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SUMMARIES FOR CARD INDEXES

Chromatographic separation and determination of niobium, tantalum and titanium: I. MARTIN and R. J. MAGEE, *Talanta*, 1963, 10, 1119. (Department of Chemistry, The Queen's University, Belfast, Northern Ireland.)

Summary—Following a critical study of the composition of solvent mixtures which separate niobium, tantalum and titanium by partition chromatography, a solvent mixture has been developed which gives ideal R_f values for these elements. Its composition is 2.2*M* hydrofluoric acid-2*M* nitric acid-diethyl ketone. Separation is complete in about 30 min. The method has been applied to the determination of these elements.

The use of metal-specific indicators in precipitation titrations—VIII: Titration of micro amounts of arsenic with standard lead solution, using PAR and SNAZOXS: RICHARD PÜSCHEL, *Talanta*, 1963, 10, 1125. (Medizinisch-chemisches Institut und Pregl-Laboratorium der Universität Graz, Austria.)

Summary—In hot aqueous medium buffered with hexamethylenetetramine 0.15–1.5 mg of arsenic may be titrated directly as arsenate, using a 0.01*M* solution of lead as titrant. PAR and 7-(sulpho-1-naphthylazo)-8-hydroxyquinoline sulphonic acid (SNAZOXS) are used as indicators. The standard deviation is 7.2 μg of arsenic.

The determination of tertiary amines in the presence of primary and secondary amines: M. MILLER and D. A. KEYWORTH, *Talanta*, 1963, 10, 1131. (Universal Oil Products Company, Des Plaines, Illinois, U.S.A.)

Summary—Tertiary amines in the presence of primary and secondary amines can, in most cases, be determined after reaction of phenylisothiocyanate with the primary and secondary amine to form a derivative of thiourea. The unreacted tertiary amines are then titrated with anhydrous hydrogen chloride in methyl isobutyl ketone (MIBK). This method has been successful for all aliphatic primary and secondary amines, and for most aromatic amines. Of the secondary amines tested, *N*-sec-alkylanilines and sterically hindered *o*-substituted *N*-alkylanilines failed to react although, when there was *p*-substitution of the ring, all of the *N*-sec-alkylanilines examined did react. The primary and secondary amines are treated in MIBK with phenylisothiocyanate at room temperature, and the unreacted tertiary amines are titrated with anhydrous hydrogen chloride in MIBK. The bridge solution of the reference calomel electrode is lithium chloride-saturated MIBK. Duplicate determinations normally do not differ from the mean by more than 0.03 meq of tertiary amine nitrogen per g of sample. Twenty times as much primary and secondary amine nitrogen as tertiary amine nitrogen can be tolerated.

The recovery of rhodium, iridium, palladium and platinum from ores and concentrates by wet assay, and a comparison with recovery by fire assays: G. G. TERTIPIS and F. E. BEAMISH, *Talanta*, 1963, 10, 1139. (Department of Chemistry, University of Toronto, Toronto, Canada.)

Summary—A wet method for recovering micro amounts of rhodium, iridium, palladium and platinum from ores and concentrates is reported. It involves stepwise dissolution of the roasted sulphide concentrate. The calcined material is leached with *aqua regia* or with concentrated hydrochloric acid followed by *aqua regia*. The leached residue is chlorinated, silicon is volatilised as silicon tetrafluoride from the chlorinated residue, and the final residue is fused with sodium peroxide. From the resulting solution the base metals are removed by a cation-exchange technique. A chromatographic method followed by solvent-extraction procedures is used to separate the above four platinum metals from the effluent from the small cation exchanger. The efficiency of the method is compared with that of both the copper-nickel-iron and the classical (lead) fusion methods, applied to the same ore and concentrate.

The determination of traces of iron in samples of platinum by neutron-activation analysis: D. F. C. MORRIS and R. A. KILLICK, *Talanta*, 1963, 10, 1153. (Department of Chemistry, Brunel College, London W.3, England.)

Summary—A neutron-activation analysis method for the determination of traces of iron in samples of purified platinum is described. The nuclear reactor BEPO at Harwell has been used as the neutron source. A rapid radiochemical separation procedure using carriers has been employed to decontaminate the iron activity from most other induced activities. The analysis is completed by discriminated γ -scintillation counting. Results of analyses of seven samples of platinum are quoted. The method of analysis has the advantage that it obviates difficulties caused by "reagent blanks" or by contamination from traces of inactive iron after irradiation. Interference resulting from nuclear reactions of elements other than iron in the samples appears to be of no consequence in the present case.

Spectrophotometric studies of lower oxidation states of technetium: G. B. S. SALARIA, CHARLES L. RULFS and PHILIP J. ELVING, *Talanta*, 1963, 10, 1159. (Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.)

Summary—The spectrophotometric behaviour of lower oxidation states of technetium, obtained by reducing pertechnetate under different conditions, by various methods, has been examined. Contrary to some of the previously advanced conclusions regarding the ascorbic acid reduction of pertechnetate, it was found that the technetium is reduced to a quadrivalent state. The latter product does not appear to involve a tightly-bound ascorbate species; neither does it react or complex with α -picolinic acid to give a new species.

Summaries for card indexes

Electron microscopy studies of nickel dimethylglyoximate: KAZUYOSHI TAKIYAMA and LOUIS GORDON, *Talanta*, 1963, **10**, 1165. (Division of Engineering and Department of Chemistry, Case Institute of Technology, Cleveland 6, Ohio, U.S.A.)

Summary—Nickel dimethylglyoximate crystals precipitated from homogeneous solution are well formed and convenient for microscopic study. The crystals are precipitated in solution as long needles with a rectangular cross-section. The direction of the long axis, *i.e.*, the direction of the long dimension of the needle, is the c-axis; the shortest axis is either the a- or b-axis. When the single crystal was slowly heated in the electron microscope, it began to sublime at 120° with changes occurring in its surface structure. Above 400° the Debye-Scherrer diffraction rings appeared as the crystal changed to nickel oxide.

Precipitation of metal chelates from homogeneous solution: F. H. FIRSCHING, *Talanta*, 1963, **10**, 1169. (Department of Chemistry, University of Georgia, Athens, Georgia, U.S.A.)

Summary—The precipitation of metal chelates from homogeneous solution is reviewed.

Complexometric titration of yttrium and the lanthanons—1: A comparison of direct methods, S. J. LYLE and MD. M. RAHMAN, *Talanta*, 1963, **10**, 1177. (Londonderry Laboratory for Radiochemistry, University of Durham, South Road, Durham City, England.)

Summary—A comparison is made of a number of direct complexometric titrations previously published for the determination of yttrium and the lanthanons. Working and 'optimum' pH ranges are obtained for what are considered to be the best indicators, Alizarin Red S screened with Methylene Blue, Eriochrome Black T, Copper-Naphthyl Azoxine and Xylenol Orange. The precision and accuracy of the selected methods are determined by carrying out replicate titrations on standard solutions of cerium^{III}, yttrium and ytterbium. The results, together with additional observations made on the behaviour of indicators in the different methods, suggest that Xylenol Orange at pH 5.8 to 6.4 is most satisfactory and convenient for direct titrations.

Complexometric titration of yttrium and the lanthanons—II: Methods for their determination in oxalates: S. J. LYLE and MD. M. RAHMAN, *Talanta*, 1963, **10**, 1183. (Londonderry Laboratory for Radiochemistry, University of Durham, South Road, Durham City, England.)

Summary—Complexometric methods for the determination of yttrium and the lanthanons in oxalate precipitates are investigated. In the method recommended, excess EDTA is added to a suspension of the oxalate, and solution is effected at pH 10 with ammonia-ammonium chloride buffer. The excess EDTA is titrated with standard zinc solution to the blue to red colour change of Eriochrome Black T indicator. It is more convenient, and generally more satisfactory, than the method previously suggested, in which magnesium is the back-titrant at pH 10.2 to 10.5. Both of these methods are superior to the back-titration with lanthanum using Arsenazo as indicator at pH 8 to 9 in the presence of oxalate, and more convenient than methods in which the oxalate is removed by wet oxidation before titrating directly with EDTA. The zinc titration method is particularly suitable for chemical-yield measurement in radiometric determinations of yttrium and lanthanons precipitated as oxalates for "counting" purposes.

Precipitation from homogeneous solution of palladium using indane-1,2-dioxime: L. S. BARK and D. BRANDON, *Talanta*, 1963, **10**, 1189. (Department of Chemistry and Applied Chemistry, Royal College of Advanced Technology, Salford 5, Lancashire, England.)

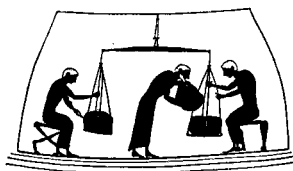
Summary—The preparation of indane-1,2-dioxime and its use for the precipitation of palladium from homogeneous solution is described. The complex $\text{PdC}_{18}\text{H}_{14}\text{O}_4\text{N}_4$ has a complex:metal weight ratio greater than those with reagents normally used for the gravimetric determination of palladium. The effect of foreign ions on the precipitation is investigated and the optimum analytical conditions are established.

Use of masking agents in chelatometric titrations—III: β -Mercaptopropionic acid: KOICHI YAMAGUCHI and KEIHEI UENO, *Talanta*, 1963, **10**, 1195. (Department of Organic Synthesis, Faculty of Engineering, Kyusushu University, Fukuoka, Japan.)

Summary— β -Mercaptopropionic acid has been investigated as a masking agent in EDTA titrations. With the use of this reagent at pH 10, it is possible to determine nickel^{II}, manganese^{II}, calcium^{II} and magnesium^{II} in the presence of bismuth^{III}, cobalt^{II}, iron^{III}, copper^{II} and mercury^{II}.

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- ² S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*. Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
- ³ A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.
- ⁴ W. Jones, *Brit. Pat.* 654321, 1959.

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CHROMATOGRAPHIC SEPARATION AND DETERMINATION OF NIOBIUM, TANTALUM AND TITANIUM

I. MARTIN and R. J. MAGEE

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(Received 25 July 1962. Accepted 19 February 1963)

Summary—Following a critical study of the composition of solvent mixtures which separate niobium, tantalum and titanium by partition chromatography, a solvent mixture has been developed which gives ideal R_f values for these elements. Its composition is 2:2*M* hydrofluoric acid-2*M* nitric acid-diethyl ketone. Separation is complete in about 30 min. The method has been applied to the determination of these elements.

BECAUSE of the lanthanide contraction, the atomic volumes of niobium and tantalum are almost identical and chemical resemblance between them is very close. Their analytical chemistry is characterised by generally weak chemical behaviour, and complicated by the effects of association imposed by other elements. This results in close similarity of their individual reactions, which produces difficulties in separating the two elements from one another. The difficulties in separation and analysis of these metals have been stressed by several authors.^{1,2,3} Colter,⁴ discussing the importance of niobium as a metal in nuclear technology, states that, although there are a number of methods used for the extraction of niobium from columbite, the major difficulty in all of them is separation from the accompanying tantalum. Elwell and Wood³ in a recent review emphasise that in the analytical separations involving niobium and tantalum, the presence of other metals, particularly titanium and zirconium, may introduce difficulties. In this laboratory the difficulties caused by the presence of titanium have been experienced in recent work.⁵ It was the intention of this work to achieve a separation of niobium, tantalum and titanium by partition chromatography. The number of chromatographic methods available for the separation of niobium and tantalum (and titanium) is not large. The first separation of this type was by Wood,⁶ based on the elution of the ammonium fluoro-salts of the metals from a cellulose column with ketone solutions containing various concentrations of hydrofluoric acid.

Partition methods on paper employing hydrofluoric acid and ketones have been used by Hunt and Wells⁷ and by Scott and Magee.⁸ Bruniux *et al.*⁹ have reported the separation of niobium and tantalum on paper by electrophoresis. The largest quantities separated are 50 μg . The same authors have also achieved a separation by paper chromatography using the oxalates and a solvent-mixture composed of ethyl methyl ketone and 10*M* hydrochloric acid. Microgram amounts were separated. None of the methods employing paper chromatography include titanium in the separation. This paper describes the separation and determination of niobium, tantalum and titanium, using partition chromatography in systems involving hydrofluoric acid/mineral acid, alcohol and ketones.

EXPERIMENTAL

Reagents

Titanium solution: 0.66 g of titanium dioxide was dissolved in a mixture of nitric and hydrofluoric acids in a 30-ml platinum crucible. The solution was evaporated to dryness, the residue taken up in 1 ml of 40% hydrofluoric acid and the resulting solution diluted to 20 ml with water to give a concentration of 2% of titanium. This solution was stored in a Polyethylene bottle.

Niobium solution: 0.8 g of niobium pentoxide was treated in the same way as for the titanium solution. The concentration was 2% of niobium in 0.6M hydrofluoric acid.

Tantalum solution: 1.0 g of tantalum metal was dissolved in a mixture of nitric and hydrofluoric acids and treated in the same way as the other two metals to give a 2% tantalum solution in 1M hydrofluoric acid. This solution should be made up freshly each week.

Preliminary investigations

Experiments were carried out on Whatman No. 1 paper using mixtures of (1) 2M nitric acid, (2) 5.5M hydrochloric acid, and (3) 6M sulphuric acid, with alcohols and ketones, and 0.6M hydrofluoric acid. The aqueous acid mixture was shaken with the appropriate alcohol or ketone until the organic phase was saturated. The organic phase was used as the mobile phase. Where the organic component was miscible with the aqueous phase, mixtures varying from 99.9 to 95% in the organic component were used.

TABLE I.—HYDROFLUORIC ACID-NITRIC ACID SYSTEM

0.6M HF + 2M HNO ₃ with	R _f values		
	Ti	Nb	Ta
Methyl isobutyl ketone	0	0 → 0.10	1.00-slight tail
Methyl propyl ketone	0	0.1 → 0.35	1.00
Dipropyl ketone	0	0	0.42-0.80
Diethyl ketone	0	0	1.00-excellent separation
Acetone*	0.64	0.75	1.00
Ethyl alcohol*	0.5 → 0.95	0.5 → 0.95	1.00
Butyl alcohol	0.25	0.43	0.85-good separation
Amyl alcohol	0	0	0.90

* R_f values varied with concentration of aqueous phase in the solvent-mixture.

TABLE II.—HYDROFLUORIC ACID-HYDROCHLORIC ACID SYSTEM

0.6M HF + 5.5M HCl with	R _f values		
	Ti	Nb	Ta
Methyl isobutyl ketone	0	0	0.93
Methyl propyl ketone	0	0 → 0.6	1.0
Dipropyl ketone	0	0	0.4 → 0.8
Diethyl ketone	0	0 → 0.5	0.95
Acetone	0.89	0.92	0.98
Ethyl alcohol	0.8 - 0.9	0.8 - 0.9	1.0
Butyl alcohol	0.1 - 0.5	0.1 - 0.5	0.97
Amyl alcohol	0.31	0.51	0.93

RESULTS AND DISCUSSION

The results obtained for the hydrofluoric acid-nitric acid and hydrofluoric acid-hydrochloric acid systems are shown in Tables I and II, respectively.

Substitution of 6M sulphuric acid produced much the same effect on the ketone chromatograms as did hydrochloric acid. Any movement of the elements was almost

invariably associated with tailing and streaking. Separations using alcohol solvents were in this case disappointing, no separations being obtained despite considerable movement of the elements on the paper. While these solvent-mixtures give a satisfactory separation of tantalum-niobium or titanium, the separation of niobium and titanium was not satisfactory. It appeared that to achieve the complete separation of all three elements, it would be desirable to increase the R_f value of niobium to about

TABLE III

No.	Solvent-mixture	R_f values		
		Ti	Nb	Ta
1	2.2M HF-2M HNO ₃ -diethyl ketone	0.05	0.55	1.0
2	2.2M HF-5.5M HCl-dipropyl ketone	0.00	0.45 - 0.55	0.90 - 1.0
3	2.2M HF-5.5M HCl-hexone	0.00	0.3 - 0.4	0.95 - 1.0

0.5, keeping those for tantalum and titanium at 1.0 and 0.0, respectively. A possible method of achieving this was by alteration of the hydrofluoric acid concentration. In solvent extraction work there is no appreciable extraction of niobium until the molarity of the hydrofluoric acid is increased above 4. Addition of mineral acids, however, lowers the molarity at which niobium begins to be extracted. In the present work this is in the region of 2M in hydrofluoric acid. In choosing solvent mixtures which would give a complete separation of all three elements attention was paid to this factor and to the evidence of the above work. As a result of this assessment, the three solvent-mixtures shown in Table III were selected for further examination. Solvent-mixture No. 1 is a fast solvent, a good "run" occupying about 30 min. Solvent-mixtures Nos. 2 and 3 are slower but not unreasonably slow. While all three produce the separations predicted, solvent mixture No. 1 provides the best separation of all. Band definition, reproducibility and speed are all good. No significant hydrolysis is observed.

Spraying reagents

All of the usual reagents which have been used for the determination of niobium and tantalum were investigated. These included thiocyanate, pyrogallol, tannin and 8-hydroxyquinoline. With the exception of 8-hydroxyquinoline, all of these reagents proved unsatisfactory as spraying reagents on a chromatogram. Using the method of Scott and Magee,⁸ 8-hydroxyquinoline was satisfactory but slow. Attempts were made to improve this reagent and a dilute solution of the reagent in dilute sodium hydroxide was found to be most suitable. On spraying this solution on the dried chromatogram the colours of the elements developed immediately: yellow bands for niobium and tantalum, and orange for titanium. The reagent requires to be prepared fresh daily.

Procedure

Place the solvent-mixture (2.2M hydrofluoric acid-2M nitric acid-diethyl ketone) in the solvent trough of a Shandon Chromatank at least 1 hr before the experiment is to be started. Cut strips of Whatman No. 1 paper of 50 cm × 16 cm. At a distance approximately 12 cm from the end of a strip, rule a line across the paper. Spot the metal fluorides along this line, using a volume of 0.01 ml. The spots should still be slightly damp when the strips are inserted into the tank. Allow the solvent-mixture to run down the paper for a distance of about 16 cm from the line. Remove the strip from the tank and allow to dry in the air. Attach the strip to the strip holder and spray with 8-hydroxyquinoline reagent. (0.5% solution of 8-hydroxyquinoline in 0.25N sodium hydroxide) Examine the strip, when niobium and tantalum will be observed as yellow bands and titanium as an orange band at the R_f -values indicated in Table III.

Standards, limits of detection, synthetic mixtures

Standards of 20, 100, 200 and 300 μg were prepared for each element. For all three elements the limit of detection was 20 μg .

Synthetic mixtures of "unknown" composition were analysed by one of us (I.M.). Estimations were carried out by comparison of band intensities and areas with a set of standards. The results are shown in Table IV.

TABLE IV

	Nb, μg	Ti, μg	Ta, μg
{Actual	300	300	200
{Found	285	290	190
{Actual	100	20	100
{Found	95	20	95
{Actual	50	200	30
{Found	45	190	25

Application of the method to quantitative determinations

To extend the method to quantitative determinations, it is necessary to ensure that the precipitation of the oxinates on the paper is complete. Secondly, a method of removal from the paper is required. If these two requirements are met, it should then be possible to determine the metals colorimetrically, assuming that extraction from the paper is complete.

It was found that by spraying as described, precipitation on the paper was complete, providing hydrolysis has not taken place during the running of the chromatogram.

Removal of the oxinates from the paper and subsequent extraction into chloroform, using the method of Scott and Magee⁸ was investigated. Hot 2M hydrochloric acid was used for the removal from the paper. The pH values used in the extraction were: niobium 8.5, tantalum 10.0, titanium 9.0. With this method some hydrolysis of the elements, particularly tantalum, occurred and complete extraction into the chloroform layer was not always obtained. The method, however, yields better results when the standards are put through the same procedure. Using this method to prepare calibration curves is, however, tedious. Investigations showed that more satisfactory results were obtained in the case of niobium and titanium by cutting the developed bands from the chromatogram, igniting in a 5-ml platinum crucible, and dissolving the oxides in 40% hydrofluoric acid and nitric acid, adding 6M sulphuric acid and heating to fumes of sulphuric acid. The residue is taken up in hydrochloric acid and the strychnine thiocyanate method⁵ applied. Reproducible results for "unknown" mixtures were obtained. The results for niobium, titanium and tantalum are shown in Table V.

TABLE V

	(1)	(2)	(3)	(4)	
Nb,	{Actual	100	100	25	—
μg	{Found	95	105	23	—
Ti,	{Actual	100	20	60	—
μg	{Found	95	22	56	—
Ta,	{Actual	100	50	50	250
μg	{Found	105	—	—	230

Tantalum is best treated by bisulphate fusion, oxalate leaching⁸ and determined by the pyrogallol method.⁹ Results for amounts of tantalum below 100 μg were, however, unreliable.

