_2SO_4	1·0 × 10^{-4} to 2·0 × 10^{-3}	16	95
CH_3COOH	1·0 × 10^{-4} to 1·0	2 to 6	59
NaOH	1·0 × 10^{-4} to 2·0	1 to 30	79, 95, 96
NaCl	1·0 × 10^{-4} to 2·0	1 to 14	68, 96
KCl	4·0 × 10^{-4} to 1·0 × 10^{-2}	20 to 30	79

TABLE II.—ACID-BASE TITRATIONS

Acid	Base	Concn. range, *g-equiv/litre*	Freq. range, *Mc/sec*	Comments	Refs.
HCl	NaOH	3·0 × 10^{-4} to 5·0	0·5 to 120	(Normal monobasic behaviour)	5, 6, 28, 52, 61, 72, 75, 88, 89, 90, 95, 97–100, 101
HCl	KOH	5·0 × 10^{-3} to 0·5	4	„	53, 76
HCl	$Ba(OH)_2$	0·025	30	„	29
H_2SO_4	NaOH, KOH	0·1	1 to 40	„ Suggestion of break at $NaHSO_4$	101 63
H_2SO_4	NH_4OH	2·0 × 10^{-5} to 2·0 × 10^{-4}	30	—	42
HCl	Na_2CO_3	1·0 × 10^{-3} to 1·0	1 to 30	Two breaks on adding Na_2CO_3 to acid	5, 28, 56, 66, 97
HNO_3	Na_2SiO_3	0·1 to 0·25	2	—	98
CH_3COOH	NaOH	0·01 to 0·60	10 to 130	—	71, 102, 103
CH_3COOH	$Ba(OH)_2$	0·025	30	—	29
CH_3COOH	NH_4OH	5·0 × 10^{-3} to 1·0	1 to 35	Excellent end-point obtained	6, 63
Picric Phthalic Malonic Tartaric	NaOH	1·0 × 10^{-3} to 3·0 × 10^{-2}	5	One break corresponding to the first H atom	104
H_3PO_4	NaOH	—	8 to 20	Three breaks	97
H_3PO_4	NaOH	0·025 to 0·25	130	Two breaks	71
H_3PO_4	NaOH	0·2	10, 20, 30	One break	31
H_3PO_4	KOH	3·0 × 10^{-4}	4 to 7	Three breaks, estimated K_1 K_2 and K_3	48

Various phenols, enols, and imides have been titrated with 0·05*N* lithium hydroxide at a frequency between 15 and 20 Mc/sec.[105] Glycine was satisfactorily determined by dissolving in excess standard sodium hydroxide, and back-titrating with hydrochloric acid.[106] Salts of alkaloids and other weak organic bases have been titrated with 0·1*N* sodium hydroxide at 27 Mc/sec in water and in aqueous alcohol as solvents; the method is satisfactory[107] if K_b is not less than 10^{-9}.

It has been frequently observed that potentiometric and conductimetric titrations in which a precipitate is formed are liable to errors due to contamination of the electrodes. The "external electrode" technique has been fully explored for such reactions, and the results are summarised in Tables III and IV.

TABLE III.—CHLORIDE* DETERMINATIONS

Chloride	Titrant	Concentration range, *g-equiv/litre*	Freq. range, *Mc/sec*	Refs.
NaCl KCl	$AgNO_3$	1·0 × 10^{-4} to 1·0	0·1 to 350	5, 28, 29, 45, 58, 61, 63, 66, 71, 81, 97, 108
HCl	$AgNO_3$	1·0 × 10^{-4} to 0·1	4 to 30	31, 48
Cl^-	$Hg(NO_3)_2$	0·025	30	29
Cl^-	$Hg(ClO_4)_2$	0·01	30	69, 109†

* Bromide and iodide ions could doubtless be determined by similar titrations, as has indeed been found for the reverse titrations.[67]

† The method described is claimed to be superior to potentiometric or conductimetric titration.

TABLE IV.—SULPHATE DETERMINATIONS

Sulphate	Titrant	Concentration range, *g-equiv/litre*	Freq. range, *Mc/sec*	Refs.
$(NH_4)_2SO_4$	$BaCl_2$	0·05 to 0·10	8 to 20	97
Na_2SO_4	$BaCl_2$	1·0 × 10^{-4} to 0·1	0·5 to 18·5	52, 61, 76 110,* 111*
$MgSO_4$	$BaCl_2$	0·01	10 to 30	31*
SO_4^{2-}	$(CH_3COO)_2Ba$	0·015	5	112*
SO_4^{2-}	$(CH_3COO)_2Ba$	0·005 to 0·05	15 to 20	113
SO_4^{2-}	$Pb(NO_3)_2$	0·005 to 0·05	15 to 20	113
SO_4^{2-}	octa-ammino-μ-amino-μ-nitrodicobalt^{III} tetranitrate	0·005 to 0·05	15 to 20	113
SO_4^{2-}	Hexamminocobalt^{III} bromide	0·005 to 0·05	15 to 20	113

* The use of 30 to 50% by volume of ethanol, together with seed crystals of barium sulphate, has been recommended in these titrations. Such additions had been found advantageous in similar low-frequency determinations.[114]

The RF titration has been applied to the determination of fluoride ions, an analysis which is difficult to carry out by more conventional precipitation methods. Although objection has been raised to the use of thorium nitrate as a titrant,[115] this reagent has been reported to be satisfactory for titration at 5 Mc/sec over a wide range of fluoride ion concentration.[116,117] Lanthanum acetate has been used as titrant at frequencies within the range 2 to 20 Mc/sec and at concentrations between 0·01 and 0·025 g-equiv/litre of fluoride.[45,102,118] The stoichiometry of this reaction has been confirmed by independent standardisations of the fluoride and lanthanum solutions,[102] the fluoride in the form of hydrofluoric acid was neutralised by standard sodium hydroxide and the lanthanum acetate solution titrated with disodium EDTA at pH 4·0 to 5·5 using Xylenol Orange as indicator.

A few applications have been made to redox titrations. Ferrous ammonium sulphate has been titrated with potassium permanganate at frequencies from 4 to 20 Mc/sec, and concentrations within the range 0·01 to 0·1 g-equiv/sec.[5,48,76] More recently ferrous ethylenediamine sulphate has been titrated with potassium dichromate.[31]