The method is satisfactory (for niobium and titanium) but colorimetric methods for tantalum are not sufficiently sensitive. The Scott-Magee method is satisfactory if one adheres to a long calibration procedure, but using this chromatographic system hydrolysis of tantalum does occur with resultant incomplete precipitation of tantalum oxinate.

Zusammenfassung—Nach kritischer Untersuchung verschiedener Lösemittelgemische zur verteilungschromatographischen Trennung von Niob, Tantal und Titan wurde eine Zusammensetzung gefunden, die ideale R_f -werte für diese Elemente ergibt. Die Lösung besteht aus 2·2n HF-2n HNO₃-diethylketon. Die Trennung ist in 30 Minuten komplet und wurde auf die Bestimmung der Elemente angewendet.

Résumé—A la suite d'une étude critique de la composition des mélanges de solvants utilisés pour séparer le niobium, le tantale et le titane par chromatographie de partage, un mélange de solvants donnant des valeurs de R_f optimales pour ces éléments a été mis au point. Dans le mélange se trouvent 2·2N HF-2N HNO₃-diethyl cétone. La séparation est totale en 30 minutes environ. La méthode est appliquée au dosage de ces éléments.

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ÜBER DIE VERWENDUNG METALLSPEZIFISCHER INDIKATOREN BEI FÄLLUNGSTITRATIONEN—VIII*

TITRATION VON MIKROMENGEN ARSENAT MIT BLEIMASS- LÖSUNG GEGEN PAR UND SNAZOXS

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Zusammenfassung—0,15 bis 1,5 mg Arsen werden als Arsenat in heisser, wässriger, mit Hexamethylentetramin gepufferter Lösung direkt mit 0,01 m Bleilösung titriert. Als Indikatoren werden PAR und 7-(4-Sulfo-1-naphthylazo)-8-hydroxychinolin-5-sulfonsäure (SNAZOXS) verwendet. Die Standardabweichung beträgt 7,2 µg Arsen.

IN den bisherigen Beiträgen zu dieser Reihe wurden die Titration von Molybdat,¹ Wolframat,² Sulfat³ und Phosphat⁴⁻⁶ beschrieben. Die Verwendung bestimmter Farbstoffe, die bislang nur als chelometrische Indikatoren oder als photometrische Reagentien zur Bestimmung von Metallen in Gebrauch waren, ermöglicht bei Fällungstitrationen noch sehr geringe Mengen bei niederen Konzentrationen exakt zu erfassen; im Falle von Phosphat beispielsweise erhält man mit Cer (III) oder Blei als Titrans noch im Mikrogrammbereich scharfe Endpunkte gegen Eriochromschwarz T oder PAR.⁶ Die Nützlichkeit der erarbeiteten Methoden erwies sich auch anhand ihrer Anwendung auf praktische Probleme. So hat sich die direkte Titration von Molybdat und Wolframat bei der routinemässigen Analyse von Molybdänkonzentraten, von Wolframlegierungen und Hartmetallen gut bewährt.⁷ Die Titration von Phosphat mit Cer (III) wurde zur Bestimmung von Phosphor in organischen Substanzen⁸ und in biologischem Material⁹ angewandt. Diese Methodik wurde von anderer Seite mit Erfolg zur Analyse von Nucleinsäuren verwendet.¹⁰ Auf die theoretischen Voraussetzungen für die Verwendung chelatochromer Indikatoren bei Fällungstitrationen haben wir hingewiesen und die sich daraus ergebenden praktischen Vorteile anhand einer Literaturzusammenfassung erörtert.¹¹

Auch an dieser Stelle sei unser Hinweis wiederholt, dass Fällungstitrationen vor allem zur *direkten Bestimmung von Anionen* in Betracht kommen, denn Metallionen (mit Ausnahme des Silbers) lassen sich bedeutend eleganter, mit grösster Genauigkeit bis in den Ultramikrobereich,¹² und unter Einhaltung bestimmter Bedingungen und/oder unter Zuhilfenahme von Maskierungsmitteln auch hochselektiv auf chelometrischem Wege direkt titrieren.

Die Vorteile der direkten Phosphattitration⁴⁻⁶ und die Reaktionsanalogie zwischen Phosphat und Arsenat legten es nahe, die Möglichkeit zu prüfen, kleine Arsenmengen durch eine direkte Titration zu erfassen.

Bereits 1939 berichtete Evans¹³ kurz über die Titration von Arsenat mit Bleimasslösung in pyridingepuffertem Wasser-Aceton-Medium gegen Diphenylcarbazon als

* VII. Mitteilung: *Mikrochim. Acta*, 1960, 352.

Indikator. Dieser Weg scheint—nach Durchsicht der seither erschienenen Literatur—weder weiter untersucht, noch praktisch angewandt worden zu sein. In neuerer Zeit wurde von Bakács-Polgár, Szekeres und Láng^{14,15} die Titration von Arsenat in ammoniakalisch gepuffertem Medium mit Magnesiummasslösung beschrieben. Hierbei erwies es sich als notwendig, Alkohol zuzusetzen, um die Bildung des Niederschlages in einer vernünftigen Zeit zu erreichen. Nach unseren Erfahrungen gelingt es nicht, diese Methode auf Milligrammbruchteile Arsen zu verfeinern, da die Fällung bei so geringen Arsenmengen viel zu langsam verläuft.

Die Möglichkeit, wie zur Bestimmung von Phosphat, Cer (III) als Titrans zu verwenden, entfällt, da es das Arsenat reduziert. Arsenit fällt unter den Titrationsbedingungen weder mit Cer (III), noch mit Blei. Das Cer (III) könnte durch Lanthan ersetzt werden, der Indikator Eriochromschwarz T wird aber durch Wasserstoffperoxid in der Hitze zerstört, welches zugesetzt werden muss, um Arsenit zu Arsenat zu oxidieren. So erstreckten wir unsere Untersuchungen auf die Titration des Arsenats mit Bleimasslösungen und stellten fest, dass es sich in wässriger, mit Hexamethylentetramin gepufferter, heisser Lösung gegen PAR oder SNAZOXS ausgezeichnet bestimmen lässt.

Die Kurzbezeichnung SNAZOXS haben Guerrin, Sheldon und Reilley¹⁰ für die Verbindung 7-(4-Sulfo-1-naphthylazo)-8-hydroxychinolin-5-sulfonsäure vorgeschlagen, deren Indikatoreigenschaften sie untersucht und beschrieben haben. Dieser Farbstoff liegt im neutralen und schwach sauren Bereich als rotes Anion vor, das mit einer Reihe mehrwertiger Metallionen, darunter auch mit Pb^{2+} , gelbe, lösliche Chelate bildet. Im Verlaufe weiterer, an anderer Stelle veröffentlichter Untersuchungen¹⁷ haben wir festgestellt, dass das SNAZOXS dem PAR insoferne überlegen ist, als es nicht bereits mit geringsten Verunreinigungen durch Metallionen reagiert, die in die Analysenlösung eingeschleppt werden können. Dieser Vorteil mag in vielen Fällen eine Vorbehandlung der Untersuchungslösung mit einem Kationenaustauscher erübrigen.

Die Fällungsgeschwindigkeit des Bleiarsenats ist bei Vorliegen von 0,1 mg Arsen in 10-30 ml Lösung noch ausreichend, so dass mit rascher Tropfenfolge gearbeitet werden kann. Sowohl mit PAR, als auch mit SNAZOXS erhält man im Endpunkt einen scharfen Farbumschlag auf Zusatz von einem Tropfen 0,01 m Bleilösung. In Analogie zu Phosphat reagieren auch hier 5 Mole Pb^{2+} mit 3 Molen AsO_4^{3-} wahrscheinlich unter Bildung von $Pb_5(OH)(AsO_4)_3$.

Liegt das Arsen als Arsenit vor, so lässt es sich durch Aufkochen unter Zusatz von etwas Wasserstoffperoxid quantitativ in Arsenat überführen. Beide Indikatoren sind unter den Titrationsbedingungen gegen Wasserstoffperoxid stabil.

EINFLUSS VON FREMDIONEN

Es ist nicht möglich, diese Titration in Gegenwart von Phosphat durchzuführen, da dieses unter analogen Bedingungen quantitativ ausfällt. Ferner war zu erwarten, dass Cl^- , Br^- , J^- und SO_4^{2-} stören würden, da sie alle mehr oder weniger schwerlösliche Bleisalze bilden. Der Einfluss dieser Ionen wurde systematisch untersucht und wird durch Abb. 1 dargestellt. Die im Diagramm wiedergegebenen Mehrverbrauche stellen das Mittel aus jeweils vier bis fünf Einzelbestimmungen dar.

Zunächst überrascht der Befund, dass Iodid auf die Titration ohne Einfluss ist. Durch das zugegebene Wasserstoffperoxid wird es nämlich zu Jod oxidiert und beim Kochen aus der Lösung entfernt, was sich mit Stärkepapier nachweisen lässt. Das

Redoxpaar Bromid/Brom weist ein positiveres Normalpotential auf und das Bromid wird daher durch Wasserstoffperoxid nicht oxidiert.

Der Einfluss von Sulfat ist erheblich, der von Bromid und Chlorid geringer. Der durch einige Milligramme dieser Ionen verursachte Mehrverbrauch ist auf 0,01 ml reproduzierbar (Standardabweichung), daher kann man, wenn Art und Menge des Störions bekannt sind, vom abgelesenen Verbrauch entsprechende Korrekturen abziehen, ohne die Exaktheit des Verfahrens zu beeinträchtigen. Die Endpunkte sind

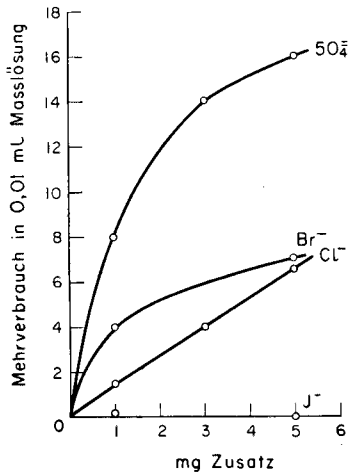


ABB. 1.—Titration von 0,01 mMol Arsenat mit 0,01 m Bleilösung in Gegenwart steigender Mengen von Cl⁻, Br⁻, J⁻ und SO₄²⁻.

auch in Gegenwart einiger Milligramme dieser Störionen scharf; mehr als 5 mg Sulfat führen aber zu einem zunehmend unscharfen Endpunkt. Mehr als 10 mg Acetat bedingen ebenfalls einen Mehrverbrauch an Masslösung und einen ziehenden Endpunkt. Auch grössere Elektrolytkonzentrationen stören; so ist bei 500 mg KNO₃ in 25 ml Untersuchungslösung ein Mehrverbrauch von 0,07 ml 0,01 m Bleilösung festzustellen, höhere Salzkonzentrationen ergeben grössere Mehrverbräuche und ausserdem einen ziehenden Indikatorumschlag.

Mehrwertige Metallionen stören, entweder, weil sie mit den verwendeten Indikatoren reagieren, oder, weil sie mit dem Arsenat Fällungen ergeben können, und müssen daher vor der Titration, am besten durch Ionenaustausch oder extraktiv, aus der Probelösung entfernt werden.

Tabelle 1 enthält die Ergebnisse einer grossen Zahl von Titrationen, sowohl gegen PAR, als auch gegen SNAZOXs, ohne und mit Zusatz von störenden Ionen und von Fremdelektrolyt.

Aus den Titrationen von 0,15 bis 1,5 mg Arsen in reiner Lösung in einem Volumen von etwa 25 ml errechnet sich die Standardabweichung gemäss $s = \sqrt{\frac{\sum(\bar{x}_j - x_{ij})^2}{N - M}}$ zu $s = \pm 7,2 \mu\text{g As}$, entsprechend $\pm 13,4 \mu\text{g AsO}_4^{3-}$.

Der Vorteil des beschriebenen Verfahrens gegenüber den gebräuchlichen Redoxverfahren liegt vor allem in seiner Einfachheit, dem scharfen Endpunkt und in der titerbeständigen Bleimasslösung. Seine Anwendung ist auf Lösungen mit geringer bis

TABELLE 1.—TITRATION VON ARSENAT MIT 0,01 m BLEILÖSUNG

As, Gegeben, mg	Verbrauch korr. 0,0100 m Bleilösung, ml	As, Gefunden, mg	As, Differenz, µg	Zusatz	
0,150	0,34	0,153	+3		a
	0,37	0,166	+16		a
0,375	0,85	0,381	+6		a
	0,85	0,381	+6		a
0,749	1,68	0,755	+6		a
	1,65	0,742	-7		a
1,124	2,47	1,110	-14		a
	2,51	1,128	+4		a
1,498	3,33	1,496	-2		a
	3,32	1,492	-6		a
1,498	3,35	1,505	+7		b
	3,34	1,501	+3		b
	3,33	1,496	-2		b
	3,32	1,492	-6		b
	3,32	1,492	-6		b
	3,31	1,487	-11		b
	3,34	1,501	+3		b
	3,33	1,496	-2		b
0,749	1,67	0,750	+1		bd
	1,75	0,787	+38	1 mg SO ₄ ²⁻	bc
	1,81	0,814	+65	3 mg SO ₄ ²⁻	bc
	1,83	0,823	+74	5 mg SO ₄ ²⁻	bc
	1,68	0,757	+8	1 mg Cl ⁻	bd
	1,71	0,769	+20	3 mg Cl ⁻	bd
	1,73	0,780	+31	5 mg Cl ⁻	bd
	1,71	0,769	+20	1 mg Br ⁻	bd
	1,74	0,782	+33	5 mg Br ⁻	bc
	1,66	0,749	0	1 mg J ⁻	bd
	1,67	0,750	+1	5 mg J ⁻	bd
	1,72	0,773	+24	100 mg KNO ₃	ad
	1,74	0,782	+33	500 mg KNO ₃	ad
	1,75	0,786	+37	1.000 mg KNO ₃	ad
	1,83	0,823	+74	200 mg NaAc	ad

- a gegen PAR als Indikator
 b gegen SNAZOXS als Indikator
 c Mittel aus vier Einzelbestimmungen
 d Mittel aus fünf Einzelbestimmungen

mässiger Elektrolytkonzentration beschränkt. Im Vergleich zu bekannten fällungs-volumetrischen Verfahren erübrigt sich hier ein Zusatz von Alkohol oder Aceton.

Diese Methode wurde auf die Bestimmung von Arsen in organischen Substanzen im Anschluss an eine Schöniger-Verbrennung angewandt und erwies sich dabei als zeitsparend und einfach, und lieferte sehr gut reproduzierbare Ergebnisse.¹⁷

LÖSUNGEN UND REAGENZIEN

Bleimasslösung: 0,01 m, wird wie bereits beschrieben (6,17) aus Bleinitrat (p.A.) unter Zusatz von 1 ml konz. HNO₃ pro Liter bereitet. Der Faktor dieser Lösung wird mit 0,0100 m ÄDTA-Lösung gegen PAR oder Erio T bestimmt.

PAR-Lösung: 100 mg käuflicher Indikator (E. Merck, Darmstadt) werden in 100 ml bidestilliertem Wasser gelöst.

SNAZOXS-Lösung: 100 mg Indikatorpulver werden in 100 ml bidestilliertem Wasser gelöst.

Hexamethylentetramin, (p.A.)

Wasserstoffperoxid, 30% ig, (p.A.)

Als ArsenstammLösung wurde eine aus Arsenitoxid (p.A.) durch Lösen in NatriumhydroxidLösung hergestellte 0,0100 m ArsenitLösung verwendet.

ARBEITSVORSCHRIFT

Die 0,15 bis 1,5 mg As als Arsenit oder Arsenat enthaltende, annähernd neutrale Probelösung wird mit einem Tropfen 30% indem Wasserstoffperoxid versetzt und mit bidestilliertem (entkationisiertem) Wasser auf etwa 25 ml verdünnt. Man lässt etwa eine Minute sieden, fügt etwa 0,5 g festes Hexamethylentetramin zu, und titriert die siedendheiße Lösung nach Zusatz von zwei Tropfen Indikatorlösung mit 0,01 m Bleinitratlösung bis zum deutlichen, *bleibenden* Farbumschlag von Gelb nach Rot (PAR), bzw. von Rotorange nach Gelb (SNAZOXS). Vom abgelesenen Verbrauch muss die statistisch ermittelte Indikatorkorrektur abgezogen werden. Da käufliche Indikatorpräparate i.A. verschiedene Farbstoffanteile aufweisen, soll die Indikatorkorrektur für jede Indikatorlösung gesondert ermittelt werden.

Berechnung

$$\text{mg As} = (V - \bar{V}_B) \cdot 0,4495 \cdot f$$

V abgelesener Verbrauch in ml 0,01 m Bleilösung

\bar{V}_B mittlere Indikatorkorrektur

f Korrekturfaktor der Bleilösung gegen 0,0100 m ÄDTA

Summary—In hot aqueous medium buffered with hexamethylenetetramine 0.15–1.5 mg of arsenic may be titrated directly as arsenate, using a 0.01M solution of lead as titrant. PAR and 7-(sulpho-1-naphthylazo)-8-hydroxyquinoline sulphonic acid (SNAZOXS) are used as indicators. The standard deviation is 7.2 μg of arsenic.

Résumé—Des quantités d'arsenic de l'ordre de 0,15 à 1,5 mg sont dosées sous forme d'arséniate par une solution aqueuse de plomb à 0,01 M, chauffée et tamponnée au moyen d'hexaméthylénetétramine. On utilise comme indicateur le P.A.R. et l'acide (sulfo-4-naphtylazo-1)-7-hydroxy-8-quinoléine sulfonique (SNAZOXS). L'écart standard s'élève à 7,2 μg d'arsenic.

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THE DETERMINATION OF TERTIARY AMINES IN THE PRESENCE OF PRIMARY AND SECONDARY AMINES*

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Summary—Tertiary amines in the presence of primary and secondary amines can, in most cases, be determined after reaction of phenylisothiocyanate with the primary and secondary amine to form a derivative of thiourea. The unreacted tertiary amines are then titrated with anhydrous hydrogen chloride in methyl isobutyl ketone (MIBK). This method has been successful for all aliphatic primary and secondary amines, and for most aromatic amines. Of the secondary amines tested, *N*-*sec*-alkylanilines and sterically hindered *o*-substituted *N*-alkylanilines failed to react although, when there was *p*-substitution of the ring, all of the *N*-*sec*-alkylanilines examined did react. The primary and secondary amines are treated in MIBK with phenylisothiocyanate at room temperature, and the unreacted tertiary amines are titrated with anhydrous hydrogen chloride in MIBK. The bridge solution of the reference calomel electrode is lithium chloride-saturated MIBK. Duplicate determinations normally do not differ from the mean by more than 0.03 meq of tertiary amine nitrogen per g of sample. Twenty times as much primary and secondary amine nitrogen as tertiary amine nitrogen can be tolerated.

INTRODUCTION

PREPARATION of amines frequently results in a mixture which may contain ammonia as well as primary, secondary and tertiary amines. In the analysis of amine mixtures a general method for the determination of total tertiary amines is often required. Since the total basic nitrogen content of an amine mixture may be conveniently determined by non-aqueous titration using a titrant such as perchloric acid in acetic acid solvent, the general approach has been a preliminary reaction of the primary and secondary amines with a selective reagent, the product of which has negligible basicity. The tertiary amine may then be titrated without interference.¹



The standard laboratory procedure has employed acetic anhydride, which converts the primary and secondary amines to amides.³ A variety of titrants, of which perchloric acid in Methyl Cellosolve is excellent, have been used to conclude the determination.⁶ However, many primary and secondary amines do not react with acetic anhydride (Table I). This fact has been recognised by Hillenbrand and Pentz,² who recommended phenylisothiocyanate for difficultly acetylated amines. More recently Siggia has used phenylisothiocyanate to analyse amine mixtures by differential reaction rates.⁵

PRELIMINARY CONSIDERATIONS

Phenylisothiocyanate reacts with primary and secondary amines to form thioureas. The phenylisothiocyanate procedure employing alcoholic hydrochloric acid as a titrant² gave poor results for several amines, and therefore many reaction variables were examined with the goal of including within the scope of the method the maximum number of amine structures possible. Several conclusions were drawn:

* Presented at the 11th Anachem Conference, Detroit, Michigan, U.S.A., 21–23 October, 1963.

TABLE I.—SOME AMINES WHICH INTERFERED WITH THE ACETIC ANHYDRIDE METHOD FOR TERTIARY AMINES IN MIXTURES

No.	Amine identification	Tertiary nitrogen, mequiv/g	
		Theoretical	Found
1	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}$ <div style="display: flex; justify-content: space-around; margin-top: 10px;"> <div style="text-align: center;">  </div> <div style="text-align: center;">  </div> </div>	3.73	7.43 7.36
2*	$\begin{array}{ccccccc} & & \text{CH}_3 & & \text{CH}_3 & & \\ & & & & & & \\ \text{C}_6\text{H}_5 & -\text{NH} & -\text{CH} & -\text{CH}_2 & -\text{CH}_2 & -\text{CH} & -\text{CH}_3 \\ & & & & & & \\ & \text{NH} & -\text{CH} & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{CH}_3 \\ & & & & & & \\ & & \text{C}_2\text{H}_5 & & \text{CH}_3 & & \end{array}$	0.00	1.60 1.57
3*	$\begin{array}{ccc} \text{C}_6\text{H}_5 & -\text{NH} & -\text{CH} & -\text{CH}_3 \\ & & & \\ & & \text{CH}_3 & \end{array}$	0.00	2.85 2.83
4	$\begin{array}{ccc} \text{C}_6\text{H}_5 & -\text{NH} & -\text{CH} & -\text{CH}_2 & -\text{CH}_3 \\ & & & \\ & & \text{CH}_3 & \end{array}$	0.00	6.80 6.84
	$\text{NH} \left(\begin{array}{ccc} -\text{CH} & -\text{CH}_2 & -\text{CH} & -\text{CH}_3 \\ & & & \\ \text{CH}_3 & & \text{CH}_3 & \end{array} \right)_2$	0.00	5.38 5.36
5*†	$\text{NH} \left(\begin{array}{ccc} -\text{CH} & -\text{CH}_3 \\ & \\ \text{CH}_3 & \end{array} \right)_2$	0.00	7.73 8.00

* By the method of Ruch *et al.*,⁶ which we consider the best of the acetic anhydride methods, but inadequacy is apparent for the indicated amines.

† Tertiary amine nitrogen by the phenylisothiocyanate method was 0.18 mequiv/g average.

1. Alcoholic and acetic acid solvents are best avoided. During titration several thioureas tended to show a slow solvolysis reaction in these solvents, with the formation of titratable products.

2. Methyl isobutyl ketone (MIBK) may be employed as a solvent in the titrant or reaction without adverse effects.

3. *N*-*sec*-Alkylanilines (Table II, Nos. 2 and 6), but not *N*-*sec*-cyclohexylaniline (Table II, No. 19) and some *ortho*-substituted anilines (Table II, No. 1) are sterically hindered, and do not react quantitatively with either acetic anhydride or phenylisothiocyanate.

4. Although sterically hindered *N*-*sec*-alkylanilines tend to react more nearly quantitatively upon heating, several heat-sensitive secondary amines are adversely affected and heating in a general procedure is therefore not recommended (Table II, Nos. 14 and 15).

5. It may be possible to determine tertiary amines even in the presence of sterically

TABLE II.—SELECTED AMINES AND THEIR RESPONSE UNDER VARIOUS REACTION CONDITIONS USING HCl IN MIBK TITRANT AND LiCl IN MIBK SALT BRIDGE

No.	Compound identification	Tertiary nitrogen, meq/10g						GLC* analysis
		MIBK solvent at 24°		MIBK 2 hr hot		Added Basic N, meq/10g		
		Theory	Found	Found	Found	Theory	Found	
1.		0.0	3.05	1.91	3.01	3.11	98.9	
		—	2.69	1.76	—	3.14	—	
		—	1.65	2.50	—	—	—	
2.		0.0	0.30	0.16	9.09	9.04	96.2	
		—	0.32	0.16	—	9.00	—	
		—	0.34	0.19	—	—	—	
3.		0.0	0.22	—	10.4	10.3	97	
		—	0.17	—	—	10.4	—	
		—	0.20	—	—	—	—	
4.		6.10	6.25	—	6.10	5.97	98.2	
		—	6.20	—	6.10	5.96	—	
		—	6.25	—	—	—	—	
5.		0.00	7.19	5.63	7.35	7.36	99.3	
		—	7.26	5.58	—	7.37	—	
		—	7.12	—	—	—	—	
6.		5.65	5.67	—	5.65	5.71	99.6	
		—	5.67	—	—	5.71	—	
		—	5.66	—	—	—	—	

TABLE II (Contd.)

No.	Compound identification	Tertiary nitrogen, mequiv/g						GLC* analysis
		MIBK, 2 hr hot		Added Basic N, mequiv/g		Found	Wt.-%	
		Theory	Found	Theory	Found			
		MIBK solvent at 24°		Basic N, mequiv/g		Found	Wt.-%	
		Theory	Found	Theory	Found	Found	Wt.-%	
7.		0.00	1.78	4.35	—	6.71 6.73	6.59 6.60	— —
8.		0.00	0.11	—	—	6.71	6.59 6.60	— —
9.		0.00	0.16 0.14	—	—	6.65	5.62 5.60	— —
10.		0.00	0.13 0.13 0.13	—	—	5.41	5.39 5.34 5.36	99.6 — —
11.		2.29	2.29	—	—	6.87	6.64 6.64	98.1 —
12.		4.38	4.28	4.25 4.22	—	8.77	8.65 8.62	97.6 —
13.		0.0	0.04 0.03	0.07	—	13.9	13.7 13.7	— —

TABLE II (Contd.)

14.	$\left(\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}-\text{NH} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3/2 \end{array} \right)$	0-00	0-02	0-90	5-41	5-39	99-6
		—	0-08	0-97	—	5-34	—
		—	—	0-97	—	—	—
15.	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{S}$	3-73	3-79	4-91	7-46	7-42	—
		—	—	4-90	—	7-41	—
		—	3-74	4-92	—	—	—
16.	$\text{C}_6\text{H}_5-\text{NH}-\text{S}$	0-00	0-00	—	5-72	5-70	—
		—	0-01	—	5-82	5-76	—
17.	$\text{CH}_3-\text{CH}-\text{CH}_2-\text{C}=\text{N}-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_3$	(Schiff's Base)	2-72	—	5-44	5-21	98-3
	$\begin{array}{c} \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	—	2-75	—	—	5-18	—
		—	2-72	—	—	—	—
18.	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(-\text{CH}(\text{CH}_3)_2)_2$	8-69	8-49	—	8-69	8-71	95-2
	$\begin{array}{c} \\ \text{CH}(-\text{CH}_3)_2 \end{array}$	—	8-46	—	—	8-61	—
		—	8-50	—	—	—	—
19.	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$	4-80	4-75	—	9-60	9-43	—
	$\begin{array}{c} \\ \text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_3 \end{array}$	—	—	—	—	9-48	—
20.	$\text{C}_6\text{H}_5-\text{NH}-\text{CH}_2-\text{CH}_2\text{OH}$	0-00	0-02	0-02	7-30	7-15	—
		—	—	—	—	7-15	—
21.	$\text{C}_5\text{H}_5\text{N}$	12-64	12-59	—	—	—	—
		—	12-58	—	—	—	—

* Gas-liquid chromatography

hindered *N*-sec-alkylanilines in favourable cases. In such favourable cases the potentiometric titration of the mixture would result in two breaks, the first of which corresponds to the amount of tertiary amine present, and the second of which corresponds to the unreacted *N*-sec-alkylaniline. A known amount of tertiary amine should be added when *N*-sec-alkylanilines are present to mark the potentiometric break for tertiary amines.

TABLE III.—ANALYSIS OF AMINE MIXTURES USING PHENYLISOTHIOCYANATE

No.	Compounds present	Weight, g	Tertiary amines, <i>mequiv/g</i>	
			Theoretical	Found
1*	$\left(\begin{array}{c} \text{CH}_3-\text{CH}- \\ \\ \text{CH}_3 \end{array} \right)_3 \text{N}$	0.5221	6.49	6.49
2*	$(\text{C}_2\text{H}_5)_2\text{NH}$	0.5890	0.00	0.00
3*	$\left(\begin{array}{c} \text{CH}_3-\text{CH}- \\ \\ \text{CH}_3 \end{array} \right)_2 \text{NH}$	0.5123	0.00	0.04
4	$\left\{ \begin{array}{l} 1 \\ 2 \end{array} \right.$	$\left\{ \begin{array}{l} 0.2911 \\ 0.3397 \end{array} \right.$	2.99	2.97
5	$\left\{ \begin{array}{l} 1 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 0.4401 \\ 0.3495 \end{array} \right.$	4.02	3.96
6	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 0.2423 \\ 0.2541 \\ 0.4391 \end{array} \right.$	1.69	1.78
7	$\left\{ \begin{array}{l} 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 0.4570 \\ 0.2728 \end{array} \right.$	0.00	0.28†
8	$\left\{ \begin{array}{l} 1 \\ 2 \end{array} \right.$	$\left\{ \begin{array}{l} 0.3132 \\ 1.4622 \end{array} \right.$	1.14	1.15
9	$\left\{ \begin{array}{l} 1 \\ 2 \end{array} \right.$	$\left\{ \begin{array}{l} 0.3445 \\ 0.5261 \end{array} \right.$	2.57	2.59
10	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 0.3678 \\ 0.4718 \\ 0.5520 \end{array} \right.$	1.71	1.74

* 1: Purity by gas chromatography (GC) 96.2% with 3.1% tertiary amine;

2: Purity by GC 97.3% with 0.2% tertiary amine;

3: Purity by GC 95.8% with 1.3% tertiary amine.

† Found tertiary deviates from theory because of actual presence of tertiary in the mixture from the tertiary impurity in 3.

6. The ordinary calomel-glass electrode system with an aqueous potassium chloride salt bridge is unsatisfactory⁴ for these potentiometric titrations, because of drift-back of the emf recorder at and approaching the end-point. When the salt bridge is replaced with MIBK saturated with lithium chloride, this drift-back is negligible.

Although many other combinations of solvents, catalysts, electrode systems and temperatures were considered, the method which correctly dealt with the largest number of amine mixtures follows, and its use is shown in Table III.

EXPERIMENTAL

Apparatus

Beaker: 250-ml, tall-form.

Electrodes: glass-calomel with MIBK saturated with lithium chloride as a bridge solution.

Potentiometric recording titrator: a Metrohm Potentiograph Model 336, available from Brinkmann, Great Neck, N.Y., U.S.A., or equivalent apparatus.

Reagents

Anhydrous hydrochloric acid in methyl isobutyl ketone: 0.2*N*: Pass dry hydrogen chloride into 200 ml of MIBK until the latter is saturated. Pour into an open beaker (in a hood), and allow to stand overnight. Titrate to determine the approximate normality of this solution and dilute with MIBK to prepare an approximately 0.2*N* solution. Determine the exact normality of this solution by titrating 0.3000 g of tris(hydroxymethyl)aminomethane (reference grade) dissolved in 100 ml of glacial acetic acid. Despite formation of a precipitate during this titration, the repeatability of duplicate titrations should not differ by more than 1 part in 500. (Perchloric acid in MIBK also has been used and is preferred where stronger acid is required.)

Methyl isobutyl ketone

Phenylisothiocyanate: Eastman Kodak, White Label.

Procedure

Weigh a sample containing approximately 5 mequiv of tertiary amine into a 250-ml tall-form titration beaker. Add 10 ml of phenylisothiocyanate, 100 ml of MIBK, and heat gently until the sample dissolves. (Do not boil—some amines decompose or are volatile.) Let stand for 2 hr at ambient temperature ($24 \pm 4^\circ$). Titrate with 0.2*N* hydrochloric acid in MIBK, making sure that the delivery tip of the titrator is below the solvent level in the titration beaker to avoid loss of hydrogen chloride by fuming.

Note: The reagent should be handled carefully in a hood to avoid unnecessary contact and breathing of vapours. Undue exposure of the reagent to atmospheric moisture should also be avoided.

CONCLUSIONS

Frequently it is not possible to know whether the amine mixture presented for tertiary amine determination will respond to the acetic anhydride method of preliminary treatment for primary and secondary amines which are weakly basic. Although phenylisothiocyanate does not react under the test conditions with most *N*-sec-alkylanilines, with sterically hindered *o*-substituted *N*-alkylaniline, nor with some Schiff's bases or amines too weak to be titrated with anhydrous hydrochloric acid in MIBK (Table II), it does react with a much larger group of primary and secondary amines more successfully than does acetic anhydride. With reasonable precautions, phenylisothiocyanate presents no handling difficulties when used as an analytical reagent. Duplicate determinations using 0.2*N* titrant do not normally differ from the mean by more than 0.03 mequiv of tertiary amine nitrogen for the range of 0.03–0.7 mequiv of tertiary amine nitrogen. Accuracy is dependent on quantitative blocking, which is normally the case except as indicated above. Using 5-g samples and 0.02*N* titrant, as little as 0.005% of tertiary amine nitrogen can be determined. Twenty times as much primary and secondary amine nitrogen as tertiary amine and 0.02*N* titrant, as little as 0.005% tertiary amine nitrogen can be determined. Twenty times as much primary and secondary amine nitrogen as tertiary amine nitrogen can be tolerated.

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Zusammenfassung—Tertiäre Amine können in Gegenwart primärer und sekundärer Amine nach Reaktion der primären und sekundären Amine mit Phenylsenföls zu Thioharnstoffderivaten meistens bestimmt werden. Sie werden mit wasserfreier HCl in Methylisobutylketon (MIBK) titriert. Die Methode war bei allen aliphatischen und den meisten aromatischen primären und sekundären Aminen erfolgreich. N-sec-Alkylaniline und sterisch gehinderte o-substituierte N-Alkylaniline reagierten nicht, dagegen reagierten alle untersuchten *p*-substituierten N-sec-Alkylaniline. Die primären und sekundären Amine werden in MIBK mit Phenylsenföls behandelt, dann werden die nicht umgesetzten tertiären Amine mit wasserfreier HCl in MIBK titriert. Die Brücke zur Kalomel-Vergleichselektrode wird mit LiCl-gesättigtem MIBK beschickt. Doppelbestimmungen weichen im allgemeinen vom Mittelwert nicht mehr als um 0,03 Milliäquivalente tertiären Aminstickstoff pro g Probe ab. Die zwanzigfache Menge prim- und sec-Aminstickstoff ist daneben zulässig.

Résumé—Les amines tertiaires en présence d'amines primaires et secondaires peuvent être dosées dans la plupart des cas, après réaction de l'isothiocyanate de phényle avec les amines primaires et secondaires qui forment un dérivé de la thiourée. Les amines tertiaires n'ayant pas réagi sont ensuite titrées par l'acide chlorhydrique anhydre dans la méthyl-isobutyl-cétone. Cette méthode a pu être appliquée avec succès à toutes les amines primaires et secondaires aliphatiques, et à de nombreuses amines aromatiques. Parmi les amines secondaires contrôlées, les N-sec-alcoylanilines et les N-alcoylanilines o-substituées ne donnent pas la réaction; cependant les N-sec-alcoylanilines *p*-substituées réagissent. Ce traitement des amines primaires et secondaires par l'isothiocyanate de phényle dans la méthyl-isobutyl-cétone s'effectue à température ordinaire, et les amines tertiaires n'ayant pas réagi sont titrées par de l'acide chlorhydrique anhydre également en solution dans la méthyl-isobutyl-cétone. L'électrolyte de l'électrode de référence au calomel est constitué par une solution saturée de chlorure de lithium dans la méthyl-isobutyl-cétone. Les dosages en double ne diffèrent pas normalement de la moyenne par plus de 0,03 mg d'azote d'amine tertiaire par g d'échantillon. Un taux d'azote contenu dans les amines primaires et secondaires de l'ordre de vingt fois celui de l'azote de l'amine tertiaire, ne gêne pas le dosage.

THE RECOVERY OF RHODIUM, IRIDIUM, PALLADIUM AND PLATINUM FROM ORES AND CONCENTRATES BY WET ASSAY AND A COMPARISON WITH RECOVERY BY FIRE ASSAYS

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Summary—A wet method for recovering micro amounts of rhodium, iridium, palladium and platinum from ores and concentrates is reported. It involves stepwise dissolution of the roasted sulphide concentrate. The calcined material is leached with *aqua regia* or with concentrated hydrochloric acid followed by *aqua regia*. The leached residue is chlorinated, silicon is volatilised as silicon tetrafluoride from the chlorinated residue, and the final residue is fused with sodium peroxide. From the resulting solution the base metals are removed by a cation-exchange technique. A chromatographic method followed by solvent-extraction procedures is used to separate the above four platinum metals from the effluent from the small cation exchanger. The efficiency of the method is compared with that of both the copper-nickel-iron and the classical (lead) fusion methods, applied to the same ore and concentrate.

INTRODUCTION

THE platinum metals are found in nature in the metallic state as inter-platinum metal alloys or alloyed with gold, iron, copper and sometimes with nickel and cobalt. They are also found as compounds with arsenic, antimony, sulphur and possibly selenium. The platinum metal compounds are associated with copper, nickel and iron sulphide ores. In the ores of the Sudbury district, Ontario, Canada, the total content of the platinum metals is of the order of 0.5 ppm.¹

The recovery of the platinum metals from ores and certain concentrates involves two steps: a concentration of the metals in either a solid or aqueous medium followed by wet separations of the precious metals.

The available methods of extraction from ores and the subsequent separational techniques have been discussed in a recent review.²

In addition to the classical method by which the noble metals are collected in a fused lead alloy, two recent methods have been proposed. In one the collection is made by reducing the natural base-metal content of the ores to form a collecting alloy of iron, copper and nickel. In the second method, collection is made by a fused tin alloy, in which case tin is an additive constituent. The acceptance of the lead fusion method for the platinum metals was based initially upon its success for gold and silver and not on direct experimental results. Nevertheless, one must accept as a fact that the classical methods have, in general, predicted with reasonable accuracy the recoveries attained by commercial methods. Recently, the efficiency of the classical lead assay for each of the six platinum metals has been examined experimentally.³⁻⁸ Evidence was presented to indicate that the lead assay, applied under

optimum conditions, provided quantitative extraction of platinum, palladium and rhodium. Even in these favourable applications it became evident that a re-assay of the slag was generally advisable. It is a surprising fact that the procedural texts dealing with fire assaying seldom direct the re-assay of slags, with the obvious inference that a single extraction by the fused lead is sufficient to extract the noble metals quantitatively. This technique is analogous to failure to wash the wall of a beaker free of precipitate during the filtration of a solution to be analysed, or failure to provide for a second extraction in the quantitative application of immiscible solvents.

In the case of the more resistant platinum metals, *e.g.*, iridium and ruthenium, the recovery by lead is adversely affected through their relative insolubility in lead alloys. In the case of iridium the collective mechanism is largely associated with the high density of the metal, resulting in a non-homogeneous metal phase. Thus one may expect some degree of ineffective collection.

Methods of assay based on more acceptable principles are obviously required. Because iron, copper and nickel were common associates of the platinum metals it was hoped that these base metals might be used as collectors. In a series of papers⁹⁻¹⁶ it was made evident that these base metals could indeed be used as quantitative collectors for even microgram amounts of noble metals present in an assay ton of ore or concentrate. In principle, the natural base-metal content could be used for collecting, or, in the absence of a sufficient amount, iron, copper and nickel oxides could be added to provide the optimum weight of alloy.

Clearly, it was desirable to compare the efficiency of the two assay methods as applied to a natural ore or concentrate. However, a comparison of this type is open to the suspicion that such assay procedures, requiring as they do a fortuitous juxtaposition of the collector and noble metal, might each fail to effect a quantitative collection. Thus, to meet this possibility, it was necessary to devise a complete wet procedure which would ensure the conversion of the noble metal minerals to a dissolved constituent known to be amenable to the most effective wet procedures.

Toward this end the present research includes results provided by the classical fire assay; by the iron-copper-nickel collection; and by a complete wet procedure. The noble metals used were rhodium, iridium, palladium and platinum. Osmium and ruthenium were omitted, partly because the problem was sufficiently difficult in their absence, and partly because of the reasonable certainty that methods for their determination could be integrated into the proposed scheme.

In the present investigation, the calcined natural sulphide concentrate was brought into solution by a stepwise dissolution. Either *aqua regia* or hydrochloric acid followed by *aqua regia* were used as primary leaching reagents. Complete dissolution was accomplished by chlorinating the leached residue, volatilising silicon as silicon tetrafluoride from the chlorinated residue, and fusing the remaining residue with sodium peroxide. After a cation-exchange removal of the base metals from the resulting solution, a chromatographic method followed by solvent-extraction techniques was used to separate the platinum metals in the effluent.

EXPERIMENTAL

Apparatus and reagents

The apparatus and reagents have been described previously.^{16,17}

Methyl isobutyl ketone: Fisher Certified Reagent (Fisher Scientific Co.).

Unless otherwise specified, all other chemicals were of reagent grade.

Assay crucibles, 30-g, were supplied by the A.P. Green Fire Brick Co. Ltd., Toronto, Canada.

Sulphide concentrate was obtained from Falconbridge Nickel Mines Ltd., Richvale, Ontario, and was made from ores of the Sudbury district of Ontario, Canada. The percentages of the main constituents were: iron 40.70, copper 5.20, nickel 6.14, sulphur 34.00, silica 5.10, lime 2.0, alumina 4.5, and magnesia 2.0.

Standard solutions

Rhodium: The rhodium solution was standardised gravimetrically with thiobarbituric acid¹⁸ and was found to contain 0.504 mg of rhodium per ml.