TABLE V.—MISCELLANEOUS RF TITRATIONS

Ion determined	Titrant	Concn. range *g-equiv/litre*	Freq. range, *Mc/sec*	Notes	Refs.
CNS^-	$AgNO_3$	2·5 × 10^{-4} to 1·0	1 to 30	—	28, 29, 69, 119
CNS^-	$Hg(NO_3)_2$	2·5 × 10^{-4} to 0·1	5, 30, 350	0·1% error*	29, 58,119
CrO_4^{2-}	$BaCl_2$	0·1	2, 5, 11	—	66
$C_2O_4^{2-}$	Th^{4+}	0·05 to 0·25	2, 350	—	58, 65
Th^{4+}	$C_2O_4^{2-}$	0·025 to 0·05	30	0·04% error	120†
KCN	$AgNO_3$	0·05	6	sharp break at $KAg(CN)_2$	67
KI	$Na_2S_2O_3(HCl)$	0·025	30	—	29
Be(HCl soln)	NaOH or NH_4OH	0·01 to 0·03	2, 22	CO_2^- free reagents and N_2 atmosphere	118, 121
Ca^{2+}	$C_2O_4(NH_4)_2$	—	100	Used for lime in slag. pH 5·2–5·4 and 50% MeOH.	57
Ca^{2+}	$C_2O_4(NH_4)_2$	0·01	6	pH 6–6.5	122
Mg^{2+}, Ca^{2+}, Ba^{2+} and mixtures.	$C_2O_4(NH_4)_2$	1·0 × 10^{-3} to 3·0 × 10^{-3}	6·5	2% error in presence of EtOH	111
Mg^{2+}	NaOH	8·0 × 10^{-4} to 5·0 × 10^{-3}	6·5 —	Ca does not interfere	111
Pb^{2+}, Tl^+, Ba^{2+}	$Cr_2O_7^{2-}$	0·01	6	pH 6–6·5	122
Zn^{2+}, Cu^{2+}, Cd^{2+}	NaHS	0·001 to 0·1	8	—	40
Tl^+	$Na(C_6H_5)_4B$	0·1	25 to 30	0·5% error	123‡
Ce^{4+}	$C_2O_4(NH_4)_2$	0·01	6	pH 6–6·5	122
Ag^+, Cu^{2+}	$K_4Fe(CN)_6$	0·01	6	pH 6–6·5	122
Ag^+	KCl, KBr, KI, NH_4CNS, 2-mercapto benzothiazole, Bismuthiol II	0·05	6	—	67

* One break was observed in the titration of Hg^{2+} with CNS^-; two breaks for the reverse titration ($Hg[CNS]^+$).

† Of several ions considered for titrant, oxalate was found most satisfactory; the interference of several ions was investigated.

‡ The interference of several ions was studied.

A very large number of miscellaneous determinations, mainly precipitation methods, have been reported and these are conveniently summarised in Table V. Water hardness determination by titration with "soap solution" has been reported;[124] and the precipitation of many ions with cupferron reagent[125] studied over the concentration range 5·0 × 10^{-4} to 1·0 × $10^{-3}N$. Complex formation between various cations and glycine has been investigated,[39] and several bivalent and tervalent cations titrated at a frequency of 100 Mc/sec with 0·02*M* solution of 8-hydroxyquinoline. With the latter it was found that for sharp breaks, the pH of the electrolyte solution needed careful adjustment. For example, with a 0·02*M* solution of iron a definite end-point was obtained at pH 3·4 whereas at pH 4·8 the curve, under similar experimental conditions, was a straight line.[126]

In addition to the numerous examples of titrations listed in the previous Table, the RF technique has been extensively applied in complexing reactions involving EDTA, dimethylglyoxime, pyridine and many other reagents. Table VI lists the work reported with EDTA.

TABLE VI.—RF TITRATIONS INVOLVING EDTA

Cations determined	Concn. range, *g-mole/litre*	Freq., *Mc/sec*	Comments	Ref.
Cu^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}.	0·01	30	0·1% error	127
UO$_2$$^{2+}$	0·01	30	NaOH via EDTA pH 3·5 to 4·0, and direct titrn.	128
La^{3+}	3 × 10^{-4} to 0·01	30	NaOH via EDTA, and direct, pH 2·8 to 3·0	129
Gd^{3+}, Ce^{3+}	3 × 10^{-4} to 0·01	30	Direct, pH 10	129
Pr^{3+}, Nd^{3+}, Ce^{3+}	3 × 10^{-4} to 0·01	30	In HAc/Ac$^-$ buffer at pH 5·3 0·5 to 1·0% error	129
"Ca Bentonite"	0·1 to 3·0	0·1 and 3	Colloidal	81
Ni^{2+}	0·01 to 0·05	5	NaOH via EDTA	130
Cu^{2+}	1·0 × 10^{-4} to 0·01	5	Direct	130
La^{3+}	0·01 to 0·1	10 to 30	—	102

In general, RF titrimetry is found to give qualitative evidence regarding the ability of cations to chelate with EDTA[131] which is in agreement with the order of "formation constants".[132] The method is not suitable where weak EDTA complexes are formed, *e.g.* with Tl^{I} or Ag^{I}; because of the low selectivity of the reagent, few separations are feasible.[130]

Other complexing agents have been studied and information regarding complex formation in solution has been deduced. Thus, in RF titration at 30 Mc/sec with pyridine, copper, nickel and zinc show breaks in the titration curve at mole ratios of 1:1, 1:2, 1:3, 1:4, 1:5 and 1:6; nickel titrated with dimethylglyoxime showed breaks[133] at 1:1·1, 1:2, and 1:3·3

However, it seems probable that some of the very indistinct breaks recorded may represent instrument fluctuations; further evidence is required before the breaks representing hitherto unknown co-ordination numbers may be safely interpreted.

We consider next applications of the RF technique to non-aqeous solutions; most of these are acid-base reactions and are reported in Table VII.

Sulphuric acid titrated by potassium acetate in glacial acetic acid at 5 Mc/sec behaves as a monobasic acid.[144] The lithium halides may be titrated by KCNS in pyridine solution.[144]

Applications to dielectric constant measurement

The measurement of dielectric constants was one of the earliest applications of radiofrequencies to the study of chemical systems, and the RF technique just described can equally well follow changes in dielectric constant as in conductance during the course of a reaction. Mixtures may be analysed by measurement of dielectric constant if a calibration curve relating to the components has previously been constructed.

The heterodyne-beat method for determining dielectric constants, using a fixed-frequency crystal oscillator at 500 kc/sec, has been described.[145] The resonance method employing a 3·5-Mc/sec crystal oscillator, is claimed to be satisfactory over the dielectric constant range 1–80.[146] A frequency-deviation method, calibrated by observing the deviations produced by a standard capacitor, uses a 1-Mc/sec crystal oscillator.[147] A 10-Mc/sec oscillator, with concentric-cylinder cell, operates a pen recorder by its anode current.[148]

TABLE VII.—ACID-BASE TITRATIONS IN NON-AQUEOUS SOLVENTS

Acid	Base	Solvent	Concn. range, *mole/litre*	Freq. range, *Mc/sec*	Refs.
Phthalic	Na methoxide	Methanol/ acetone	0·01 to 0·1	15 to 20	5
Phthalic	Methylamine	Aniline	—	30	64
$HClO_4$(0·1*N*) in glacial acetic acid	Aniline and substituted anilines*	Glacial acetic acid	$1 \cdot 0 \times 10^{-3}$ to $1 \cdot 0 \times 10^{-2}$	130	134
$HClO_4$ (0·1*N*) in glacial acetic acid	Various organic bases†	Glacial acetic acid	0·1	5 to 20	45, 104, 135, 165
$HClO_4$ (0·1*N*) in glacial acetic acid	Various organic bases†	Benzene/methanol/glac. acetic acid	$1 \cdot 0 \times 10^{-4}$ to $1 \cdot 0 \times 10^{-2}$	2 to 15	136, 137
$HClO_4$ (0·1*N*) in glacial acetic acid	Salts of various carboxylic acids	Glacial acetic acid	0·1	—	138
$HClO_4$ (0·1*N*) in glacial acetic acid	Amino acids, teramycin, actinomycin	—	—	30‡	139, 140
Various weak carboxylic acids and phenols¶	Na methoxide K methoxide		—	5	141, 142
Oxine	Na methoxide	Dimethyl formamide	0·1	15 to 20	45
NH_4^+ halides	Na methoxide	Dimethyl formamide	$1 \cdot 0 \times 10^{-4}$	5	143
Salicylic o-nitro phenol Benzoic Lactic Tartaric**	Alcoholic KOH	Pyridine	0·001	5	104

* Pairs of such amines can be determined when their molecular weights differ by about 20.