Iridium: The iridium solution was standardised gravimetrically with 2-mercaptobenzothiazole¹⁹ and was found to contain 0.732 mg of iridium per ml.

Palladium: Spectrographically pure palladium wire was dissolved in *aqua regia*, and was then converted to chloride by successive treatments with concentrated hydrochloric acid. The solution was filtered, made up to 1 litre with water containing 10 ml of concentrated hydrochloric acid, and standardised gravimetrically with the sodium salt of dimethylglyoxime. The palladium solution was found to contain 0.506 mg of palladium per ml.

Platinum: A standard solution was similarly prepared by dissolving spectrographically pure platinum wire. The platinum solution was standardised gravimetrically with benzenethiol¹⁸ and was found to contain 0.608 mg of platinum per ml.

Multicomponent precious metals standard solution: Aliquots of the above standard precious metals solutions were placed in a 1-litre flask and diluted to the mark with 20 ml of concentrated hydrochloric acid and water. The solution contained 5.0, 3.7, 5.0 and 9.1 μg of rhodium, iridium, palladium and platinum, respectively, per ml.

Analysis of Sulphide Concentrate for Rhodium, Iridium, Palladium and Platinum

A. Wet extraction

In general, platinum metal concentrates will contain sulphides. Thus, wet oxidising treatments produce sulphates which introduce an interference in many of the wet methods of separation and determination. Air oxidation removes most of the sulphur, and in those instances where the determination of osmium and ruthenium is not a requirement this method is simple and effective. Where osmium and ruthenium are to be determined, sulphur may be removed as hydrogen sulphide by roasting in hydrogen. This process will be the subject of a later paper. The calcine resulting from roasting in air contains constituents which are not quantitatively corroded by any single acid. Therefore stepwise leaching of the calcine with a mixture of the leaching reagents was necessary. Because of the restrictions imposed by the methods^{20,17,21} to be used for the analysis of the solution, a choice of the leaching reagents had to be made. Chloride solutions could be most conveniently obtained by using either hydrochloric acid or its mixture with nitric acid as leaching reagents. Hydrochloric acid leaching before that with *aqua regia* offered the following advantages:

- (1) There is no vigorous reaction which might involve losses.
- (2) The bulk of the metal present in the sample would be converted to the desired chloride form without additional treatment of the solution.
- (3) The leached residue would contain only small amounts of metals, which are readily converted to the chloride form.

The method applied for the dissolution of the sulphide concentrate and for the recovery of the four platinum metals is described below.

Procedure 1: Sixty g of the sulphide concentrate were placed in a 6-inch porcelain dish and roasted in the assay furnace at 980° for 2 hr with frequent stirring by means of an iron rod. To minimise losses of the sample which adhered to the iron rod after each stirring, the iron rod was gently touched on the inside surface of the dish after stirring. The cooled calcine weighing about 48.3 g was placed in a 400-ml beaker and leached as follows:

Sixty ml of *aqua regia* diluted to 90 ml with water were added to the sample in a 400-ml beaker covered with a watch glass and containing a glass stirring rod for frequent stirring of the mixture. The mixture was heated for 16 hr on a steam bath and diluted with 125 ml of water, and the residue was allowed to settle. The supernatant liquid was filtered into a 600-ml beaker using Whatman No. 42, 11-cm filter paper. The residue in the original beaker was leached once more as above. Two more leachings were made with 100 ml of undiluted *aqua regia*. All of the above filtrations were made through the original filter paper, and the filtrates and washings were received by the same 600-ml beaker. This was made possible by partially evaporating the filtrate from each leaching. After the fourth leaching, the residue in the beaker was washed with 3.0 ml of hydrochloric acid, and was then transferred to the filter paper. The filtrate in the 600-ml beaker was evaporated to 150 ml on a steam bath, and was treated successively with concentrated hydrochloric acid to remove the oxides of

nitrogen completely. After each addition of the acid the beaker was tightly covered with a watch glass until reaction ceased. Evaporation was continued with the watch glass raised by glass hooks. Five or six 125-ml portions of concentrated hydrochloric acid were found to be adequate for the removal of the nitrogen oxides and for the conversion of the metals to a chloride form. The solution was evaporated to 100 ml (solution A) and set aside to be used later as described below. The filter paper and the leached residue, when dry, were placed in a porcelain crucible and ignited in an electric oven at 550° for 30 min. The amount of concentrate remaining undissolved by the above treatment was 4.0 g or less. The residue was mixed well with 1.0–1.5 g of 200-mesh graphite, and was then placed in a porcelain boat and subjected to dry chlorination at 650–700° for 6–7 hr.¹⁵ Any residue deposited on the inside surface of the chlorination tube was readily leached with concentrated hydrochloric acid. The leached solution from the boat, *etc.*, was added to a 400-ml beaker, and the solution was evaporated, cooled, diluted with water and finally filtered through a 9-cm glass fibre filter to give a residue B and a filtrate B. The filtrate B was set aside to be combined with the filtrate from C and D and solution A.

The residue B in the glass filter was placed in a 50-ml polyethylene beaker and treated three times with hydrofluoric acid, heating to dryness each time on a steam bath. The residue was transferred to a 150-ml beaker by means of 3.0M hydrochloric acid, and was treated several times with concentrated hydrochloric acid to convert the fluorides to chlorides. The solution was diluted with water and filtered through a Whatman No. 42, 7-cm filter paper, thus obtaining a residue C and a filtrate C. The filter paper with the residue C was ignited, reduced in hydrogen at 550° for 45 min, and chlorinated in the presence of sodium chloride.¹⁵ The chlorinated residue was leached with hydrochloric acid and the resulting solution was filtered through a 5-cm glass fibre filter to provide a filtrate D, the residue being discarded.

The filtrates B, C and D were combined with solution A, and the resulting solution was evaporated on a steam bath to incipient dryness. The subsequent treatment of the evaporated residue, and the method of removing base metals by cation-exchange have been described.¹⁵ The separation and determination of the four metals in the effluent were made according to the method described below. The results are recorded in Table I, Samples No. 1–5.

TABLE I.—ANALYSIS OF SULPHIDE CONCENTRATE FOR RHODIUM, IRIIDIUM, PALLADIUM AND PLATINUM BY WET METHOD

Procedure	Sample no.	Rhodium,		Iridium,		Palladium,		Platinum,	
		ppm	oz/ton	ppm	oz/ton	ppm	oz/ton	ppm	oz/ton
1	1	0.184	0.0054	0.017	0.0005	0.517	0.0151	0.867	0.0253
1	2	0.164	0.0048	0.067	0.0020	0.507	0.0148	1.083	0.0317
1	3	0.167	0.0049	0.064	0.0019	0.500	0.0146	0.904	0.0264
1	4	0.134	0.0039	0.067	0.0020	0.467	0.0136	0.923	0.0270
1	5	0.134	0.0039	0.074	0.0022	0.487	0.0142	1.066	0.0312
2	6	0.154	0.0045	0.084	0.0025	0.567	0.0166	0.954	0.0279
2	7	0.140	0.0041	0.090	0.0026	0.500	0.0146	1.040	0.0304
2	8	0.117	0.0034	0.050	0.0015	0.554	0.0162	0.870	0.0254
2	9	0.100	0.0029	0.050	0.0015	0.580	0.0169	0.940	0.0275

Procedure 2: Thirty g of the sulphide concentrate were roasted to give a calcine of about 24 g. The subsequent procedure was similar to the above but with the following modifications:

(a) The cooled calcine was leached with concentrated hydrochloric acid, three times, using 100 ml of the acid each time; and then was leached once with 60 ml of *aqua regia*.

(b) The leaching residue, weighing about 2 g, was reduced in hydrogen and chlorinated in the presence of sodium chloride.¹⁵

(c) The residue from the hydrofluoric acid treatment was fused with sodium peroxide in a nickel crucible.²²

Results are listed in Table I, Samples No. 6–9. The leaching procedure is illustrated in Fig. 1.

Observations

Constituents of the complex solution of the concentrate, or of the iron-copper-nickel button, obtained as previously described,¹⁵ introduced difficulties after the partial evaporation of the effluent. When the solution was reduced to a few drops, a persistent green colour developed. Repeated passage through the exchanger failed to remove the colour. Addition of hydrochloric acid resulted in the development of a yellow colour. Addition of the green solution to the chromatographic

paper, and subsequent development, resulted in a persistent green colour superimposed on the rhodium-iridium band but above the palladium band.

It was evident that metals present in the concentrate were either not converted to cationic species during the dissolution of the sample, or were converted to a cationic form not adsorbed by the cationic exchanger under the conditions applied above for the removal of the base metals. Kember and Wells,³⁰ dealing with the position of metals on strips developed with hexone-pentanol-hydrochloric acid solvent systems, reported that certain transition metals (chromium, hafnium, thorium, titanium, zirconium, vanadium, *etc.*) should be found along with the rhodium and iridium band and well above that of palladium. Interference from these elements in the recovery and determination

WET METHOD

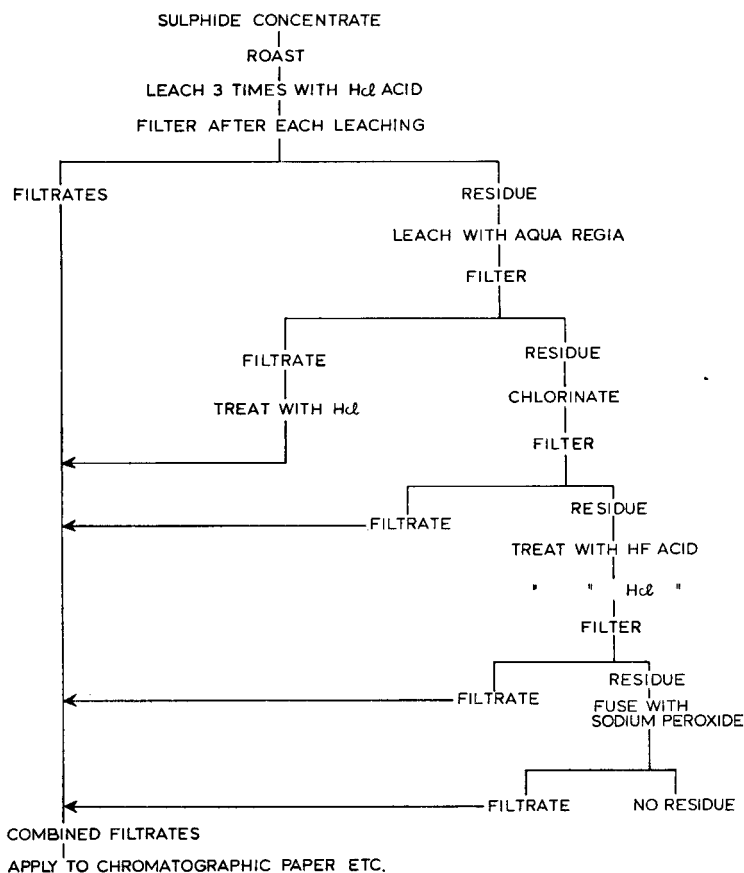


FIG. 1

of rhodium and iridium was eliminated, during the course of recovering the latter metals, by reduction and chlorination of the ignited Rh-Ir section of the chromatographic paper. These transition metals were converted to a black-green insoluble mass which strongly adhered to the bottom of the chlorination crucible.

Dissolution of the chlorinated residue resulted in a solution free from the green colour.

The effect of the presence of the transition metals on the movement of palladium and platinum on the chromatographic paper during the development of the strip was found to be negligible, since neither palladium nor platinum was found associated with the rhodium and iridium bands.

Losses of the platinum metals to the exchanger were investigated by salting sample solutions with aliquots of the multicomponent precious metals solution before feeding to the exchanger. These losses were found to be insignificant.

*Chromatographic Separation of Rhodium, Iridium, Palladium
and Platinum in Standard Solutions*

The most acceptable methods yet proposed for separating microgram quantities of the platinum metals (excluding ruthenium and osmium) can be classified as follows:

- (1) Precipitation of metals.²³
- (2) Solvent extraction.^{24,25}
- (3) Ion exchange.²⁶
- (4) Chromatography.²⁰

Although all of these methods were potentially applicable, the chromatographic method was preferred because of simplicity of technique, time required and the accuracy obtained.

The method of Kember and Wells²⁰ was used with some modification. It became evident that the amount of sodium chlorate recommended was sufficient to overcome the combined reducing action of both paper and solvent, and thus some iridium was found entrained in the palladium band. This difficulty was avoided by substituting sodium chloride for the sodium chlorate solution, although the former encourages the formation of a double band with platinum. In this case iridium was fixed quantitatively with rhodium. Diffusion by the platinum was observed, and to ensure quantitative recovery of the platinum, both palladium and platinum sections were combined; subsequently, palladium was separated from platinum by the *p*-nitrosodimethylaniline method.²¹ Results presented in Table II proved the efficiency of the above extension of the Kember-Wells method,²⁰ which allowed the determination of iridium with only one chromatographic operation. The method used is recorded below.

TABLE II.—SEPARATION OF RHODIUM, IRIIDIUM, PALLADIUM AND PLATINUM
BY PAPER CHROMATOGRAPHY

Added				Recovered			
Rhodium, <i>μg</i>	Iridium, <i>μg</i>	Palladium, <i>μg</i>	Platinum, <i>μg</i>	Rhodium, <i>μg</i>	Iridium, <i>μg</i>	Palladium, <i>μg</i>	Platinum, <i>μg</i>
25.0	18.4	25.0	45.5	24.2	17.1	23.0	44.0
				24.0	17.6	*	*
				24.2	19.4	23.5	46.0
				23.8	18.4	23.5	46.0
				24.2	17.9	24.0	46.5
				24.0	17.9	24.0	46.0
				25.8	19.4	23.5	46.0
				23.5	17.4	23.0	47.0
				24.8	17.2	23.0	47.0
				26.0	16.8	23.5	46.5
			Average, <i>μg</i>	24.5	17.9	23.5	46.1
			Deviation, <i>μg</i>	±1.0	±1.1	±0.5	±1.0
			Error, <i>μg</i>	-0.5	-0.5	-1.5	+0.6

* These samples were destroyed during the analysis.

Procedure: Five ml of the multicomponent precious metals standard solution containing 25.0, 18.4, 25.0 and 45.5 *μg* of rhodium, iridium, palladium and platinum, respectively, were placed in a 00 Coors 10-ml capacity porcelain crucible, wide form, and evaporated carefully to 1 or 2 drops under a 250-watt infrared heat lamp. To the cooled sample 1 drop of concentrated hydrochloric acid was added, and the mixture was then swirled to mix and to dissolve any residue formed on the wall of the crucible during the evaporation of the solution. The sample was applied by means of a glass dropper, elongated to an almost capillary end, to a line drawn 5.8 cm from one end of a strip of Whatman No. 3 MM chromatographic paper, 40 cm in length. Small amounts of the sample were applied at a time, with the short dimension of the paper held vertically, drying the paper between each application with the aid of an infrared heat lamp placed at a distance of 60–70 cm. By holding the paper in a vertical position with its long dimension horizontal, sagging of the wet paper, and breaking under its own weight, were avoided. By this method one could apply eight samples to papers held in a rack.

The crucible and dropper were washed three times with 2 drops of a 1% sodium chloride solution used each time, and the washings were applied to the above line. The band was kept as narrow as possible, approximately 1.5 cm in width. A jar 14.5 cm in diameter and 46 cm high accommodated

four paper strips dipped into two 15-ml porcelain boats, glazed inside, each containing a 60:30:10 isobutyl ketone-concentrated hydrochloric acid-isopentyl (isoamyl) alcohol mixture. The papers were held by glass strips at a point 2.5 cm from the end of the paper, the latter dipping into the above solvent mixture contained in the porcelain boat. 20 ml of the solvent mixture were placed at the bottom of the jar to aid saturation of the atmosphere with solvent vapour. Separations by downward diffusion were carried out at about 24°, and chromatograms were developed for 14 hr. During this time the solvent front reached within 2.5–3 cm of the bottom of the strip. The lid of the jar supporting the papers was removed and placed in a dust-free atmosphere. Excess solvent was removed from the boats with Kleenex paper. To ascertain the location of the bands, the control strip was set aside on a track, and after 15 min was sprayed downward with 1.0M tin^{II} chloride in 3.5M hydrochloric acid solution. The positions of the metals were given by the usual colours and in the following order: rhodium together with iridium, yellow-orange; palladium, brown; platinum, yellow. The two bands of rhodium and iridium were close to each other, but were well separated from the palladium band. Each of the remaining strips, having been dried in a dust-free atmosphere for 20–25 min, was cut in two sections at a point between the rhodium-iridium and palladium band. Thus one section contained rhodium together with iridium, and the other contained palladium together with platinum. The control strip, developed as described above, served as a guide to determine the point at which each of the remaining strips was to be cut. The cut was made at a distance of 1 cm beyond the furthest detected position of the palladium. Care was exercised in handling the strips since these were fragile and became increasingly brittle as the solvent evaporated. The R_T and R_L values obtained are listed in Table III.

TABLE III.—POSITION OF THE METALS ON THE STRIPS

Metal	Amount, μg	R_T	R_L
Rh + Ir (1st band)	Rh: 25.0	3	
Rh + Ir (2nd band)	Ir: 18.4		13
Pd	25.0	37	51
Pt	45.5	63	80

Recovery and separation of palladium from platinum

The strip containing the palladium and platinum was grasped by the undeveloped lower end, and the developed end was lowered into a 30-ml beaker, where it was broken up into small pieces with the end of a glass stirring rod. The strip was then cut below the undeveloped portion at a point 2.0–2.5 cm from the leading front of the solvent, and this piece, containing the undeveloped portion of the strip together with part of the developed portion, was discarded. This was done to remove any gold present in the ore from the palladium-platinum section. Previous work indicated the relative position of the gold deposit. The glass rod was wiped clean with a small piece of filter paper, which was placed in the beaker containing the palladium-platinum chromatograph, and the organic matter was ignited overnight by placing the beaker in an electric oven at 400–450°. The cooled ash was treated with *aqua regia*, and palladium with platinum were then converted to chlorides with concentrated hydrochloric acid by heating on a steam bath in the usual manner. The cool beaker and watch glass were washed with 5 ml of acidulated water adjusted to pH 2–3 by hydrochloric acid. After 5 min the solution was transferred to a 75-ml pear-shaped separatory funnel, and the volume of the solution was brought up to 10 ml with the acidulated water. Palladium was then separated from platinum by extracting the palladium-*p*-nitrosodimethylaniline red species with chloroform.²¹

Determination of palladium

The chloroform extracts, in a 30-ml beaker, were evaporated to near dryness by placing the beaker upon a glass on a steam bath. Complete evaporation directly on the steam bath resulted in creeping of the organic matter. The remaining solution was evaporated to dryness by allowing it to stand at room temperature. After the removal of the organic matter with fuming nitric acid and 30% hydrogen peroxide, and conversion of the metal to a chloride form with concentrated hydrochloric acid, palladium was determined spectrophotometrically according to the method of Yoe and Kirkland²¹ using 1-cm matched silica cells. The results have been listed in Table II.

Determination of platinum

The aqueous phase of the palladium extraction with chloroform was drained into a 50-ml

calibrated volumetric flask containing 1 ml of the concentrated sodium acetate-hydrochloric acid buffer solution, and 0.7 ml of the 0.5% *p*-nitrosodimethylaniline reagent. The separatory funnel was rinsed twice with 3 ml of 95% ethanol and the washings were combined with the aqueous phase in the volumetric flask, taking care to wash the neck of the flask. The colour was developed by placing the flask in a water bath heated at $85 \pm 2^\circ$ on a hot plate for 1 hr. The flask was air cooled for 5 min, and was then cooled with tap water. The volume of the solution was brought up to the mark with 95% ethanol, and platinum was determined immediately at 525 $m\mu$ using 1-cm silica cells.²⁷ Results have been listed in Table II.

Recovery of rhodium and iridium

The rhodium-iridium section was placed on a Kleenex paper of appropriate size. The paper strip was cut at the points adjacent to the strip supports. The remaining section containing the rhodium and iridium metals was wrapped with the Kleenex paper, rolled and placed in an A2, medium-porosity, porcelain crucible (or in a 0000 Coors porcelain crucible); which was placed in a larger crucible. This protection was necessary in order to avoid losses resulting from the fragility of the paper. The papers were ignited by heating overnight at 400–450°. The cooled ash was reduced in hydrogen at 500–550° for 45 min, and was then subjected to dry chlorination in the presence of sodium chloride.¹⁵ The chlorination product was leached with 1.0M hydrochloric acid. The leached solution, together with the washings from the chlorination crucible, were added to a 250-ml beaker, and the solution was evaporated, cooled, diluted with water, and finally filtered through the same A2 porcelain crucible, applying mild suction. The filtrate was evaporated somewhat, and was then transferred to a 30-ml beaker where it was evaporated to dryness on a steam bath.

Separation and determination of rhodium and iridium

A drop or two of redistilled hydrobromic acid were added to the above residue, and the mixture was dissolved with water. Rhodium was separated from iridium by solvent extraction, and each metal was determined spectrophotometrically; rhodium in the organic phase and iridium in the aqueous phase, as described previously.¹⁷ Results have been listed in Table II.

Classical Assay

The approach to the lead fusion method for the determination of the four platinum metals in ores and concentrates required some consideration of the optimum flux composition. In a series of investigations^{4,7,8} it has been shown that the collection of rhodium, palladium and platinum is relatively effective in a slightly basic slag, and that iridium⁵ is best collected in a near neutral or slightly acid slag. The acidity of the slag (silicate degree) is expressed in terms of ratio of acid oxygens to basic oxygens. Thus an acid slag would be represented by $\text{Na}_2\text{O}\cdot\text{SiO}_2$ and a basic slag by $3\text{Na}_2\text{O}\cdot\text{SiO}_2$. The calculations of the required composition of the flux must include the acid and basic oxygens associated in the ore or concentrate; this information is obtained by any suitable method of analysis. Investigations^{5,28} revealed also that nitre assays produced recoveries comparable to those obtained by the normal fusions, and these are sometimes preferred when prior roasting to remove sulphur increased the possibility of mechanical losses. The amount of nitrate required for a 40-g button was determined experimentally through ascertaining the reducing power of the ore and the nitrate-lead equivalent.

For the basic fusion the following flux constituents were used: sodium carbonate, 35.0 g, litharge, 170.0 g, potassium nitrate 45.0 g, and silica, 19.5 g. In addition, 5 mg of silver powder and sufficient litharge to produce the 40-g button were added. 30 g of concentrate, ground to pass a 45-mesh screen, were thoroughly mixed with the above flux, transferred to an assay-ton clay pot, and fused at 1000–1150°.

The acid slag consisted of 35.0 g of sodium carbonate, 148.0 g of litharge, 40 g of potassium nitrate and 65 g of silica.

Reduction of button weight and the cleaning process were accomplished by scorification. Two lead buttons were transferred to the scorifier and heated at 900° for an appropriate time. The scorified button, weighing 30–35 g, was cupelled by heating to normal cupellation temperatures. The cupels were preheated to 900° for 15 min before use. The silver-platinum metals bead (about 10 mg) was analysed as described below in the analysis of the standard silver beads. Results are listed in Table IV.

It was necessary also to develop a reliable method for the analysis of a silver bead which included iridium in its composition. Although collection by silver and subsequent wet treatments are acceptable techniques in the case of gold, platinum and palladium, the fact that the more insoluble platinum metals, particularly iridium, do not form homogeneous alloys vitiates the efficiency of the classical silver collection and its subsequent wet treatment.

TABLE IV.—ANALYSIS OF SULPHIDE CONCENTRATE FOR RHODIUM, IRIDIUM, PALLADIUM AND PLATINUM BY LEAD FUSION

Sample no.	Rhodium,		Iridium,		Palladium,		Platinum,	
	ppm	oz/ton	ppm	oz/ton	ppm	oz/ton	ppm	oz/ton
(I) Basic Slag (~0.5 S.D.*)								
1	0.124	0.0036	0.021	0.0006	0.477	0.0139	0.816	0.0239
2	0.107	0.0031	0.013	0.0004	0.477	0.0139	0.833	0.0244
3	0.100	0.0029	0.026	0.0008	0.503	0.0147	0.735	0.0215
(II) Acidic Slag (~1.5 S.D.)								
1	0.037	0.0011	0.025	0.0007	0.553	0.0162	0.735	0.0215
2	0.034	0.0010	0.022	0.0007	0.577	0.0169	0.810	0.0237
3	0.037	0.0011	0.037	0.0011	0.563	0.0165	0.766	0.0224

* S.D., or silicate degree, is the ratio of the number of acid oxygens to basic oxygens.

A modified nitric acid parting method was developed, and was proved by application to standard solutions of the four platinum metals.

Standard silver beads

Five ml of the standard solution containing the four metals were added to a lead boat constructed from a 4 × 5-inch rectangular sheet of lead foil, 0.004 inch thick. The solution was evaporated to dryness in a steam cabinet, pure silver powder (10 mg) was added, and the boat was folded into a ball and wrapped with a 2 × 4-inch portion of the lead foil. The lead ball weighing 27 g was cupelled by heating to normal cupellation temperatures. Blanks were prepared as described above without adding the precious metals solution.

The method of analysis of the silver bead is illustrated in Fig. 2, and additional details are included in the procedure described below.

Procedure: The solution (filtrate D) obtained from filtrate C, after reprecipitation of silver as silver chloride, was treated with fuming nitric acid followed by *aqua regia* to destroy the residual ammonium salts, which interfered in the chromatographic separations.²⁰ Removal of nitrogen oxides and conversion of the salts to a chloride form were accomplished by successive treatments of the residue with concentrated hydrochloric acid and evaporation to dryness on a steam bath. The residue was dissolved with water acidified with hydrochloric acid, and the solution was combined with the filtrates (B). The residues A and C were combined by placing them in a 0000 Coors porcelain crucible, where they were ignited and reduced in hydrogen. The crucible with the reduced residues was placed in a 30-ml beaker, and the residues were treated twice with 8 ml of *aqua regia*, and were heated on a steam bath. The salts were converted to a chloride form, and the nitrogen oxides were removed in the usual manner by successive treatments with concentrated hydrochloric acid. After the dissolution of the residue with 1.0M hydrochloric acid and filtration of the resulting solution, the filtrate was combined with those of B and D, and the combined solution was applied to the chromatographic paper to separate rhodium plus iridium from palladium plus platinum as described above. The filter paper with the residue was placed in the original crucible, where it was ignited, and the crucible was set aside to receive the rhodium-iridium section of the strip from the chromatographic separation applied to the combined filtrates. The rhodium and iridium residues were chlorinated, and separations and determinations were made as described above. The results are listed in Table V.

TABLE V.—ANALYSIS OF STANDARD SILVER BEADS FOR RHODIUM, IRIDIUM, PALLADIUM AND PLATINUM

Added				Found			
Rhodium, μg	Iridium, μg	Palladium, μg	Platinum, μg	Rhodium, μg	Iridium, μg	Palladium, μg	Platinum, μg
25.0	18.4	25.0	45.5	23.0	14.0	21.0	44.0
				22.0	15.0	21.0	43.0
				24.0	16.2	23.4	43.9
				23.6	13.0	22.5	43.5
				*	*	24.4	44.2
				23.4	14.5	23.6	43.9

* These samples were destroyed during the analysis.

TABLE VI.—ANALYSIS OF SULPHIDE CONCENTRATE FOR RHODIUM, IRIDIUM, PALLADIUM AND PLATINUM BY THE COPPER-NICKEL-IRON FUSION METHOD

Sample no.	Rhodium		Iridium		Palladium		Platinum	
	ppm	oz/ton	ppm	oz/ton	ppm	oz/ton	ppm	oz/ton
1	0.137	0.0040	0.058	0.0017	0.500	0.0146	0.804	0.0235
2	0.087	0.0026	0.045	0.0013	0.434	0.0127	0.983	0.0287
3	0.134	0.0039	0.050	0.0015	0.497	0.0145	1.000	0.0292
4	0.137	0.0040	0.050	0.0015	0.417	0.0122	0.980	0.0286

DISCUSSION

A condensation of Tables I, IV, and VI is presented in Table VII. These data represent the average recoveries from one assay ton of concentrate of the four platinum metals by the three methods.

TABLE VII.—COMPARISON OF RESULTS FROM THREE METHODS

Method applied	Rhodium, μg	Diff, μg	Iridium, μg	Diff, μg	Palladium, μg	Diff, μg	Platinum, μg	Diff, μg
Lead fusion	3.5		0.8		14.5		24.0	
Cu-Ni-Fe fusion	3.7	+0.2	1.5	+0.7	14.0	-0.5	28.2	+4.2
		+0.6		+0.4		+1.6		+0.6
Wet extraction	4.3		1.9		15.6		28.8	

The greatest discrepancy in the values is found with iridium obtained by the classical assay. With this method iridium is relatively insoluble in both collectors, lead and silver, and thus the mechanism of recovery is largely, if not entirely, a mechanical one depending upon the high density of the metal. This fact is made evident by the appearance of the silver bead containing iridium, the latter revealing its presence by surface excrecences.²⁹

In the case of the iron-copper-nickel alloy, the iridium, in small amounts at least, is apparently collected as a homogeneous alloy with the base metals,¹⁵ and the acid treatments of the alloy result in complete dissolution of each of the four metals. Furthermore, the presence of nickel in the slag of the classical assay has been shown to encourage high losses,³⁰ whereas in the iron-copper-nickel collection advantage is taken of this affinity for nickel and platinum metals in that the former is removed to form the alloy.

The results with the complete wet assay are generally higher than those from either of the alloy extractions. This finding is not unexpected, since complete dissolution of the concentrate should convert the platinum metals to forms which respond to the separational techniques such as ion exchange and chromatography. There can be little doubt that the most reliable method for the determination of the platinum metals in all natural sources is the complete wet procedure. However, this method is cumbersome, and is reliable only in the hands of an experienced and careful operator.

It should be noted that the results in Table VII constitute the first instance in which the results from the classical assay of a natural concentrate for platinum, palladium, rhodium and iridium are compared with a proved wet extraction. To the

best of the authors' knowledge it is also the first instance in which the results for the recoveries of the four metals are compared with recoveries based on a method involving new fundamental principles.

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Zusammenfassung—Eine naßchemische Methode zur Rückgewinnung von Mikromengen Rh, Ir, Pd und Pt aus Erzen und Konzentraten wird angegeben. Dabei wird das geröstete Sulfidkonzentrat stufenweise in Lösung gebracht. Das kalzinierte Material wird mit Königswasser oder zuerst mit konzentrierter Salzsäure und dann mit Königswasser ausgelaugt. Der Rückstand wird chloriert, Kieselsäure als SiF_4 abgetrieben und der Rest mit Natriumperoxyd geschmolzen. Aus der Lösung werden die unedlen Metalle durch Ionenaustausch entfernt. Durch Chromatographie und nachfolgende flüssig-flüssig-Extraktion werden die genannten vier Platinmetalle aus dem Eluat des Kationenaustauschers abgetrennt. Die Ergiebigkeit der geschilderten Methode wird mit den Kupfer-Nickel-Eisen- und den alten (Blei-) Schmelzmethoden am selben Erz und Konzentrat verglichen.

Résumé—On décrit une méthode de récupération par voie humide de microquantités de rhodium, d'iridium, de palladium et de platine à partir de minerais et d'échantillons concentrés. Cette méthode fait intervenir la dissolution graduelle du concentré de sulfures calciné. Le matériel calciné est extrait par lessivage au moyen d'eau régale ou d'acide chlorhydrique concentré suivi d'eau régale. Le résidu du lessivage est chloré, le silicium volatilisé sous forme de tétrafluorure, et le produit obtenu est fondu avec du peroxyde de sodium. A partir de ces solutions résultantes, les métaux de base sont chassés par une technique d'échange de cations. Une méthode chromatographique suivie de procédés d'extraction par les solvants permet enfin de séparer les quatre métaux envisagés des résidus venant de l'échangeur de cations. On donne une comparaison de l'efficacité de ce procédé avec les deux méthodes classiques du cuivre-nickel-fer et de la méthode de fusion au plomb, appliquées au traitement de ces échantillons concentrés et minerais.

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THE DETERMINATION OF TRACES OF IRON IN SAMPLES OF PLATINUM BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A neutron-activation analysis method for the determination of traces of iron in samples of purified platinum is described. The nuclear reactor BEPO at Harwell has been used as the neutron source. A rapid radiochemical separation procedure using carriers has been employed to decontaminate the iron activity from most other induced activities. The analysis is completed by discriminated γ -scintillation counting. Results of analyses of seven samples of platinum are quoted. The method of analysis has the advantage that it obviates difficulties caused by "reagent blanks" or by contamination from traces of inactive iron after irradiation. Interference resulting from nuclear reactions of elements other than iron in the samples appears to be of no consequence in the present case.

THE contamination of many reagents by traces of iron makes chemical methods for determining very small quantities of the element difficult. Also, electrodes used in spectrographic analysis are frequently contaminated with iron.¹ However, in radioactivation analysis, since carriers are usually employed in any radiochemical separations, the method is free from difficulties caused by "reagent blanks" or by contamination from traces of inactive material during chemical operations after irradiation. A further advantageous feature of radioactivation is that samples generally require little pretreatment before irradiation.² In the present paper a procedure for the determination of traces of iron in samples of purified platinum by neutron-activation analysis is reported.

The nuclear characteristics of iron relevant to activation with thermal neutrons are summarised in Table I.³⁻⁵ It has been estimated⁶ that with a thermal neutron flux of 10^{12} neutrons.cm⁻².sec⁻¹, it should be possible under ideal conditions to determine *ca.* 1×10^{-7} g of iron, utilising the activated form, ⁵⁹Fe. Possible conflicting nuclear reactions, such as ⁵⁹Co(*n, p*)⁵⁹Fe and ⁶²Ni(*n, α*)⁵⁹Fe, which may limit the neutron-activation analysis of iron, are listed by Koch,⁷ and their consequence is discussed later in this paper.

In order to avoid errors from self-shielding, standardisation has been provided by irradiating similar known quantities *a* and *b* of a sample with a very small known amount of iron mixed with *b*. As is usual, all samples and comparators have been irradiated in duplicate, at least.

EXPERIMENTAL

Irradiation

Samples of powdered platinum sponge of 1 g were accurately weighed, and were sealed in silica irradiation tubes of 6-mm internal diameter. Standardisation was provided by the addition of weighed portions (*ca.* 0.1 g) of a standard solution of iron (100 mg of Fe/litre, as Fe^{III} in 1M H₂SO₄) to 1-g samples of platinum in silica irradiation tubes. The liquid was allowed to soak into the metal

powder, which was then carefully dried at 70°, after which the tubes were sealed. As is general practice, these operations were performed in a special room detached from the main radiochemical laboratory, to avoid the possibility of radioactive or chemical contamination.

Comparators containing the added iron, together with samples to which no iron had been added, were packed with silica wool in standard aluminium screw-top cans and sent to the Atomic Energy Research Establishment, Harwell, for activation. Irradiations were for 1 month in the nuclear reactor BEPO with a thermal neutron flux of 1.2×10^{12} neutrons.cm⁻².sec⁻¹.

TABLE I.—NUCLEAR DATA FOR THERMAL NEUTRON ACTIVATION OF IRON

Target nuclide	Abundance, %	Isotopic activation cross section, barns	Product on thermal neutron irradiation	Radiation and energy, MeV	Half-life
⁵⁴ Fe	5.84	2.5 ± 0.4	⁵⁸ Fe	EC (100%) —Mn x	2.7 y
⁵⁶ Fe	91.68		⁵⁷ Fe	stable	
⁵⁷ Fe	2.17		⁵⁸ Fe	stable	
⁵⁸ Fe	0.31	0.98 ± 0.10	⁵⁹ Fe	β ⁻ 0.13 (1%), 0.271 (46%), 0.462 (53%), 1.560 (0.3%), γ 0.14 (0.9%), 0.191 (2.4%), 0.34 (0.3%), 1.10 (56%), 1.29 (44%)	45 d

Radiochemical separation

After irradiation the samples and comparators were left to "cool" for 4 days, and then were put through a radiochemical procedure to separate radio-iron from a number of interfering activities. Various radiochemical procedures for iron have been described.⁸ For the present study a rapid procedure designed to take advantage of gamma-spectrometry was developed. The samples of platinum were dissolved in *aqua regia* in the presence of iron carrier. Decontamination of high order was obtained by extraction of the iron into methyl isobutyl ketone (4-methyl-2-pentanone or hexone) from hydrochloric acid solution.^{9,10} Further purification was effected by anion-exchange¹¹ and by acid sulphide scavenging. Iron was finally precipitated and counted as the 8-hydroxyquinolate (oxinate), Fe(C₉H₆ON)₃. The chemical yields were determined gravimetrically, and were usually about 80%.

Preparation and standardisation of carrier

Fe carrier: 1 mg of Fe/ml (as FeCl₃.6H₂O in 1M HCl). Weigh out 4.84 g of FeCl₃.6H₂O and make up to 1 litre in 1M HCl.

Treat 25 ml of the carrier solution with dilute NH₄OH until a faint precipitate persists, and dissolve the precipitate in the minimum volume of 1M HCl. Then add a solution of 3 g CH₃CO₂NH₄ in 125 ml of H₂O, followed by oxine solution (2% in 1M CH₃CO₂H) from a burette, with constant stirring, until an excess is present (12–15 ml are required). Digest the dark precipitate at 80–90° on a water-bath for 30 min, filter through a sintered-glass crucible (porosity No. 3), wash successively with 1% CH₃CO₂H and H₂O, dry to constant weight at 130–140°, cool, and weigh.

Since iron is finally weighed as the 8-hydroxyquinolate in the radiochemical procedure, the carrier is standardised gravimetrically through this compound.

Radiochemical separation procedure

Treat each irradiated sample and comparator in the following manner:

Step 1: Remove a silica irradiation tube from the can, open it and transfer the contents quantitatively to a 150-ml beaker containing 2 ml of Fe carrier and 5 ml of 12M HCl. Wash out the tube thoroughly with warm 6M HCl and transfer the washings to the beaker. Heat at 60° on a water-bath and add the minimum quantity of 16M HNO₃ necessary to dissolve the platinum. Remove HNO₃ by heating more strongly and adding 5 ml of 12M HCl in several portions. Cool and transfer the solution to a 50-ml centrifuge tube.

Step 2: Dilute the solution to 20 ml with H₂O. Extract Fe^{III} by agitating with two 5-ml portions of methyl isobutyl ketone. Separate and combine the organic phases, and wash several times with 5-ml portions of 6M HCl. Then back-extract the Fe^{III} by agitating with 10 ml of 1M HCl.

Step 3: Evaporate the aqueous phase to dryness and dissolve the residue with 3 ml of 12M HCl. Pour the solution on a 5-cm × 1-cm column of Deacidite FF anion-exchange resin (100–200 mesh) in the Cl⁻-form. Add a further 2 ml of 12M HCl to the column. Then elute the Fe^{III} with 25 ml of 0.5M HCl into a 50-ml centrifuge tube.

Step 4: Add 1 ml of Sb^{III} carrier (2 mg of Sb/ml as SbCl₃ in 3M HCl) and heat to 80°. Saturate with H₂S, centrifuge and discard the precipitate of Sb₂S₃. Transfer the supernate to a clean 50-ml centrifuge tube and boil to expel H₂S. Add dilute NH₄OH until a faint precipitate persists, and dissolve the precipitate in the minimum volume of 1M HCl. Add 10 ml of CH₃CO₂NH₄ solution (0.3 g/ml) and 10 ml of oxine solution (2% in 1M CH₃CO₂H) with constant stirring. Centrifuge and discard the supernate. Wash the precipitate well with 10-ml portions of H₂O and transfer it to a weighed aluminium counting tray. Dry at 130° for 15 min, cool, and weigh to determine the chemical yield.

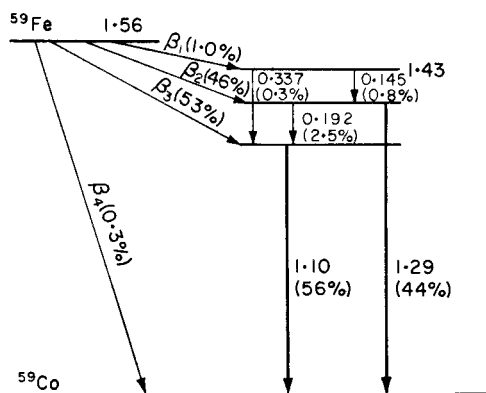


FIG. 1.—Decay scheme of iron-59.^{12,13}

Measurement of radioactivity

Geiger-Müller and gamma spectral measurements on the separated samples of iron^{III} 8-hydroxyquinolate showed that they were not radio-chemically pure, and that they contained a trace of ¹⁹²Ir. This radionuclide has a half-life of 74.37 days and emits β -particles and γ -rays; the γ -ray energies with their relative unconverted abundances in parentheses⁹ are as follows

0.13633 (1.9), 0.2959 (360), 0.3085 (350), 0.3165 (1000), 0.4166 (16)
0.4680 (640), 0.5884 (71), 0.605 (140), 0.613 (84), 0.79 (1), 0.885(5), MeV.

The decay scheme of ⁵⁹Fe is shown in Fig. 1. The two major γ -rays emitted by ⁵⁹Fe are of considerably higher energy than those emitted by ¹⁹²Ir and γ -spectra measurements indicated that by application of a sufficient bias voltage the 1.10- and 1.29-MeV γ -rays of ⁵⁹Fe could be counted without interference from ¹⁹²Ir—for example, see Fig. 2.