† Lower limit of $K_b = 10^{-12}$; poor indication if K_b less than 10^{-10}.

‡ Using a ceramic cell of permittivity about 80.

¶ Two breaks with oxalic and similar dibasic acids; each OH group of polyhydric phenols is observed.

** Lactic and tartaric acids showed one break only.

The Hall RF Titrimeter circuit has been modified specifically for the determination of dielectric constant; this uses the normal external-band electrodes, at frequencies of 2, 5 and 11 Mc/sec.[66] Many other titrimeter circuits are amenable to this type of measurement.

Apparatus and methods for the determination of dielectric constant have been reviewed,[149,150] and the applications of the technique to the analysis of mixtures are recorded in Table VIII.

Miscellaneous chemical applications

The position of absorption bands in a column of ion-exchange resin may be determined by the RF technique;[155,156] and chromatographic zones may be followed in a similar manner.[47,157] The rate constants for ester hydrolyses have been determined by following conductance changes during the course of the reaction. A calibration curve, the titration of acetic acid with sodium hydroxide, is used and the method is applicable to reactions of half-life of 10 sec or less.[74,93,158] The rate of precipitation of barium sulphate in aqueous solution has been determined as a function of the concentrations of the ions and of the number of moles of precipitate already formed.[159] The RF titration of lead with potassium dichromate solution has been studied, with particular regard to co-precipitation of other ions. Using the differential method an error of less than 0·2% is claimed. In this investigation the Beckmann Conductometer was used.[160]

TABLE VIII.—ANALYSIS OF MIXTURES BY MEASUREMENT OF DIELECTRIC CONSTANT

System	Freq., *Mc/sec*	Comments	Ref
$H_2O/MeEtCO/C_6H_6$	4	H_2O content within 0·2% error	151
$H_2O/EtOH$	10 to 30	—	31
H_2O/mono-, di- and tri-hydric alcohols	4,5	particularly sensitive to $EtOH/H_2O$	152
H_2O/Me_2CO	5	accurate temp. control required	82
H_2O/ powdered materials	7	—	2
H_2O/salts/MeOH/dioxan	9	water content to 0·2% at optimum % dioxan *e.g.* NaCl. . . 35% dioxan NH_4NO_3. . . 69% dioxan	51
H_2O/dioxan/KCl	Various	—	153
H_2O/oil emulsion*	10	salinity does not interfere but suspended solids must be absent	148
acetone/toluene/ benzene, *o*- and *m*-xylenes	7	—	2
hexane/benzene, *o*- and *p*-xylenes	5	accurate temp. control required	82
continuous monitoring of toluene in distillation	2	toluene content to within ±1%.	154

* Sodium chloride has been determined in such emulsions by titration with 0·1*N* $AgNO_3$ at 20 Mc/s.[102]

CONCLUDING REMARKS

The main advantage of having external electrodes is that precipitation reactions may be followed more easily than with the conventional cell. It has been pointed out[24] that for a given conductance change within the cell the RF indication will be less than the LF resistance change; however, if the measuring technique under RF conditions is better, the overall accuracy may be improved. The conductance at radio-frequency is a function of the LF conductance, and not a measure of some new property. It is, perhaps, worth mentioning that any beaker or test-tube may be used as a conductivity cell in the RF method and that accurate results can be obtained with quite simple apparatus. Moreover, the same apparatus may often be used to follow changes in dielectric constant.

Note added in proof

The out-of-balance voltage of a Twin-T Bridge, powered by a General Radio signal generator at frequencies between 10 and 30 Mc/sec, has been measured to follow the course of titrations. Transfer plots relate this voltage to the low-frequency conductance of the solution, κ_0. The equation: $\Delta E_p = (EZ).\Delta Y_{ac}$ is obtained, where ΔE_p is the out-of-balance voltage, and ΔY_{ac} the change in admittance of the cell-equivalent circuit; E is the generator voltage, and Z the detector impedance.[161]

The importance of a correctly-designed cell has again been emphasised, and several types have been described.[162]

A 130-Mc/sec oscillator is described, in which changes in grid-current are followed; a band-electrode cell is used.[163] The lower limits of concentration with this oscillator are as follows:[164]

HCl v. bases, 1 μg/ml of HCl.

CH_3COOH v. bases, 20 μg/ml of CH_3COOH.

Cl^- v. $AgNO_3$, 2 μg/ml of Cl^-.

SO_4^{2-} v. $BaAc_2$, 10 μg/ml of SO_4^{2-}.

A heterodyne beat oscillator for the accurate determination of dielectric constants is described; it uses a Pierce crystal oscillator, beating with a Clapp variable oscillator, the mean frequency being 1 Mc/sec. Cells with rigid electrode assemblies are described, and measurements on benzene and chlorobenzene solutions are reported.[166]

Zusammenfassung—Die Theorie radiofrequenter Messungen, die von bedeutung für die Chemie sind, wird dargelegt und ein geeigneter Apparat diskutiert. Anwendungen, besonders auf dem Gebiete der analytischen Chemie, werden zusammenfassend behandelt.

Résumé—Les auteurs donnent un aperçu de la théorie des mesures de fréquence radio d'importance chimique, et discutent l'appareillage convenable. Les applications sont passées en revue, spécialment en chimie analytique.

REFERENCES

[1] A. L. Berry, U.S. Pat. 2076441, 1937.
[2] F. C. Alexander, *Electronics*, 1945, **18**, 116.
[3] P. Debye and H. Falkenhagen, *Physik. Z.*, 1928, **29**, 121, 401.
[4] S. K. Chatterjee and B. V. Sreekantan, *Indian J. Phys.*, 1948, **22**, 229.
[5] F. W. Jensen and A. L. Parrack, *Ind. Eng. Chem. Anal.*, 1946, **18**, 595.
[6] G. G. Blake, *J. Sci. Instr.*, 1947, **24**, 101.
[7] C. N. Reilly and W. H. McCurdy, *Analyt. Chem.*, 1953, **25**, 86.
[8] H. F. Calcote, *Rev. Sci. Instr.*, 1949, **20**, 349.
[9] W. van Tongeren, *Chem. Weekblad.*, 1951, **47**, 281.
[10] W. J. Blaedel, T. S. Burkhalter, D. G. Flom, G. Hare and F. W. Jensen, *Analyt. Chem.*, 1952, **24**, 198.
[11] W. J. Blaedel, H. V. Malmstadt, D. L. Petitjean and W. K. Anderson, *ibid.*, 1952, **24**, 1240.
[12] J. L. Hall, *ibid.*, 1952, **24**, 1236.
[13] P. W. West, *Chem. Age*, 1953, **68**, 133.
[14] O. L. Kaptsan and V. A. Teplyakov, *Zhur. Analit. Khim.*, 1953, **8**, 131.
[15] K. Cruse and R. Huber, *Angew. Chem.*, 1954, **66**, 625.