The final precipitates of iron^{III} 8-hydroxyquinolate were therefore finally counted with a 1.5-inch diam. × 1-inch NaI(Tl) crystal scintillation counter with sufficient discriminator bias voltage applied to the output to cut out γ -rays of energy < 0.8 MeV. The observed counting rates were corrected for background and chemical yield. An additional check that only ⁵⁹Fe activity from the final precipitates was being counted was obtained from decay measurements. Decay curves were straight lines corresponding quite well with published values³ for the half-life of ⁵⁹Fe.

RESULTS

In Table II are shown results of neutron-activation analyses of purified samples of platinum.

DISCUSSION

Consideration must be given to the possibility that elements other than iron in the samples could give rise on irradiation to ⁵⁹Fe. Two elements suggest themselves: cobalt and nickel. These do not give rise to significant amounts of radio-iron with

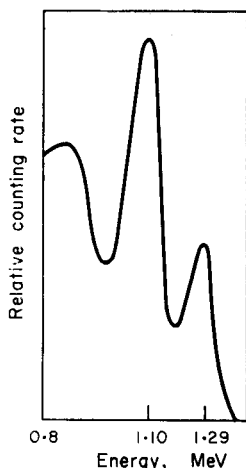


FIG. 2.—Gamma-ray spectrum of a final precipitate for energies > 0.8 MeV.

TABLE II.—IRON CONTENTS OF SAMPLES OF PLATINUM DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

Sample	Iron content, ppm
Pt 1	2.4, 2.8
Pt 3	3.6, 4.1, 4.2, 3.9, 4.4, 4.5
Pt 4	4.0, 4.3
Pt 5	7.7, 8.3
Pt 6	6.4, 6.8
Pt 7	2.3, 2.7
Pt 8	2.9, 3.4

thermal neutrons, but may give rise to some with fast neutrons, of which there is a proportion (possibly as much as 17% of the thermal flux) in the irradiation positions used in the present work. Mellish *et al.*¹⁴ have measured the cross section for the reaction $^{59}\text{Co}(n, p)^{59}\text{Fe}$ as 5.7 millibarns and a calculated value is 7.0 mb. Corresponding measured and calculated cross sections for the reaction $^{62}\text{Ni}(n, \alpha)^{59}\text{Fe}$ are 0.025 and 3.9 mb, respectively.

In order to obtain information on the extent of possible interference from cobalt, samples of platinum Pt 3, platinum Pt 3 + 100 μg of Co, and platinum Pt 3 + 100 μg of Fe were irradiated together and put through the radiochemical procedure. In this manner it was found that the ^{59}Fe activity produced from 100 μg of cobalt corresponded to that from 1.2 μg of iron.

Since platinum samples analysed for iron contained only 0.01–0.13ppm of cobalt,¹⁵ there is no interference of consequence arising from the production of ^{59}Fe from a nuclear reaction of cobalt. Moreover, since the (n, α) cross section of ^{62}Ni is less than the (n, p) cross section of ^{59}Co and ^{62}Ni has an isotopic abundance of only 3.66%, it appears that possible interference with iron analyses from a nuclear reaction of nickel may be discounted in the case of the matrices considered in the present study.

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Zusammenfassung—Die Bestimmung von Eisenspuren in gereinigtem Platin durch Neutronenaktivierungsanalyse wird beschrieben. Als Neutronenquelle wurde der Reaktor BEPO in Harwell verwendet. Durch eine schnelle radiochemische Trennmethode mit Trägern wurde die Eisenaktivität von den meisten anderen Aktivitäten abgetrennt. Die Analyse wird durch Gamma-Szintillationszählung mit Impulshöhendiskrimination abgeschlossen. Analysenergebnisse von sieben Platinproben werden angeführt. Die Methode hat den Vorteil, daß "Blindwerte" aus Reagentien oder Verunreinigung mit inaktiven Eisen nach der Bestrahlung nicht auftreten. Störungen durch Kernreaktionen anderer Elemente außer Eisen scheinen im vorliegenden Fall bedeutungslos zu sein.

Résumé—On décrit une méthode d'analyse par activation de neutrons pour la détermination de traces de fer dans des échantillons de platine purifié. La source de neutrons était constituée par le réacteur nucléaire BEPO de Harwell. Un procédé rapide de séparation radiochimique utilisant les traceurs a été employé pour décontaminer l'activité du fer d'un certain nombre d'activités induites parasites. L'analyse se complète par un comptage au moyen d'un scintillateur γ . On donne des résultats concernant l'analyse de 7 échantillons de platine. Cette méthode d'analyse offre l'avantage de supprimer les difficultés causées par les réactifs "à blanc" ou par la contamination due aux traces de fer inactif après irradiation. Les interférences dues aux réactions nucléaires des éléments autres que le fer présents dans les échantillons ne semblent pas de conséquences dans le cas présent.

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SPECTROPHOTOMETRIC STUDIES OF LOWER OXIDATION STATES OF TECHNETIUM

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Summary—The spectrophotometric behaviour of lower oxidation states of technetium, obtained by reducing pertechnetate under different conditions by various methods, has been examined. Contrary to some of the previously advanced conclusions regarding the ascorbic acid reduction of pertechnetate, it was found that the technetium is reduced to a quadrivalent state. The latter product does not appear to involve a tightly-bound ascorbate species; neither does it significantly react or complex with α -picolinic acid to give a new species.

The lower oxidation states of technetium resulting from chemical or electrochemical reduction of technetium^{VII}, present as pertechnetate in solution, have not been clearly defined for a variety of reactions.¹ Surveys of the polarographic reduction patterns of technetium^{VII} solutions,^{2,3} supplemented by more detailed studies,⁴⁻⁶ begin to decrease the uncertainties involved in characterising the lower oxidation levels.

Spectrophotometric data should provide further information regarding the technetium species involved, but the data so far reported are limited and somewhat contradictory. The absorption spectrum of pertechnetate ion is well known^{7,8} and a technetium^V-thiocyanate system has been carefully characterised.⁹ Spectra have also been given for technetium^{IV} and technetium^{III},^{10,11} and undefined lower states,¹⁰ sometimes over very narrow ranges of wavelength and for unspecified concentrations.

The present paper presents additional data relating to the spectrophotometry of technetium ter- and quadrivalent states. Based on evidence now available, a re-interpretation is suggested for the technetium^V,^{VI}- α -picolinate spectrophotometric method.¹⁰

EXPERIMENTAL

Apparatus

A Beckman Model 2400 DU instrument was used with 1.000-cm quartz cells for the spectrophotometric measurements. Polarographic measurements were made with a Fisher Elecdropode and an H-cell thermostatically controlled at $25.0 \pm 0.1^\circ$; one leg of the cell contained a saturated calomel electrode (S.C.E.). pH was measured with a Leeds and Northrup No. 7664 pH meter.

Reagents

Technetium solutions: A solution of ammonium pertechnetate in water (pH 4) containing 46.75 mg of ⁹⁹Tc/ml and 3×10^{-6} mc of ^{99m}Tc/g of ⁹⁹Tc was obtained from the Oak Ridge National Laboratory; coulometric studies substantiate the stated concentration.^{4,5} Pertechnetate stock solution I was prepared by diluting 10 ml of this solution to 250 ml; 10 ml of solution I were further diluted to 100 ml to give stock solution II (technetium concentration: 1.89 mM).

Ascorbic acid, α -picolinic acid and sulphosalicylic acid solutions: 10% w/v aqueous solutions were prepared from reagent-grade chemicals (ascorbic acid was U.S.P.).

Tin^{II} chloride solution: 20 g of SnCl₂·2H₂O were dissolved in 6M hydrochloric acid with warming, then diluted to 100 ml with the same acid.

Nitrogen: Oil-pumped and used without further purification for purging all solutions of oxygen.

Buffer solutions: A pH 1 buffer solution was prepared by diluting to 200 ml a mixture of 97 ml of 0.2M hydrochloric acid and 2.983 g of potassium chloride. A pH 2 buffer solution was prepared by diluting to 500 ml a mixture of 26.5 ml of 0.2M hydrochloric acid and 125 ml of 0.2M potassium chloride. The measured pH values of these buffer solutions were 1.0 and 2.0, respectively.

All other chemicals used were C.P. grade.

Polarographic procedure

Twenty-five ml of pertechnetate solution II and 25 ml of ascorbic acid solution were diluted to volume in a 250-ml volumetric flask with pH 2 buffer. About 15-ml portions of this solution (technetium^{VII} concentration 0.189 mM) were transferred to the H-cell at different intervals of time after preparation of the solution, deoxygenated with nitrogen for 10 to 15 min, then polarographed over the potential range of 0.0 to -1.5 V vs. S.C.E. $E_{\frac{1}{2}}$ and i_d were determined graphically, utilising the maximum deflections.

Spectrophotometric procedures

(1) In a 10-ml volumetric flask, 0.5 ml of pertechnetate solution II was well mixed with 5 ml of pH 2 buffer and 1 ml of ascorbic acid solution, heated at *ca.* 70° under an infrared lamp for 20 min, cooled and diluted to volume with pH 2 buffer; the spectrum of the resulting solution was measured at different intervals of time against a blank containing 1 ml of ascorbic acid solution diluted to 10 ml with pH 2 buffer. This procedure was also used with 0.5 ml of α -picolinic acid solution present in addition to the ascorbic acid.

(2) In a 10-ml volumetric flask, 0.5 ml of pertechnetate solution II was thoroughly mixed with 4 ml of pH 1 buffer solution and 0.2 ml of tin^{II} chloride solution, then diluted to volume with pH 1 buffer. The absorption spectrum was measured against a blank containing 0.2 ml of tin^{II} chloride solution diluted to 10 ml with pH 1 buffer. A similar procedure was employed with the addition of 1 ml of sulphosalicylic acid solution in addition to the tin^{II} chloride.

RESULTS AND DISCUSSION

Al-Kayssi, Magee and Wilson¹⁰ reduced technetium^{VII} in hydrochloric acid solution with either tin^{II} chloride or ascorbic acid to give a postulated quadri- or quinquevalent state complex with α -picolinic acid; the resulting pink solution showed a molar absorptivity (ϵ) of about 4,400 at 480 $m\mu$.

On treating pertechnetate with ascorbic acid by the same method¹⁰ but in the absence of α -picolinic acid, reduction occurs very slowly (*cf.* Table I) with the molar

TABLE I.—SPECTRA AND POLAROGRAPHY AT 25° OF TECHNETIUM^{VII} SOLUTION REDUCED BY ASCORBIC ACID

Elapsed time, hr	Molar absorptivity, ϵ^a		Wave I ^b i_d , μA
	418 $m\mu$	490 $m\mu$	
0	0	0	(6.25)
2	21	42	—
24	516	824	5.12
48	1160	1860	4.19
72	1600	2690	4.25
96	1850	3210	3.64
120	1990	3460	2.94
144	2075	3650	2.29
168	2120	3820	1.42
192	2180	3880	0.82
216	2190	3950	0.44
	(2380)	(4300)	(0.00)

^a Solution was 0.095 mM in technetium; a complete spectrophotometric run took about 30 min.

^b $E_{\frac{1}{2}}$ was between -0.150 and -0.158 V vs. S.C.E; the value of 6.25 μA is the current obtained for a similar technetium solution in the absence of ascorbic acid.

absorptivities finally approaching 4,300 at 485 $m\mu$ (maximum) and 2,380 at 418 $m\mu$ (minimum). The prior or subsequent addition of α -picolinic acid in this procedure results in no change in the position or intensity of these absorption characteristics (curve A of Fig. 1).

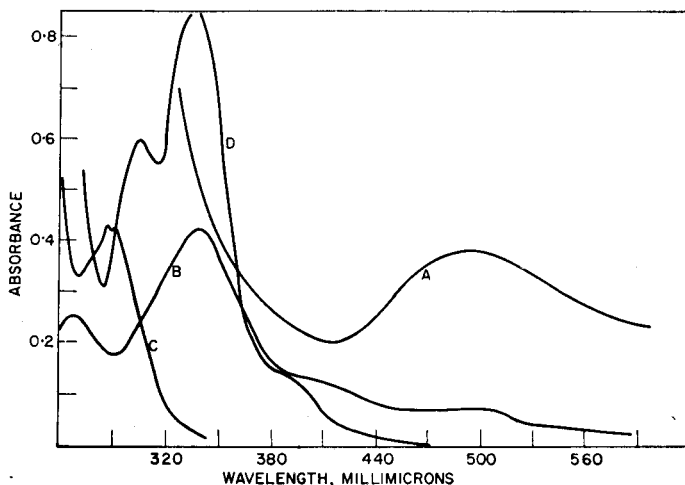


FIG. 1.—Absorption spectra:

- (A) 0.095 mM technetium^{IV} solution resulting from ascorbic acid reduction;
 (B) partially re-oxidised technetium^{III} via coulometry (56% technetium^{VII} and 44% technetium^{III}) equivalent to 0.090 mM ;
 (C) 0.095 mM pertechnetate ion;
 (D) 0.189 mM $(TeCl_6)^{3-}$ ion.

The rate of decrease in the first polarographic reduction wave of pertechnetate^{4,5} in the presence of ascorbic acid is in agreement with the increase in molar absorptivity. The half-wave potential of this wave, which represents the reduction of technetium^{VII} to technetium^{III}, is not significantly shifted by the presence of the ascorbic acid; the slope is also unchanged. While this wave does shift in the expected manner⁴ as a function of pH, it is irreversible (slope criterion) and its failure to shift here is not incontrovertible evidence of the non-existence of ascorbate complexes of the reduced technetium state or states.

The partial extraction by chloroform of the "quadri- or quinquevalent α -picolinate complex" of technetium has been noted.¹⁰ In the present study, the red solutions obtained by the reduction of pertechnetate with ascorbic acid were made 0.05–6 M in sulphuric acid and extracted with equal volumes of chloroform. Radiometric assay of the two layers indicated an extraction of 2.5–5.5%, corresponding to a low distribution coefficient of 0.03–0.06. Better extraction of technetium^{IV}, for example, is obtained with ether from 0.0–6 M hydrochloric acid solution. However, these results correspond to distribution coefficients of less than 0.1, and are not indicative of the existence of significant amounts of organic solvent soluble technetium-ascorbate species.

In order to ascertain whether the ascorbate-reduced solution contained any technetium^{III}, a yellow-green technetium^{III} solution, prepared by the macroscale reduction at a mercury cathode of an acidic pertechnetate solution,⁵ was rapidly examined spectrophotometrically after dilution. (The spectrum obtained had nothing

in common with that observed for technetium^{III} in pH 7 phosphate solution between 400 and 750 m μ .⁶) The appreciable amount of technetium^{VII}, which developed as a result of rapid air oxidation, was determined polarographically and the spectrophotometric curve was corrected by subtracting the absorbance from technetium^{VII} to give curve B of Fig. 1; inaccuracies in this correction, from the presence of technetium^{IV} or technetium^V, may account for the apparent features at 270 and 290 m μ ; however, the peak at 340 m μ is essentially free of any effects from technetium^{VII}.

Based on the absence in the ascorbate-reduced solution (curve A of Fig. 1) of the 340-m μ peak observed in the technetium solution, it can be safely asserted that the ascorbate-reduced solution does not contain appreciable amounts of technetium^{III}; this is confirmed by the presence in the ascorbate-reduced solution of an absorption maximum at 485 m μ which is absent in the technetium^{III} solution.

The nature of the technetium^{IV} species obtained by ascorbate reduction, as indicated by its spectrum (curve A of Fig. 1), is different from the technetium^{IV} species obtained by reduction in hydrochloric acid (curve D of Fig. 1). The latter spectrum is that of pertechnetate, which was allowed to stand for about 1 month in 9M hydrochloric acid, then examined against a blank of 9M hydrochloric acid; the molar absorptivity of 9,100 at 338 m μ is in general agreement with the value of 11000, reported for spectrophotometry in 1M hydrochloric acid after reduction in 9M hydrochloric acid.¹¹

Consequently, it may be concluded that ascorbic acid, in the absence of thiocyanate, reduces pertechnetate very slowly to a technetium^{IV} species, which shows a maximum at 485 m μ with a molar absorptivity of 4,300 to 4,400 as previously reported.¹⁰ The red colour of the technetium^{IV} species and the absence of a precipitate of technetium dioxide suggests the formation of an ascorbate complex, but the polarographic behaviour of the partially reduced solution is contrary to such a postulation, *i.e.*, formation of a technetium^{IV}-ascorbate complex should involve a shift in $E_{\frac{1}{2}}$, which does not occur.

Miller *et al.*⁶ coulometrically reduced technetium^{VII} in pH 7 phosphate buffer to a pink quadrivalent state, which absorbed at 515 m μ with an ϵ of 380. Apparently, the technetium^{IV} forms a stable red-coloured complex as indicated by the shift of the absorption maximum from 485 to 515 m μ and the decrease in molar absorptivity from 4,300 to 380. Similar pink or pale-violet solutions were obtained by the present authors after coulometric reduction of technetium to a quadrivalent state in non-complexing acidic media.^{4,5}

Reduction of 0.189 mM pertechnetate in 0.1M hydrochloric acid by tin^{II} chloride, which is complete in about 30 min, gives an orange-coloured solution (maximum at 445 m μ , $\epsilon = 670$). Polarography of this solution does not show any portion of the wave from the reduction of technetium^{VII} to technetium^{III} ($E_{\frac{1}{2}} = +0.02$ V *vs.* S.C.E.). The polarographic wave, which does appear at $E_{\frac{1}{2}}$ of -0.41 V *vs.* S.C.E., is that from the reduction of tin^{II}; however, the current is 224 μ A, compared to 206 μ A observed for tin^{II} alone. The increase may be caused by reduction of tin^{IV} formed and to further reduction of technetium to the metal (the reduction of technetium^{III} to technetium⁰ normally occurs at $E_{\frac{1}{2}}$ of *ca.* -0.9 V at the acidity involved).

Reduction of pertechnetate in 0.1M hydrochloric acid by tin^{II} chloride in the presence of sulphosalicylic acid gives in 30 min a solution having an absorption maximum at 430 m μ of $\epsilon = 1120$. The changes in absorption would indicate formation

of a sulphosalicylate complex by the reduced technetium. Earlier workers¹⁰ have reported for a similar operation a maximum at 460-470 m μ , without mentioning the molar absorptivity; this maximum was ascribed by them to a technetium^V complex.

Acknowledgments—One of the authors (G. B. S. S.) wishes to thank the National Academy of Sciences (U.S.A.) for an appointment supported by the International Cooperation Administration under the Visiting Research Scientist Program.

Zusammenfassung—Das spektralphotometrische Verhalten durch Reduktion von Pertechmetat unter verschiedenen Bedingungen und nach verschiedenen Methoden erhaltener niedriger Oxydationsstufen von Tc wurde untersucht. Im Gegensatz zu einigen früher gezogenen Folgerungen über die Reduktion von Pertechmetat mit Ascorbinsäure wurde gefunden, daß Tc zur vierwertigen Stufe reduziert wird. Das Produkt enthält offenbar kein Ascorbat fest gebunden; auch reagiert es nicht nennenswert mit α -Picolinsäure zu einer neuen Verbindung.

Résumé—On examine le comportement spectrophotométrique de l'état inférieur d'oxydation du technetium, obtenu par réduction du pertechmetate dans différentes conditions et par diverses méthodes. Contrairement à de nombreuses conclusions antérieures, la réduction du pertechmetate par l'acide ascorbique, il a pu être montré que le technétium est réduit à l'état d'oxydation (IV). Ce dernier ne semble pas être fortement lié aux molécules d'acide ascorbique et ne réagit pas, d'une manière caractéristique, ni ne fournit de complexe avec l'acide α -picolinique.

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ELECTRON MICROSCOPY STUDIES OF NICKEL DIMETHYLGLYOXIMATE

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Summary—Nickel dimethylglyoximate crystals precipitated from homogeneous solution are well formed and convenient for microscopic study. The crystals are precipitated in solution as long needles with a rectangular cross-section. The direction of the long axis, *i.e.*, the direction of the long dimension of the needle, is the *c*-axis; the shortest axis is either the *a*- or *b*-axis. When the single crystal was slowly heated in the electron microscope, it began to sublime at 120° with changes occurring in its surface structure. Above 400° the Debye-Scherrer diffraction rings appeared as the crystal changed to nickel oxide.

NICKEL dimethylglyoximate precipitated from homogeneous solution (PFHS)^{1,2} is composed of more perfect and larger crystals than that prepared by the conventional method.^{1,2} The red crystal appears needle-shaped when viewed under a light microscope. The crystals were examined by electron microscopy several years ago^{3,4,7} and were found to sublime as a result of electron bombardment. The X-ray crystal structure of nickel dimethylglyoximate recrystallised from nitrobenzene has been determined by Godycki and coworkers.^{5,6}

The present investigation was made to confirm the crystal structure of the PFHS product and to observe alterations in the crystal upon heating to 800°

EXPERIMENTAL

Preparation of crystals of nickel dimethylglyoximate

*Precipitation by the conventional method:*² A nickel solution, containing 80 mg of nickel, 5 g of ammonium chloride and 5 ml of aqueous ammonia in 400 ml of the solution, was mixed with an equal volume of a 0.1% solution of dimethylglyoxime in 1:1 aqueous alcohol.