[16] P. Delahay, *New Instrumental Methods in Electrochemistry*, Interscience, New York, 1954.

[17] F. M. Biffen and W. Seaman, *Modern Instruments in Chemical Analysis*, McGraw-Hill, New York and London, 1956.

[18] J. J. Lingane, *Electroanalytical Chemistry*, Interscience, New York, 1958.

[19] H. H. Willard, L. L. Merritt and J. A. Dean, *Instrumental Methods of Analysis*, Van Nostrand, New York, 3rd Ed. 1958.

[20] G. G. Blake, *Conductometric Measurements at Radio Frequencies*, Chapman and Hall, London, 1950.

[21] K. Cruse and R. Huber, *Die Hochfrequenztitration*, Verlag Chemie Weinheim, 1957.

[22] P. H. Sherrick, G. A. Dawe, R. Karr and E. F. Ewen, *Manual of Chemical Oscillometry*, E. H. Sargent, Chicago, 1954.

[23] K. Nakano, *J. Chem. Soc. Japan*, 1954, **75**, 773, 776.

[24] J. L. Hall, J. A. Gibson, H. O. Phillips and F. E. Critchfield, *Analyt. Chem.*, 1954, **26**, 1539.

[25] F. Oehme, *Analyt. Chim. Acta*, 1958, **18**, 155.

[26] D. B. Sinclair, *Proc. Inst. Radio Eng.*, 1940, **28**, 310.

[27] Wayne-Kerr Engineering Co. Ltd., Chessington, Surrey, Eng.

[28] J. L. Hall and J. A. Gibson, *Analyt. Chem.*, 1951, **23**, 966.

[29] W. J. Blaedel and H. V. Malmstadt, *ibid.*, 1950, **22**, 734.

[30] E. S. Lane, *Analyst*, 1957, **82**, 406.

[31] M. F. C. Ladd and W. H. Lee, *Lab. Practice*, 1960, **9**, 98.

[32] M. Honda, K. Nakano and A. Satuka, *J. Chem. Soc. Japan*, 1954, **75**, 1299.

[33] W. J. Blaedel and H. V. Malmstadt, *Analyt. Chem.*, 1952, **24**, 450.

[34] G. G. Gouriet, *Wireless Eng.*, 1950, **27**, 105.

[35] P. R. Aigrain and E. M. Williams, *Proc. Inst. Radio Eng.*, 1948, **36**, 16.

[36] B. J. Solley, *Wireless World*, 1945, **51**, 170.

[37] R. Huber and K. Cruse, *Angew. Chem.*, 1956, **68**, 178.

[38] M. Nishigai, H. Okabayashi and N. Tanaka, *Repts. Radn. Chem. Res. Inst. Tokyo Univ.*, 1950, **5**, 45.

[39] H. Okabayashi, K. Nakano and S. Fujiwara, *ibid.*, 1949, **4**, 23.

[40] T. Kikuchi, A. Yamada and K. Nakano, *Jap. Analyst*, 1958, **6**, 658.

[41] A. J. Arvia and P. H. Broderson, *Z. phys. Chem. (Frankfurt)*, 1956, **6**, 381.

[42] N. Tanaka and M. Nishigai, *Rept. Inst. Sci. Technol. Univ. Tokyo*, 1952, **6**, 131.

[43] M. Masui, *J. Pharm. Soc. Japan*, 1954, **74**, 530.

[44] M. Masui, *ibid.*, 1953, **73**, 921.

[45] J. P. Dowdall, D. V. Sinkinson and H. Stretch, *Analyst*, 1955, **80**, 491.

[46] M. Ishibashi, T. Fujinaga and M. Mitamura, *Jap. Analyst*, 1953, **2**, 195.

[47] F. Baumann and W. J. Blaedel., *Analyt. Chem.*, 1956, **28**, 2.

[48] B. Ricca and A. Bellomo, *Ann. Chim.*, 1955, **45**, 1217.

[49] K. Nakano, *J. Chem. Soc. Japan*, 1953, **74**, 227.

[50] J. K. Clapp, *Proc. Inst. Radio Eng.*, 1948, **36**, 356.

[51] F. W. Jensen, M. J. Kelly and M. B. Burton, *Analyt. Chem.*, 1954, **26**, 1716.

[52] M. Paucek, *Chem. Listy.*, 1958, **52**, 1367.

[53] P. W. West, T. S. Burkhalter and L. Broussard, *Analyt. Chem.*, 1950, **22**, 469.

[54] T. Gäumann, J. Hoigné and Hs. H. Günthard, *Helv. Chim. Acta*, 1959, **42**, 426.

[55] P. H. Monaghan, P. B. Moseley, T. S. Burkhalter and O. A. Nance, *Analyt. Chem.*, 1952, **24**, 193.

[56] T. Kono, *J. Agric. Chem. Soc. Japan*, 1951, **25**, 567.

[57] S. Musha, *Sci. Rep. Res. Inst. Tohoku Univ.*, 1951, **3A**, 55.

[58] W. J. Blaedel and H. V. Malmstadt, *Analyt. Chem.*, 1950, **22**, 1413.

[59] S. Fujiwara and S. Hayashi, *ibid.*, 1954, **26**, 239.

[60] *Idem*, *Repts. Univ. Electro-Comms.*, 1950, No. 1, 119; No. 2, 315; 1951, No. 3, 91.

[61] R. Morpain and S. Courtcuisse, *Chim. Analyt.*, 1959, **41**, 290.

[62] J. Pokorny, *Chem. Listy*, 1959, **53**, 1141.

[63] K. Anderson, E. S. Bettis and D. Revinson, *Analyt. Chem.*, 1950, **22**, 743.

[64] H. A. Sack and B. Sack, *J. Rech. Cent. Nat. Rech. Sci.*, 1951, No. 15, 325.

[65] J. L. Hall, *Analyt. Chem.*, 1952, **24**, 1236.

[66] J. L. Hall, J. A. Gibson, H. O. Phillips and F. E. Critchfield, *J. Chem. Educ.*, 1954, **31**, 54.

[67] A. K. Majumdar and A. K. Mukherjee, *Analyt. Chim. Acta*, 1959, **20**, 511.

[68] K. E. Harwell and D. W. Hood, *Electronics*, 1954, **27**, 172.

[69] W. J. Blaedel and H. V. Malmstadt, *Analyt. Chem.*, 1952, **24**, 455.

[70] A. H. Johnson, U.S. Pat. 2703863, 1955.

[71] A. H. Johnson and A. Timnick, *Analyt. Chem.*, 1956, **28**, 889.

[72] *Idem*, *ibid.*, 1958, **30**, 1324.

[73] K. Ishii, S. Hayashi and S. Fujiwara, *ibid.*, 1959, **31**, 1586.

[74] D. G. Flom and P. J. Elving, *ibid.*, 1953, **25**, 541.

[75] V. A. Zarinskii and D. I. Koshkin, *Zhur. Analit. Khim.*, 1955, **10**, 111.

[76] *Idem*, *ibid.*, 1954, **9**, 29.

[77] *Idem*, *ibid.*, 1958, **13**, 298.

[78] R. B. Fischer and D. J. Fisher, *Proc. Indiana Acad. Sci.*, 1952, **62**, 160.

[79] I. I. Samitov, *Zhur. Analit. Khim.*, 1956, **11**, 149.

[80] R. J. Bever, C. E. Crouthamel and H. Diehl, *Iowa State Coll. J. Sci.*, 1949, **23**, 289.

[81] F. Kupka and W. H. Slabaugh, *Analyt. Chem.*, 1957, **29**, 845.

[82] O. A. Nance, T. S. Burkhalter, and P. H. Monaghan, *ibid.*, 1952, **24**, 214.

[83] J. C. Clayton, J. F. Hazel, W. M. McNabb and G. L. Schnable, *Chemist-Analyst*, 1954, **43**, 54.

[84] Fisher Scientific Co., report in *Rev. Sci. Instr.*, 1955, **26**, 248.

[85] Wissenschaflich-Technische Werkstatten, Weilheim/Oberbayern, Germany.

[86] F. Oehme, *Chem.-Ztg.*, 1958, **82**, 224.

[87] C. M. Proctor, *Analyt. Chem.*, 1959, **31**, 1278.

[88] G. G. Blake, *Austral. J. Sci.*, 1947, **10**, 80.

[89] *Idem*, *ibid.*, 1948, **11**, 59.

[90] *Idem*, *ibid.*, 1949, **12**, 32.

[91] V. A. Zarinskii and I. R. Mandel'berg, *Zavodskaya Lab.*, 1958, **24**, 148.

[92] J. C. Clayton, J. F. Hazel, W. M. McNabb and G. L. Schnable, *Analyt. Chim. Acta*, 1956, **14**, 269.

[93] P. J. Elving, *Disc. Faraday Soc.*, 1954, **17**, 156.

[94] J. Hoigné and T. Gäumann, *Helv. Chim. Acta*, 1959, **42**, 432.

[95] R. Arditti and P. Heitzmann, *Compt. rend.*, 1949, **229**, 44.

[96] K. Nakano, *J. Chem. Soc. Japan*, 1953, **74**, 172.

[97] M. Ishibashi, T. Fujinaga and M. Mitamura, *Bull. Inst. Chem. Res. Kyoto Univ.*, 1951, **25**, 24.

[98] J. C. Clayton, J. F. Hazel, W. M. McNabb and G. L. Schnable, *Analyt. Chim. Acta*, 1955, **13**, 487.

[99] T. Asada, *J. Electrochem. Soc. Japan*, 1953, **21**, 158.

[100] *Idem*, *ibid.*, 1953, **21**, 221.

[101] K. Nakano, *J. Chem. Soc. Japan*, 1954, **75**, 494.

[102] M. F. C. Ladd and W. H. Lee, unpublished.

[103] T. Asada, *J. Electrochem. Soc. Japan*, 1954, **22**, 16, 126, 171, 375, 417.

[104] R. Hara and P. W. West, *Analyt. Chim. Acta*, 1956, **15**, 193.

[105] G. R. Jamieson, *J. Appl. Chem.* 1959, **9**, 209.

[106] T. Kono, *J. Agric. Chem. Soc. Japan*, 1952, **26**, 41.

[107] M. Ishidate and M. Masui, *J. Pharm. Soc. Japan*,. 1953, **73**, 867.

[108] M. Ishibashi, T. Fujinaga and M. Mitamura, *Bull. Inst. Chem. Res. Kyoto Univ.*, 1951, **27**, 57.

[109] W. J. Blaedel and H. V. Malmstadt, *Analyt. Chem.*, 1950, **22**, 1410.

[110] O. I. Milner, *ibid.*, 1952, **24**, 1247.

[111] S. N. Mukherjee, P. K. Bhattacharjee and A. S. Bhattacharjee, *Sci. and Culture*, 1959, **25**, 153. *Idem*, *ibid.*, 1957, **23**, 53.

[112] G. S. Bien, *Analyt. Chem.*, 1954, **26**, 909.

[113] G. R. Jamieson, *J. Appl. Chem.*, 1957, **7**, 81.

[114] L. J. Anderson and R. G. Revelle, *Ind. Eng. Chem. Anal.*, 1947, **19**, 264.

[115] H. Dodgen and G. K. Rollefsen, *J. Amer. Chem. Soc.*, 1949, **71**, 2600.

[116] J. Harley and D. Revinson, *Div. Anal. Chem.* 119th. Meeting Amer. Chem. Soc., 1951.

[117] C. L. Grant and H. M. Haendler, *Analyt. Chem.*, 1956, **28**, 415.

[118] V. Kyte and A. I. Vogel, *Analyst*, 1959, **84**, 647.

[119] B. R. Sant and K. Mukherji, *Analyt. Chim. Acta*, 1959, **20**, 124.

[120] W. J. Blaedel and H. V. Malmstadt, *Analyt. Chem.*, 1951, **23**, 471.

[121] K. Anderson and D. Revinson, *ibid.*, 1950, **22**, 1272.