*Precipitation from homogeneous solution (PFHS):*² A nickel solution, containing 80 mg of nickel, 5 g of ammonium chloride and 3 g of hydroxylamine hydrochloride in 400 ml of the solution, adjusted to pH 7, was mixed with an equal volume of a biacetyl solution containing 0.6 g of biacetyl in 400 ml of solution.

Apparatus

Electron microscope: JEM-6A, manufactured by Japan Electron Optics Co., Tokyo, Japan.

Ultramicrotome: Ivan Sorvall, Inc., Norwalk, Conn., U.S.A.

Preparation of specimens for electron microscopy

For transmission work: The filtered precipitate specimens were washed with water, 1 drop of the water suspension mounted on a Formvar-filmed copper grid (for electron microscopy) and dried.

Replica of crystals: The specimen, mounted on a filmed grid as described above, was either shadowed with platinum-carbon or was covered with a carbon film about 200 Å thick. The specimen was dipped in chloroform for 15 to 20 min to dissolve both the Formvar film and the crystal of nickel dimethylglyoximate.

For thin-sectioned crystal: The washed precipitate was placed in a 40% gelatin-2% glycerine in water solution in a small glass tube. The gelatin solution was then solidified in a refrigerator and dried in a vacuum desiccator. The solid piece was sectioned with an ultramicrotome.

For heat treatment in an electron microscope: The water suspension of nickel dimethylglyoximate, prepared as previously described, was placed on a carbon-filmed stainless-steel grid and heated to prescribed temperatures.

RESULTS AND DISCUSSION

Crystal shape and size

Crystals of nickel dimethylglyoximate prepared by the conventional or PFHS method were laminate needles of rectangular cross-section. The crystals (*cf.* Fig. 1) prepared by the conventional method were about $5\ \mu$ long and $0.05\text{--}0.2\ \mu$ wide and those prepared by the PFHS method were about 30 to $50\ \mu$ long and $0.2\text{--}1\ \mu$ wide.

The shape of the crystals was also observed by the replica technique. As is shown in Fig. 2, the crystals are pillar-shaped with a rectangular cross-section and have smooth surfaces. The cross-section of a sectioned crystal is shown in Fig. 7.

As shown in these figures, the cross-section of the crystal is rectangular although the size and the ratio of the two axes of the crystal viewed microscopically are not definite.

Crystal structure

Nickel dimethylglyoximate recrystallised from nitrobenzene⁴ is orthorhombic; $a_0 = 16.68$, $b_0 = 10.44$, $c_0 = 6.49\ \text{\AA}$, $Z = 4$, space group D_{2h}^{26} . The high resolution electron-diffraction patterns shown in Fig. 3, taken with nickel dimethylglyoximate prepared by the conventional and the PFHS methods, support these results.

The fibre period calculated from the fibre patterns, obtained from the part of the grid where the needle crystals were oriented in parallel, as shown in Fig. 4, was $6.49\ \text{\AA}$. This is in agreement with the lattice constant of the *c*-axis.

Each single crystal selected under the electron microscope showed several kinds of spot pattern. Analysis of these patterns showed that the long axis of the needles was the *c*-axis but that the shortest axis could be either the *a*- or *b*-axis, *i.e.*, the axis which was perpendicular to lamina was not definite. Typical examples are shown in Figs. 5 and 6. Fig. 7 shows the thin-sectioned crystals, sectioned perpendicular to the *c*-axis.

Planar nickel dimethylglyoximate molecules are parallel to the (001)-plane and stacked up on a 4-fold screw axis. The distance between adjoining nickel atoms along the *c*-axis is $3.245\ \text{\AA}$.⁴ The lattice constant of the *c*-axis is the smallest and the concentration of atoms along the *c*-axis is the greatest. Because the planar molecules are opposite to each other along the *c*-axis, the Van der Waals' energy along this axis would appear to be greater than that along the other axes and the crystals would tend to grow in this direction. Because the planar molecules are rotated 90° about the *c*-axis, the concentration of atoms along either the *a*- or *b*-axis is about the same. Hence the tendency to grow along the *a*- and *b*-axes seems to be about the same, so that the shortest axis of the crystal is not definitive.

Heat treatment of single crystal

A selected ribbon-like single crystal was heated in the electron microscope. Fig. 8 shows the original crystal with its smooth surface; it also exhibited a typical spot pattern at room temperature. The crystal began to sublime slightly above 120° , at the same time exhibiting granular structure on its surface; its original electron-diffraction pattern also disappeared. At 220° and at 400° the surface structure of the crystal was

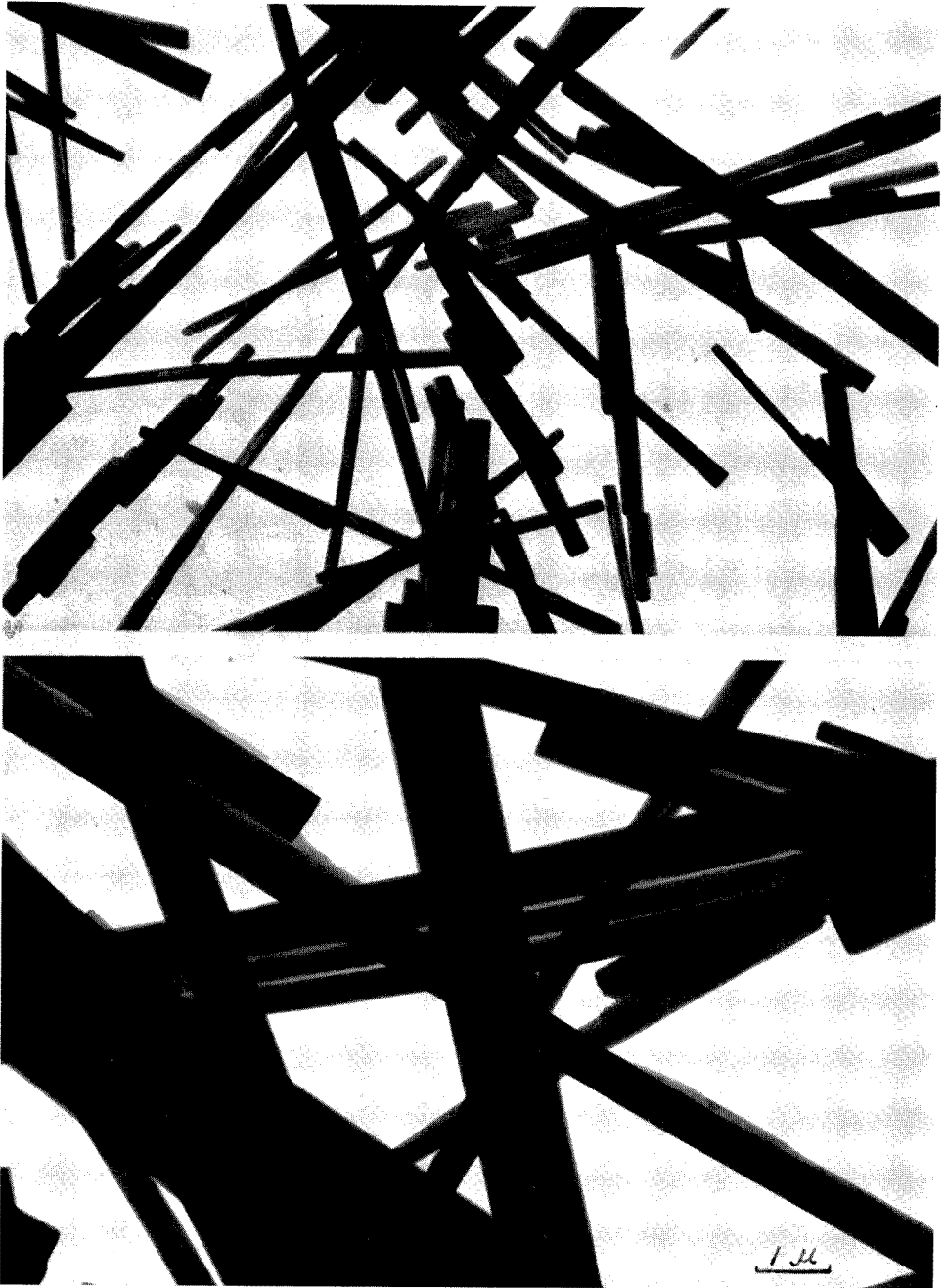


FIG. 1.—Top: Nickel dimethylglyoximate prepared by the conventional precipitation method. Bottom: Nickel dimethylglyoximate prepared by the method of PFHS.

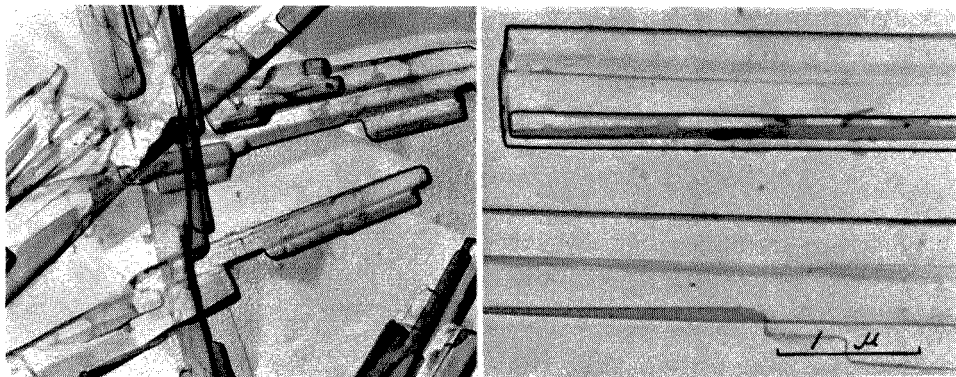


FIG. 2.—Left: Platinum-carbon self-shadowed replica of nickel dimethylglyoximate prepared by the conventional method. Right: Carbon replica of nickel dimethylglyoximate prepared by the PFHS method.

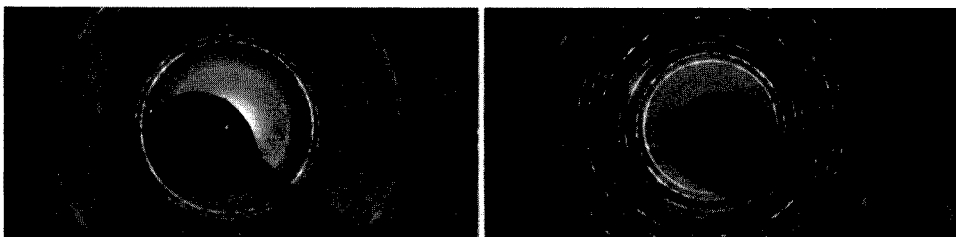


FIG. 3.—High resolution electron diffraction pattern of nickel dimethylglyoximate. Left: Precipitates prepared by the conventional method. Right: Precipitates prepared by the PFHS method.

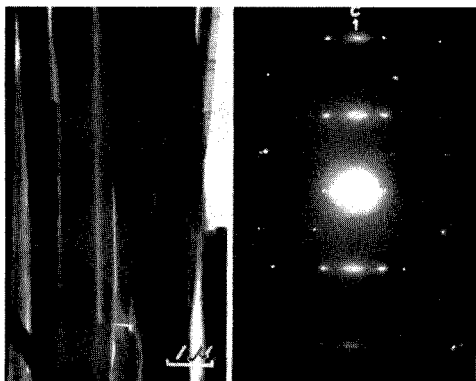


FIG. 4.—Fibre pattern obtained from the crystals prepared by the PFHS method.

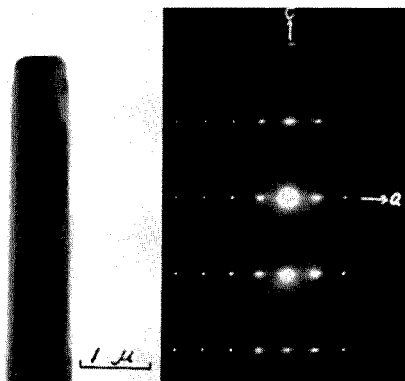


FIG. 5.—Nickel dimethylglyoximate crystal grown along the (010)-plane.

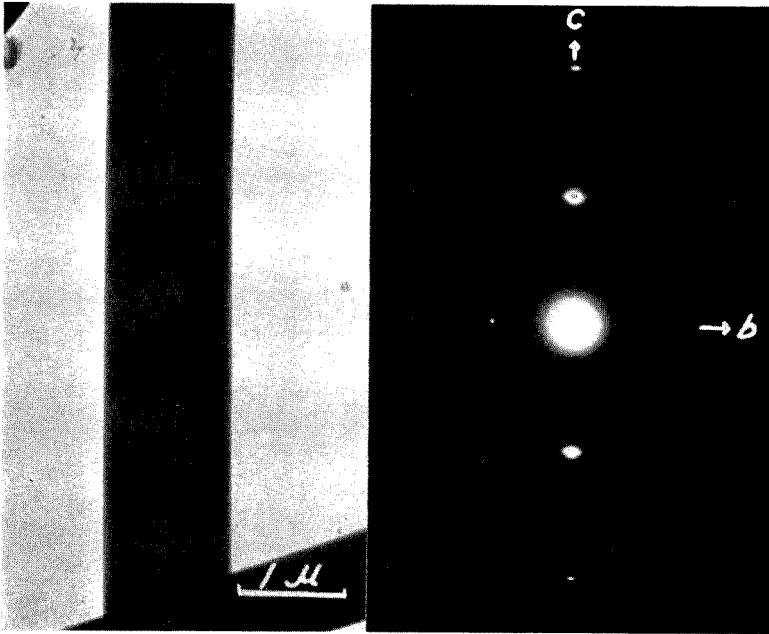


FIG. 6.—Nickel dimethylglyoximate crystal grown along the (100)-plane.

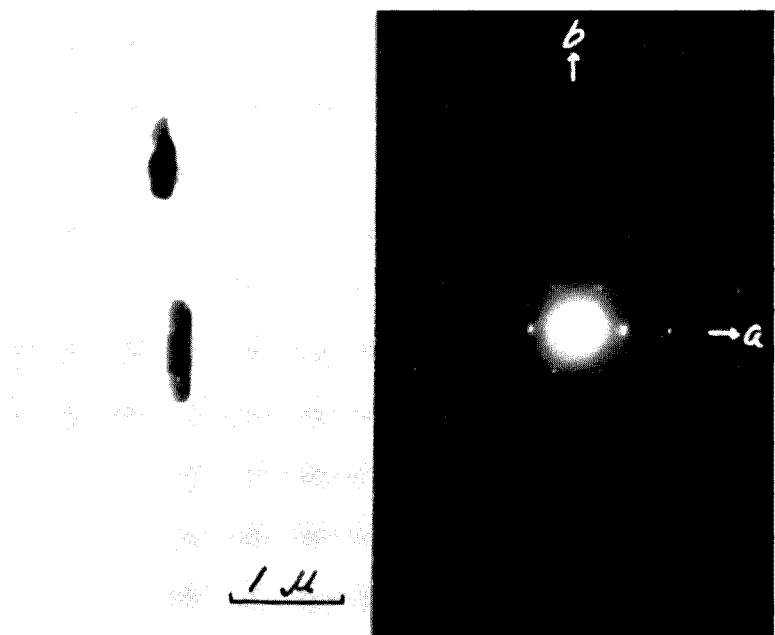


FIG. 7.—Thin section of a nickel dimethylglyoximate crystal prepared by the PFHS method.

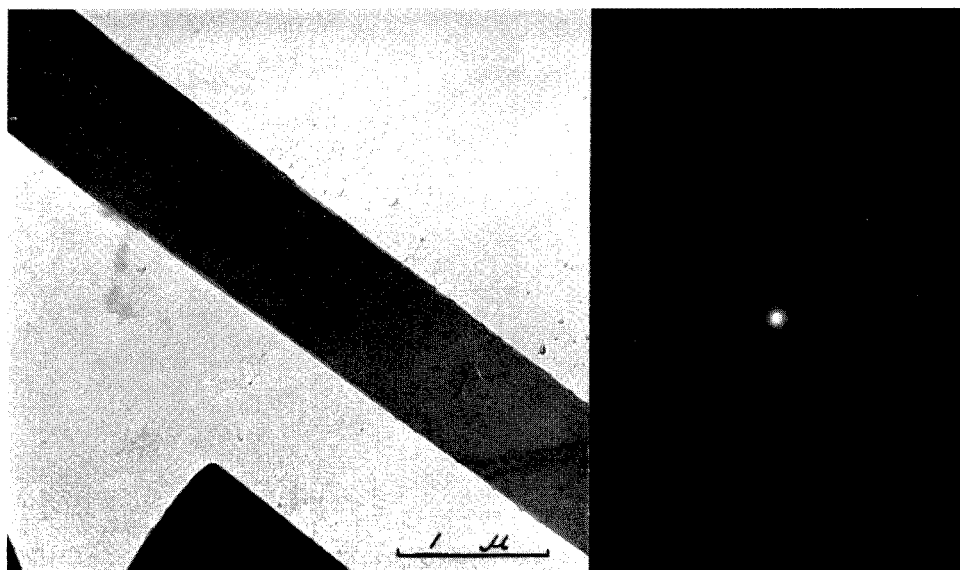


FIG. 8.—The single crystal of nickel dimethylglyoximate at room temperature.

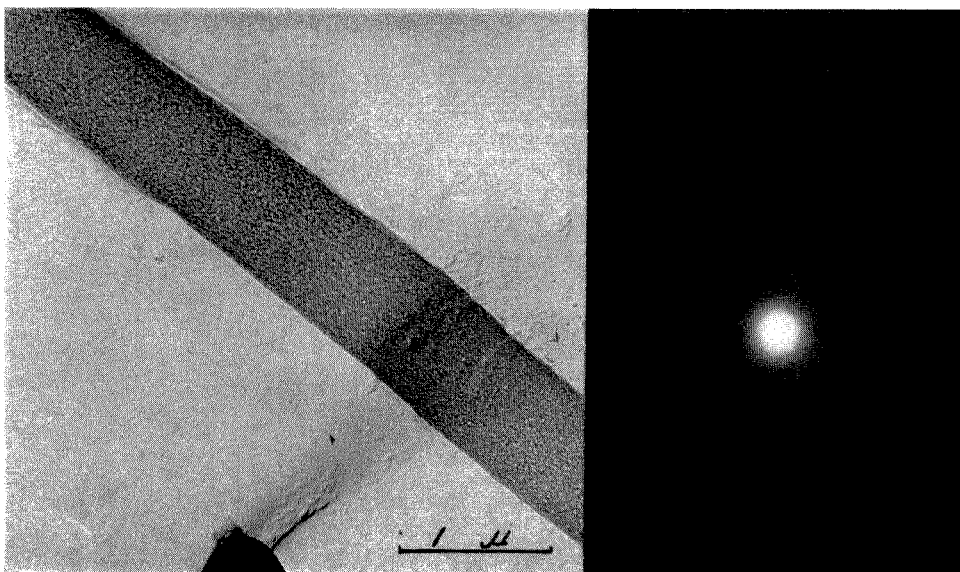


FIG. 9.—The crystal heated to 400°.

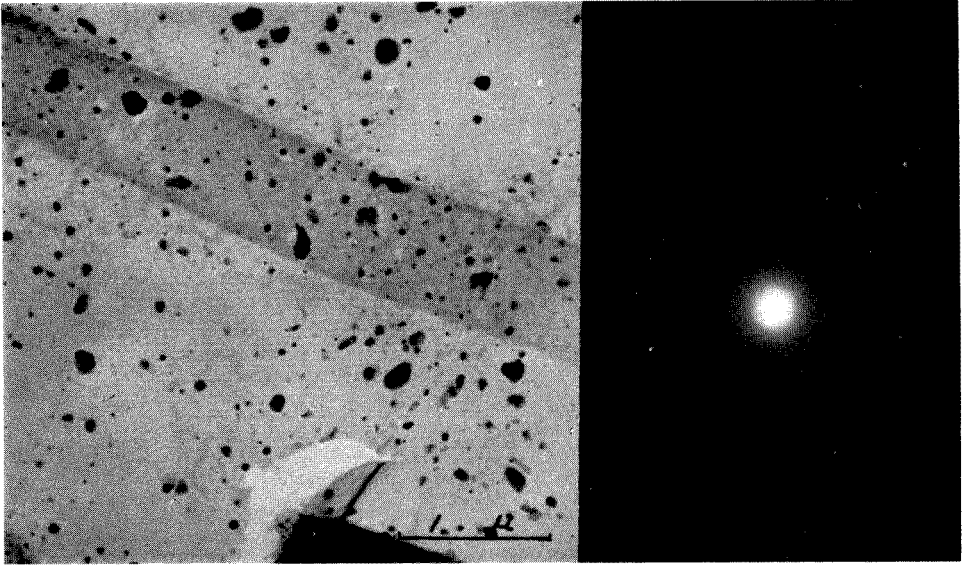


FIG. 10.—The crystal residue at 800°.

almost the same as at 120°. The crystal at 400° is shown in Fig. 9. Above 400° there appeared Debye-Scherrer diffraction rings from that part of the crystal shown in Fig. 9. Above 600° small particles appeared both on the original crystal and on the supporting film. At 800° there were numerous small particles on the supporting film and on the trace of the original crystal which was still observable as is shown in Fig. 10. The small particles were determined to be nickel oxide by a high-resolution diffraction technique.