[122] A. K. Majumdar and B. K. Mitra, *Analyt. Chim. Acta*, 1959, **21**, 29.
[123] A. R. Veis and A. F. Ievins, *Zhur. Analit. Khim.*, 1959, **14**, 143.
[124] F. W. Jensen, G. M. Watson and L. G. Vela, *Analyt. Chem.*, 1951, **23**, 1327.
[125] C. B. Riolo and T. Soldi, *Ann. Chim.*, 1959, **48**, 422.
[126] H. Goto and T. Hirayama, *Sci. Rep. Res. Tohoku Univ.*, 1954, **6A**, 224.
[127] W. J. Blaedel and H. T. Knight, *Analyt. Chem.*, 1954, **26**, 743.
[128] R. Hara and P. W. West, *Analyt. Chim. Acta*, 1955, **12**, 285.
[129] *Idem, ibid.*, 1956, **14**, 281.
[130] *Idem, ibid.*, 1955, **12**, 72.
[131] *Idem, ibid.*, 1954, **11**, 264.
[132] G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, 1951, **34**, 1503.
[133] R. Hara, *J. Pharm. Soc. Japan*, 1951, **71**, 1122, 1128, 1134, 1140, 1144.
[134] W. T. Lippincott and A. Timnick, *Analyt. Chem.*, 1956, **28**, 1691.
[135] C. B. Riolo and E. Marcon, *Ann. Chim.*, 1956, **46**, 528.
[136] M. Masui, *J. Pharm. Soc. Japan*, 1953, **73**, 1011.
[137] W. F. Wagner and W. B. Kauffman, *Analyt. Chem.*, 1953 **25**, 538.
[138] M. Ishidate and M. Masui, *Pharm. Bull.*, 1954, **2**, 50.
[139] F. Oehme, *Z. Naturforsch.* 1958, **13**, 461.
[140] *Idem, ibid.*, 462.
[141] M. Ishidate and M. Masui, *J. Pharm. Soc. Japan*, 1953, **73**, 487.
[142] K. J. Karrman and G. Johansson, *Mikrochim. Acta*, 1956, 1573.
[143] J. A. Dean and C. Cain, *Analyt. Chem.*, 1955, **27**, 212.
[144] J. P. Young, *Diss. Abs.*, 1955, **15**, 1302.
[145] J. Y. Chien, *J. Chem. Educ.*, 1947, **24**, 494.
[146] R. B. Fischer, *Analyt. Chem.*, 1947, **19**, 835.
[147] W. L. G. Gent, *Trans. Faraday Soc.*, 1949, **45**, 758.
[148] P. O. Engelden, *Instruments*, 1951, **24**, 335.
[149] F. Oehme, *Dielektrische Messmethoden*, Verlag Chemie. Weinheim, 1958.
[150] J. Hoigné and T. Gäumann, *Helv. Chim. Acta*, 1959, **42**, 437.
[151] P. W. West, T. Robichaux and T. S. Burkhalter, *Analyt. Chem.*, 1951, **23**, 1625.
[152] P. W. West, P. Senise and T. S. Burkhalter, *ibid.*, 1952, **24**, 1250.
[153] J. L. Hall, J. A. Gibson, F. E. Critchfield, H. O. Phillips and C. B. Seibert, *ibid.*, 1954, **26**, 835.
[154] B. W. Thomas, F. J. Faegin and G. W. Wilson, *ibid.*, 1951, **23**, 1750.
[155] M. Honda, *J. Chem. Soc. Japan*, 1952, **73**, 529.
[156] *Idem, Jap. Analyst*, 1953, **2**, 456.
[157] D. E. Laskowski and R. E. Putscher, *Analyt. Chem.*, 1952, **24**, 965.
[158] F. W. Jensen, G. M. Watson and J. B. Beckham, *ibid.*, 1951, **23**, 1770.
[159] R. J. Bever, C. E. Crouthamel and H. Diehl, *Iowa State Coll. J. Sci.*, 1949, **23**, 299.
[160] D. T. Sawyer and P. S. Farrington, *Analyt. Chem.*, 1957, **29**, 1688.
[161] J. M. Walker, J. L. Lambert and L. D. Ellsworth, *Analyt. Chem.*, 1960, **32**, 9.
[162] Y. Conseilleur and J. Courteix, in *Modern Electronanalytical Methods*, ed. G. Charlot, Elsevier New York 1958.
[163] E. Pungor, *Chem. Zvesti*, 1959, **13**, 823.
[164] E. Pungor and L. Balazs, *Mikrochim. Acta.*, 1960, 118.
[165] C. B. Riolo and A. F. Notarianni, *Ann. Chim. (Italy)*, 1959, **49**, 1981.
[166] H. Lumbroso and P. Rossetti, *J. Chim. Phys.*, 1959, **56**, 844.

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PRELIMINARY COMMUNICATION

A new reducing agent: Reduction of vanadium^{IV} and uranium^{VI} with ferrous ion in catechol solutions

(*Received* 25 *April*, 1960)

In a study of the polarographic behaviour of vanadium, iron, and uranium as their catechol complexes a powerful reducing system has been observed. When a ferrous solution is added to an ammoniacal solution containing either the vanadyl- or uranyl-catechol complex in the presence of excess catechol, the vanadium and uranium are reduced rapidly to V^{III} and U^{IV} species, respectively. The analytical application of this reaction has been examined briefly. The direct titration of uranyl-catechol with ferrous ion to a potentiometric or amperometric end-point indicated the above stoichiometry. Similar behaviour was also noted for the vanadyl-catechol complex.

Polarographic data indicate that the reduction potential of the ferrous-catechol/ferric-catechol couple in ammoniacal medium (pH9.5) is -0.97 volts v. Ag/AgCl. Ferrous-catechol is very unstable in a de-gassed solution containing no reducible materials. It appears that the ferrous complex will readily reduce water. The reducing strength exceeds that of chromous ion in acid solution. By employing a standard ferrous solution this strong reducing agent is readily available for titrations. The strong reducing power is attributed to the high stability of the ferric-catechol complex as compared with that of the ferrous-catechol complex.[1] Undoubtedly, the existence of vanadium- and uranium-catechol complexes contributes to the favourable titration. This behaviour is similar to the titration of bivalent cobalt with ferric chloride in the presence of 1:10-phenanthroline.[2]

The stoichiometry of the reduction for vanadium and uranium was checked by the potentiometric titration of standard solutions of each ion. The results are shown in Table I.

TABLE I. TITRATION OF VANADIUM AND URANIUM WITH FERROUS IN CATECHOL SOLUTION

Material titrated	Milliequivalents		Titration reaction
	Taken	Found	
VO^{2+}	0.238	0.237	$V^{IV} \rightarrow V^{III}$
VO^{2+}	0.245	0.244	$V^{IV} \rightarrow V^{III}$
V^{V}	0.228	0.227*	$V^{IV} \rightarrow V^{III}$
UO_2^{2+}	0.262	0.262	$U^{VI} \rightarrow U^{IV}$

* All results indicate that vanadium^{V} is reduced to vanadium^{IV} by catechol before the titration.[3,4]

The potentiometric titration curves and appropriate data are shown in Fig. 1.

Mixtures of vanadium^{IV} and uranium^{VI} cannot be differentiated so that it is necessary to remove the vanadium before titrating the uranium. The molybdate-catechol complex is also reduced under these conditions.

This is the first direct reduction that has been reported of uranium^{VI} with a stable titrant. Titanium^{III} is more difficult to prepare and use.[5,6] Further applications of this reagent are under study. The polarographic results will be published elsewhere.

Acknowledgement—I wish to thank Dr. D. D. DeFord for his interest in this work.

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JOHN W. MILLER

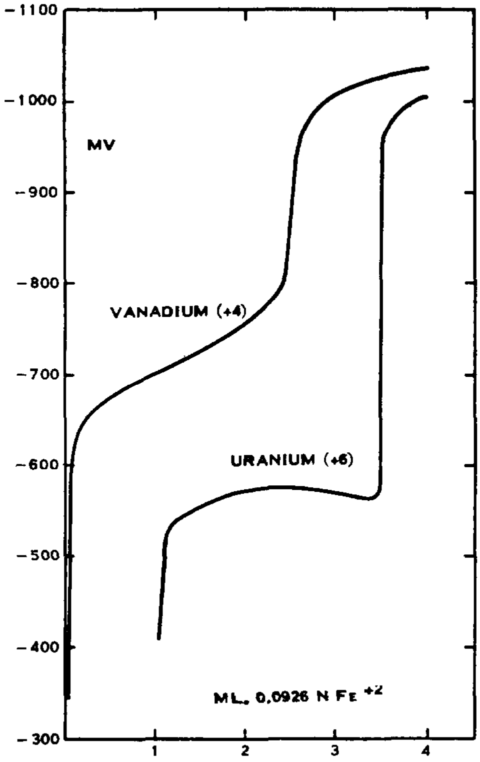

FIG. 1.—Titration curves of vanadium and uranium with ferrous in catechol solution

Vanadium titration: 60 ml 1M NH_4Cl–1M NH_3–0·1M Na_2SO_3
2400 mg catechol
5 ml 0·046N vanadate solution
Titrated with 0·0926N ferrous; mercury pool versus Ag/AgCl.

Uranium titration: 60 ml 1M NH_4Cl–1M NH_3–0·1M Na_2SO_3
2400 mg catechol
2 ml 0·131N uranyl acetate
Titrated with 0·0926N ferrous; mercury pool versus Ag/AgCl.

REFERENCES

[1] I. Banga, *Z. Physiol. Chem.*, 1938, **254**, 165; K. Laki and G. Papp, *ibid.*, 175.
[2] F. Vydra and R. Přibil, *Talanta*, 1959, **3**, 103.
[3] V. Patrovsky, *Chem. Listy*, 1954, **48**, 622.
[4] P. Blanquet, *Chemie Analyt.*, 1959, **41**, 359.
[5] J. J. Lingane and R. T. Iwamoto, *Analyt. Chim. Acta*, 1955, **13**, 465.
[6] J. H. Kennedy and J. J. Lingane, *ibid.*, 1958, **18**, 240.

Talanta, 1960, Vol. 4, pp. 294 to 295. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Quantitative Inorganic Analysis. R. BELCHER and A. J. NUTTEN. Second Edition, Butterworths Scientific Publications, London, 1960. Pp. x + 390. 35s.

THIS book is intended mainly as a practical teaching manual. It gives up-to-date instructions, with many references to the original literature, for a good selection of gravimetric and titrimetric analyses, and for a few instrumental determinations. The background and limits of applicability of each method are fully and completely discussed. It is suitable for use at all levels of undergraduate training. The Second Edition differs from the First Edition mainly in the expansion of the sections on EDTA titrations, and on balances and weighing (aperiodic and single-pan balances are now covered). Other minor improvements, resulting from new publications and from experience with the determinations, have also been made.

The cheapness of this book, and its compact presentation of detailed laboratory instructions in a form suitable for immediate use at the bench, are attractive, but it has serious faults. In concentrating on "classical" quantitative analysis, the authors fail to give their readers, most of whom will be students unable or unwilling to buy any other textbook of quantitative analysis, a balanced picture of the present state of the subject. "Microanalysis", for instance, does not even appear in the Index nor does "Ion-Exchange", although an ion-exchange method receives passing mention in the text. In spite of the authors' admonition to read up the physicochemical theory of the methods elsewhere, many student readers are likely to take the partial omission of theory from this book as evidence that the theory is not really important.

The treatment of practical techniques is, on the whole, sound and detailed, but is not free from defects. The First Edition of this book must be almost unique in the literature of analytical chemistry in containing a diagram of a chemical balance which does not show knife edges, planes, or pan stops. The Second Edition has a revised version showing the pan stops. There is a serious omission from the instructions for use of the pipette which has not been corrected in the Second Edition.

The weakest feature of the book, however, is the section on the calculations of titrimetric analysis. This is marred in parts by a reluctance to use simple mathematical equations which would have shortened and clarified the explanations. There are references to "molecules" of $KMnO_4$ and $FeSO_4$, and the term "molecular weight" is persistently used in connection with ionic compounds, although a perfectly good term, "formula weight", has long been current for this case. The account of oxidation numbers is not very clear, and is not as good as can be found in some older texts. The statement on p. 160 to the effect that the equivalent weight of a base is determined by the "number of replacable hydroxyl groups in the molecule" is unsatisfactory; hydroxylic bases are composed of ions, not molecules, and many bases of importance in analysis, such as sodium carbonate, borax and ammonia, are not hydroxylic compounds at all. This difficulty can be overcome by defining the equivalent weight in terms of the number of protons accepted by the base formula. Another sentence on p. 160 deserves to be quoted: "The molar weight of a substance is a constant, and must not be confused with a normal solution, although in many instances a normal solution contains a mole of solute and the concentrations become identical." (This is the *revised* version of the Second Edition.) It is only fair to state that this is an example of the worst writing in the book, and is not typical. It seems to show, however, how little comfort the puzzled student is likely to derive from this section. Faults like these can, it is true, be found in many other textbooks of quantitative analysis, but it is disappointing to find them so unnecessarily repeated in the second edition of a new book.

To summarise, this is a useful and, in some respects excellent book, but one which cannot be given unqualified approval as a student text.

HENRY G. HEAL

Analytical Chemistry in Nuclear Reactor Technology, 2nd Conference 1958. U.S. Atomic Energy Commission, Office of Technical Services. Department of Commerce, Washington 25, D.C. Part I Pp. vii + 298, Part II Pp. vi + 236.

THESE two paper-bound volumes contain 55 of the 70 papers presented at the second conference on analysis in reactor technology held in September 1958 at Gatlinburg, Tennessee. This conference was concerned with the problems of the analyst during the commissioning and operation of reactors; it will be recalled that the first conference in 1957 concentrated on reactor materials analysis.

Part 1 contains fourteen contributions mainly dealing with fuel alloy analyses and the range of control analyses called for in operating some experimental reactors; five papers on boron and other special determinations; a group of five papers on applications of flame photometry and polarography and finally six contributions concerned with applications of X-ray and emission spectroscopy. There are four abstracts of papers published in full elsewhere.

Part 2 contains seven papers on instrumentation (laboratory and "in-line"), nine reports on remote-control techniques, and concludes with nine papers under the heading "Nucleonics" including several dealing with radiochemical and gamma-spectrometric analysis.

The prospective reader should perhaps be warned against being misled by the title into thinking that this useful compilation is a systematic and comprehensive attempt to survey the whole field; as indicated by the editors in their preface, the objective of the conference was "to provide a forum for the exchange of information" and consequently the collected papers are in the nature of a miscellany, some indeed being rather remotely connected with reactor start-up and operation. One feels that the inclusion of a few review papers aimed at establishing trends in techniques and attempting to summarise philosophies would have increased the overall value of the conference record as now presented. If one were to try to summarise impressions, no doubt one would have to note the ever increasing activity levels the analyst must needs work at and the ingenuity and skill which have been used to adapt many of his conventional physical instrumental techniques to operation at high radiation levels; indeed, if we want to single out a group of papers, perhaps one of the most impressive presented at this symposium is that dealing with remote control developments. Other significant trends are the steadily increasing importance and widening application of such techniques as X-ray fluorescence and gamma spectrometry and the successful extensions of flame photometry to alkaline earth determination without separation in uranic solutions.

These volumes are well printed and adequately illustrated with more than 250 diagrams and reproductions from photographs, and are useful reference works to set beside the earlier volume covering the first conference.

F. J. WOODMAN

Solution of Multistage Separation Problems by Using Digital Computers. JOHN H. DUFFIN. *University of California, Radiation Laboratory. Report UCRL 8787.* U.S. Department of Commerce, Washington, D.C. 1959. pp. 266. $4.00.

THIS report is in thesis form, its object being to indicate, with appropriate detailed examples, the conditions under which digital computers may be programmed to solve multistage separation problems. Various approaches to the solution of such problems *e.g.* using mass balance, energy balance etc. are critically examined as to their range of usefulness and to the type of resulting computer programmes. The procedures are mostly iterative and the document is valuable in that it provides cross-checking of the computer data derived from the different approaches. The volume may well prove useful to chemical engineers associated with distillation and similar problems but it falls outside the working range of the majority of analytical chemists.

J. K. FOREMAN

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NOTICES

The following meetings have been arranged:

Sunday–Friday 11–16 *September* 1960: New York Meeting of **Division of Analytical Chemistry, American Chemical Society.**

Four symposia are being presented: *Resonance Methods for Analysis and Characterisation: (a) Nuclear Magnetic Resonance, (b) Electron Paramagnetic Resonance,* organised by HARLAN FOSTER. *Infrared Methods of Chemical Analysis,* organised by RICHARD C. LORD Jr. and BRYCE CRAWFORD, in conjunction with the Division of Physical Chemistry. *X-ray Absorption and Emission in Chemical Analysis,* organised by HERMAN A. LIEBHAFSKY. *Recent Advances in Analytical Chemistry,* organised by CLARK BRICKER, in conjunction with the Division of Chemical Education.

Further information may be obtained from LOCKHART B. ROGERS, Secretary-Treasurer of the Division of Analytical Chemistry, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass., U.S.A.

Wednesday 21 *September* 1960: **Polarographic Society:** *The Application of Polarography in Metallurgical Analysis*: Wolverhampton and Staffordshire College of Technology, Wolverhampton. 2.30 p.m.

Further details concerning the meeting may be obtained from Mr. R. C. ROONEY, A.R.I.C., British Cast Iron Research Association, Bordesley Hall, Alvechurch, Birmingham.

Thursday–Saturday, 6–8 *October* 1960: **Austrian Microchemical Society:** *Emich-Commemoration and Microchemical Conference.*

On behalf of the Austrian Microchemical Society and under the direction of Professor Dr. Ing. G. Gorbach, the Emich Group has arranged an Emich-Commemoration and Microchemical Conference at the Technical University of Graz on October 6, 7 and 8, 1960.

The provisional programme is as follows:

Thursday 6 *October*
Arrival and reception of the visitors in the Hotel Steirerhof.

Friday 7 *October*
Morning—Reception speech, commemoration speech and plenary lectures.
Visit to the birthplace and the grave of Emich, with the laying of a wreath at both places.
Visit to the "Emichplatzl" and lunch at the Schloßberg.
Afternoon—Individual lectures.

Saturday 8 *October*
Morning—Individual lectures.
Simultaneously with the lectures there will be demonstrations of microchemical apparatus at the Technical University of Graz as well as a visit to the Pregl-Laboratories of the University of Graz under the direction of Professor Dr. H. Lieb.

The fee for the Conference is ö.s.60,— for members or ö.s.100,— for non-members.

Those people who wish to participate in the proceedings are asked to write as soon as possible to Professor Dr. Ing. G. GORBACH, Institut fur Biochemische Technologie, Lebensmittelchemie und Mikrochemie, Technische Hochschule, Graz, Schlegelgasse 9, Austria.

Thursday 3 *November* 1960: **Royal Dutch Chemical Society:** *Symposium on Organic Analysis.*

The Section for Analytical Chemistry of the Royal Dutch Chemical Society is arranging a Symposium on Organic Analysis in the Laboratorium voor Algemenen Anorganische Chemie der Universiteit te Amsterdam on November 3, 1960.

The tentative programme is as follows:

General Introduction: Dr. Ir. E.A.M.F. DAHMEN (Kon./Shell Lab., Amsterdam);

Qualitative Detection of Elements and Functional Groups: Dr. W. I. STEPHEN (University of Birmingham, England);

Identification of Specific Organic Compounds: Mej. Dr. P. HAVERKAMP-BEGEMANN (Unilever Research Lab., Vlaardingen);

Quantitative Elementary Analysis: P. GOUVERNEUR (Kon./Shell Lab., Amsterdam);

Quantitative Determination of Groups and Specific Compounds: Dr. L. BLOM (Centraal Lab., Staatsmijnen, Geleen).

Further information can be obtained from Mej. Ir. E. HOEKSTRA, p/a Willem Smit & Co's Transformatoren fabriek N.V., Groenestraat 336, Nymegen, Netherlands.

The Polarographic Society now has a permanent address for mail; enquiries concerning the Society should be addressed to:—

The Polarographic Society, c/o Lloyds Bank Ltd., 36 High Street, Wealdstone, Middlesex.

Talanta, 1960, Vol. 4, p. 298. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Contributions to the basic problems of complexometry—III: Some advantages of acetate buffer. W. Berndt and J. Šára. (2 *May* 1960).

A study of the reduction waves of the three isomers of nitrophenol by means of the alternating current polarograph. Takeo Takahashi and Hideko Shirai. (2 *May* 1960).

Precipitation of nickel dimethylglyoximate from homogeneous solution. Eugene D. Salesin and Louis Gordon. (5 *May* 1960).

Detection of monobasic phosphorus acid esters by conversion to cholinesterase inhibitors. Harvey W. Yurow, David H. Rosenblatt and Joseph Epstein. (11 *May* 1960).

Radiometric trace analysis—I: Determination of lead with phosphate-^{32}phosphorus on filter paper without preliminary separations. P. C. Van Erkelens. (6 *May* 1960).

Radiometric trace analysis—II: Quantitative paper chromatography of lead with phosphate-^{32}phosphorus. P. C. Van Erkelens. (16 *May* 1960).

Radiometric trace analysis—III: Determination of lead with diethyldithiocarbamate and ^{204}thallium^{+3} ions. P. C. Van Erkelens. (16 *May* 1960).

Radiometric trace analysis—IV: Determination of lead with ^{204}thallium-diethyldithiocarbamate. P. C. van Erkelens. (16 *May* 1960).

Coulometric titration method for the determination of iron^{II} by electrolytically generated bromine. Takeo Takahashi and Hiroshi Sakurai. (17 *May* 1960).

PUBLICATIONS RECEIVED

Deutsche Einheitsverfahren zur Wasser-Untersuchung: Fachgruppe Wasserchemie, Gesellschaft Deutscher Chemiker. Third edition. Verlag Chemie, Weinheim, 1960. Pp. 88 in Ring Binder. DM 20.

Electrochemie Théorique: Eugenè Darmois and Geneviève Darmois. Masson et Cie., Paris, 1960. Pp. 240. 39 NF.

The Radiochemistry of Thorium: E. K. Hyde. National Academy of Sciences, Washington, D.C., NAS-NS 3004. Jan., 1960. Pp. vi + 70. $0.75.

The Radiochemistry of Fluorine, Chlorine, Bromine and Iodine: Jacob Kleinberg and G. A. Cowan. National Academy of Sciences, Washington, D.C., NAS-NS 3005, Jan. 1960. Pp. vi + 42. $0.50.

The Radiochemistry of Chromium: J. Pijck. National Academy of Sciences, Washington, D.C., NAS-N 3007, Jan., 1960. Pp. vi + 34. $0.50.

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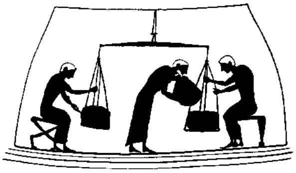

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