Although nickel dimethylglyoximate sublimes above 250° at atmospheric pressure, it sublimes at a lower temperature in the electron microscope because the pressure is about 10^{-4} mm of mercury. The specimen holder, made of molybdenum, is electrically heated; the crystal is placed on the filmed grid held at the end of the specimen holder. Thus, because the temperature of the supporting film is somewhat lower than that of the holder, the sublimed substance seems to redeposit on the supporting film and is then decomposed to oxide forming the numerous small particles.

Acknowledgment—The authors acknowledge the partial assistance of the United States Atomic Energy Commission in supporting the investigation described herein under Contract AT(11-1)1582.

Zusammenfassung—Aus homogener Lösung gefällte Dimethylglyoximnickelkristalle sind gut ausgebildet und eignen sich zur mikroskopischen Untersuchung; der Kristall gehört zu D_{2h}^{26} . Die Kristalle werden als lange Nadeln mit rechteckigem Querschnitt gefällt. Die c-Achse liegt in Längsrichtung der Nadel; die kürzeste Achse ist die a- oder b-Achse.

Beim langsamen Erhitzen des Einkristalls im Elektronenmikroskop beginnt er bei 120°C unter Veränderungen in der Oberflächenstruktur zu sublimieren. Über 400°C erscheinen die Debye-Scherrer-Beugungsringe des gebildeten NiO.

Résumé—Les cristaux de diméthylglyoximate de nickel précipité à partir de solutions homogènes sont bien formés et conviennent à des études microscopiques; le cristal appartient à la série D_{2h}^{26} . Il précipite en solution sous forme de longues aiguilles avec une coupe rectangulaire. La direction du grand axe, c'est-à-dire la direction de la plus longue dimension du cristal est l'axe-c; la plus courte est alors orientée suivant l'axe b ou c. Quand un cristal unique est chauffé lentement au microscope électronique, il commence à se sublimer à 120°C et des changements apparaissent dans la structure de la surface. Au delà de 400°C, les anneaux de diffraction de Debye-Scherrer montrent que le cristal se change en oxyde de nickel.

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PRECIPITATION OF METAL CHELATES FROM HOMOGENEOUS SOLUTION

A REVIEW

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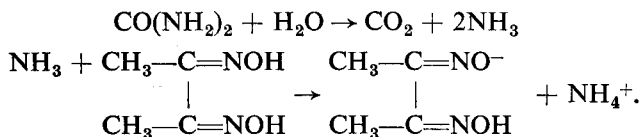
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Summary—The precipitation of metal chelates from homogeneous solution is reviewed.

SEVERAL recent review articles¹⁻⁵ have summarised the work in precipitation from homogeneous solution (PFHS). Nevertheless, a comprehensive survey of the precipitation of insoluble metal chelates by this technique is still not available. In the last few years a remarkable surge of interest has been demonstrated in this particular aspect of PFHS.

The first reported use of the precipitation of metal chelates from homogeneous solution was in 1952 by Bickerdike and Willard.⁶ Urea was hydrolysed to increase the pH gradually and precipitate nickel dimethylglyoximate:



This rather simple technique, the hydrolysis of urea, should have broad applications in this type of precipitation. Any metal chelate that is soluble in a low pH range, but insoluble in a higher pH range can be precipitated using this general method. The improved crystallinity of the precipitate should make filtration and washing much easier. Furthermore, the generally lower coprecipitation should be a distinct advantage over conventional methods of precipitation. Some typical coprecipitation results, obtained in the precipitation of zinc 8-hydroxyquinolate,²⁵ are compared in Table I.

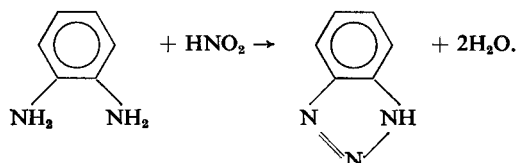
TABLE I.—COPRECIPITATION COMPARED USING HOMOGENEOUS AND CONVENTIONAL PRECIPITATION METHODS FOR PRECIPITATION OF ZINC 8-HYDROXYQUINOLATE²⁵ (ZINC TAKEN: 50.02 mg).

Diverse element taken (100 mg)	Method of precipitation	
	Homogeneous	Conventional
	Difference, mg	
Pb	+0.24	>57 >61
Ca	+0.06 -0.10	+0.33 +0.35
Mg	+0.12 -0.01	>41 >36

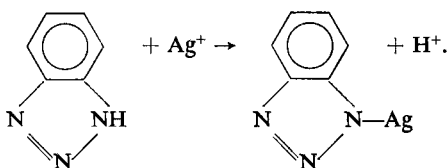
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An additional application was quickly demonstrated by Stumpf,⁷ who used the hydrolysis of urea to precipitate aluminium 8-hydroxyquinolate from an initially low pH solution.

The next important development occurred in 1955. Tarasevich⁸ reacted nitrous acid and 1,2-phenylenediamine in aqueous solution in the presence of either copper or silver:

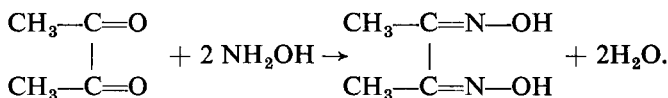


1H-benzotriazole was gradually formed and precipitated the insoluble chelates of copper and silver from homogeneous solution;



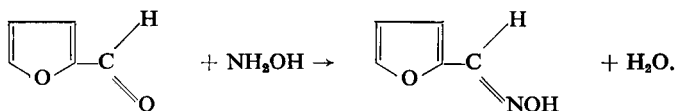
This was the first reported direct synthesis of an organic compound in aqueous solution to produce a PFHS. It opened the door to extensive investigation in this area.

Rather ironically, this type of reaction was used by Barnicoat⁹ in 1935, without being classified as PFHS. Nickel ions and hydroxylamine were reacted with the biacetyl in butter to synthesise and precipitate nickel dimethylglyoximate, thus determining biacetyl:



The significance of this type of precipitation was not recognised for 20 years.

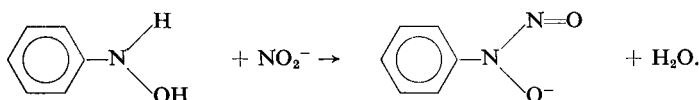
In 1959 two papers dealing with this type of precipitation^{10,11} appeared and since then the number of reports on this topic has steadily increased. Furfural and hydroxylamine were used by Pino Perez and coworkers¹⁰ to generate anin soluble palladium furfuraldoximate from homogeneous solution:



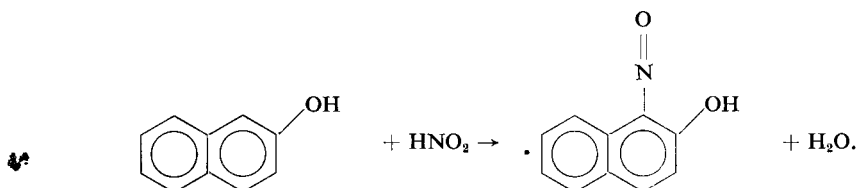
A preliminary report on the precipitation of nickel dimethylglyoximate¹¹ marked the first of a most informative series of papers by Gordon and coworkers. This process was developed independently, even though it was similar to the general scheme of Barnicoat. This paper also mentioned some preliminary work by Ramette, who used a complexation and replacement method to precipitate nickel dimethylglyoximate from homogeneous solution. This particular scheme should have a broad application, but no additional work using chelates in this general method has been published.

Three additional papers about nickel dimethylglyoximate^{12,13,14} and another concerning palladium dimethylglyoximate¹⁵ followed. Another advantage of precipitation from homogeneous solution was clearly demonstrated by this work because about 200 mg of nickel could be handled easily; the conventional precipitation is limited to about 50 mg of nickel. Nickel dimethylglyoximate obtained by PFHS has been subjected to electron microscopy studies.⁴⁶ Bark and Brandon⁴⁷ have recently precipitated palladium from homogeneous solution using the *in situ* synthesis of indane-1,2-dioxime.

Heyn and coworkers synthesised two other chelating agents *in situ*. Nitrite and phenylhydroxylamine were reacted to produce cupferron and precipitate the insoluble chelates of copper, iron and titanium from homogeneous solution:¹⁶

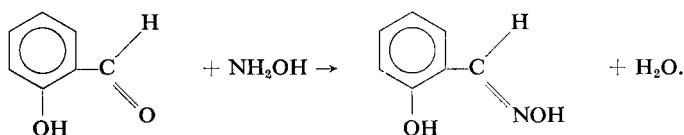


The action of nitrous acid with 2-naphthol produced a slow precipitation of cobalt 1-nitroso-2-naphtholate:¹⁷

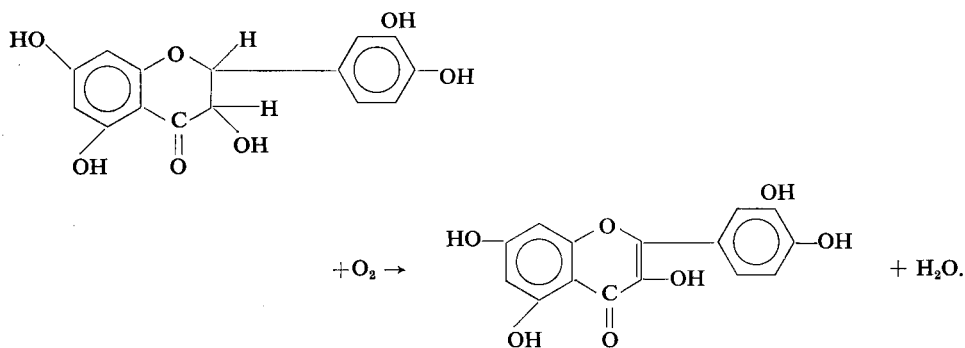


This precipitate is stoichiometric and can be weighed directly, while the conventional precipitate is contaminated and must be ignited to the oxide.

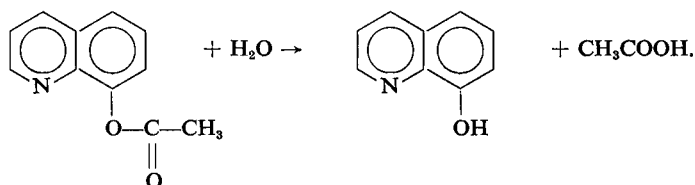
Pietrzak and Gordon¹⁸ precipitated copper salicylaldehyde oxime in the presence of copper:



Chan¹⁹ used the oxidation of 3,3',4',5,7-pentahydroxyflavanone (dihydroquercetin) in hot acid solution, exposed to air, to precipitate the insoluble tantalum and niobium 3,3',4',5,7-pentahydroxyflavonates from homogeneous solution:



The hydrolysis of esters to release the organic chelating agent in solution was the next important development. In 1960 an interesting sequence of papers by Gordon and coworkers dealing with the hydrolysis of 8-acetoxyquinoline began. The first was concerned with the preparation of the reagent:²⁰



This was followed by studies of the precipitation of thorium,²¹ aluminium,²² uranium,²³ magnesium²⁴ and zinc²⁵. Crystals formed in this way have been found useful⁴⁸ for infrared spectral studies.

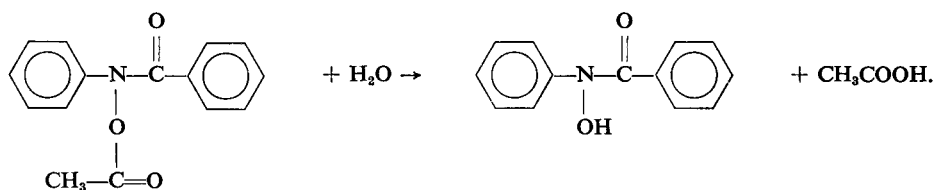
Bordner and Gordon have studied the thermogravimetric behaviour of uranium 8-hydroxyquinolates²⁶ that were precipitated from homogeneous solution.

Howick and Trigg also reported independently on the precipitation of aluminium 8-hydroxyquinolate²⁷ using the hydrolysis of 8-acetoxyquinoline.

The general results indicate that this hydrolysis scheme can be applied to the determination of many metals. The precipitates are easily handled and generally give improved separations.

Graham and coworkers have recently reported their study of the precipitation of thorium 8-quinoldate from homogeneous solution.²⁸ Apparently this ester is more troublesome to use than 8-acetoxyquinoline. Nevertheless, it should find applications in the determination of other metals.

A preliminary study has been reported by Gordon and coworkers²⁹ on the use of *N*-benzoylphenylhydroxylamine-acetate as a source of *N*-benzoylphenylhydroxylamine in order to precipitate copper slowly:



A most interesting development in this particular area of PFHS work has been several kinetic and mechanism studies. The slow processes involved are well suited to systematic studies of reactions. Salesin, Abrahamson and Gordon¹⁴ investigated the kinetics of the biacetyl and hydroxylamine reaction to form dimethylglyoxime in the presence and absence of nickel^{II} ions. Information about the nucleation process was also obtained. Howick and coworkers³⁰ have studied the effect of pH on the rate of hydrolysis of 8-acetoxyquinoline and 7-acetoxyquinoline. Wasmuth and Freiser³¹ have studied the effect of copper^{II} as a catalyst on the hydrolysis of 8-acetoxyquinoline.

The cocrystallisation of ultramicro quantities (10⁻⁸ g/ml or less) of iron and other elements with 8-hydroxyquinoline formed homogeneously in solution by the hydrolysis of 8-acetoxyquinoline was studied by Weiss and Shipman.³² The cocrystallisation of iron in trace amounts with the precipitated organic chelate appears to follow the Doerner-Hoskins equation.

All of the above methods prepare or release the organic chelating agent directly in solution. These methods represent a "bridge" between two formerly distinct areas of chemistry, organic synthesis and "wet" analytical precipitation. Many of the problems of both techniques must be solved in order to make these methods succeed. The synthesis of rather complex organic molecules in aqueous solution containing metallic ions, often at a fixed pH value, poses some rather challenging problems. Nevertheless, the success that has already been achieved strongly indicates that many more of these *in situ* methods are possible.

A related approach involving insoluble metal chelates has been progressing at a somewhat slower pace. This general scheme consists of adding all of the reagents, including the chelate, into solution, then inducing some change that will cause a precipitate to form from homogeneous solution. Bickerdike and Willard⁶ originally

TABLE II.—DIRECT SYNTHESIS METHODS FOR PRECIPITATION OF METAL CHELATES FROM HOMOGENEOUS SOLUTION

Compound formed	Reagents used	Metals determined, mg	Other metals present, mg	Coprecipitated error mg	Reference
1H-Benzotriazole	1,2-Phenylenediamine, HNO ₂	Cu —	—	—	8
N-Benzoylphenylhydroxylamine	N-Benzoylphenylhydroxylamine acetate, H ₂ O	Ag —	—	—	8
		Cu 20.4	Co 75	+0.1	29
Cupferron	Phenylhydroxylamine, NO ₂ ⁻	Cu —	—	—	16
		Fe —	—	—	16
		Ti —	—	—	16
Dimethylglyoxime	Biacetyl, NH ₂ OH	Ni 39.3	Co 40	±0.1	9, 11, 12, 13, 14
		Pd 24.3	Pt 100	+0.2	15
		Pd 28.5	Pt 20	+0.3	10
8-Hydroxyquinoline	8-Acetoxyquinoline, H ₂ O	Th 35	—	—	28
8-Hydroxyquinoline	8-Acetoxyquinoline, H ₂ O	Al 25.67	Mg 300	+0.1	22, 27
		Mg 12.84	Ba 200	+1.6	24
		Th 50.3	Ce 250	+0.18	21
		U 28.0	Pb 24	0.0	23
		Zn 50.02	Pb 100	+0.24	25
		Co 50.0	—	—	17
1-Nitroso-2-naphthol 3:3':4':5':7-Pentahydroxyflavone	2-Naphthol, HNO ₂ 3:3':4':5':7-Pentahydroxyflavanone, air	Nb 20	Zr 60	+0.3	19
		Ta 20	Zr 60	0.0	19
Salicylaldehyde	Salicylaldehyde, NH ₂ OH	Cu 43.01	Ni 100	+0.13	18

used this technique, changing the pH with the hydrolysis of urea, to induce precipitation. Recently two other applications of urea hydrolysis have been developed. Heyn and Finston³³ have studied magnesium 8-hydroxyquinolate and Kosta and Dular³⁴ have investigated niobium 8-hydroxyquinolate.

Several fundamental means of inducing a change, that will cause a precipitate to form from homogeneous solution, have been recently introduced. Howick and

coworkers used a water-miscible organic solvent system to make the original solution, containing all of the reagents, clear and uniform. Upon volatilisation of the organic solvent, precipitation occurs as the metal chelate gradually becomes more insoluble in the more water-like media. The insoluble 8-hydroxyquinolates of aluminium,^{35,36} nickel,³⁷ magnesium,³⁸ copper³⁹ and uranium⁴⁴ have been precipitated by this technique, as well as nickel dimethylglyoximate.⁴⁵

Another general volatilisation procedure has been introduced. Firsching and coworkers have used the volatilisation of a complexing agent, ammonia, to release metal ions gradually in solution and thus precipitate insoluble metal chelates. Results with the 8-hydroxyquinolates of cobalt,⁴⁰ zinc and cadmium^{41,42} have been reported. The precipitation of other 8-hydroxyquinolates as well as nickel dimethylglyoximate and copper 1-benzoinoximate using the volatilisation of ammonia has been mentioned.⁴³

TABLE III.—PRECIPITATION OF METAL CHELATES FROM HOMOGENEOUS SOLUTION BY METHODS OTHER THAN SYNTHESIS

Chelate used	Precipitation induced by	Metals determined, <i>mg</i>	Reference
1-Benzoinoxime	Volatilisation of ammonia	Cu 32	43
Dimethylglyoxime	Hydrolysis of urea	Ni 100	6
	Complexation and replacement	Ni —	11
	Volatilisation of ammonia	Ni 29	43
8-Hydroxyquinoline	Hydrolysis of urea	Al 25	7
	Volatilisation of organic solvent	Al 10.06	35, 36
	Volatilisation of ammonia	Cd 57.3	41, 42
	Volatilisation of ammonia	Co 29	40
	Volatilisation of organic solvent	Cu 30	39
	Volatilisation of ammonia	Cu 32	43
	Hydrolysis of urea	Mg 68.59	33
	Volatilisation of organic solvent	Mg 13.35	35, 38
	Volatilisation of organic solvent	Ni 30	37
	Volatilisation of ammonia	Ni 29	43
	Hydrolysis of urea	Nb 70	34
	Volatilisation of ammonia	Zn 32.9	41, 42

The hydrolysis of urea to increase pH, the volatilisation of organic solvents to make the solution more water-like, and the volatilisation of a complexing agent to release cations in solution, are all relatively simple techniques that should find numerous applications in precipitation and separation work.

Tables II and III summarise the work on the precipitation of metal chelates from homogeneous solution.

The area of precipitation from homogeneous solution involving insoluble metal chelates has been expanding steadily. Further work in this promising field should provide additional fruitful results.

Zusammenfung—Es wird eine Übersicht der Fällung von Metallchelatverbindungen aus homogener Lösung gegeben.

Résumé—On passe en revue la précipitation en solution homogène de métaux contenus dans des chélates métalliques.

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COMPLEXOMETRIC TITRATION OF YTTRIUM AND THE LANTHANONS—I

A COMPARISON OF DIRECT METHODS

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Summary—A comparison is made of a number of direct complexometric titrations previously published for the determination of yttrium and the lanthanons. Working and 'optimum' pH ranges are obtained for what are considered to be the best indicators, Alizarin Red S screened with Methylene Blue, Eriochrome Black T, Copper-Naphthyl Azoxine and Xylenol Orange. The precision and accuracy of the selected methods are determined by carrying out replicate titrations on standard solutions of cerium^{III}, yttrium and ytterbium. The results, together with additional observations made on the behaviour of indicators in the different methods, suggest that Xylenol Orange at pH 5.8 to 6.4 is most satisfactory and convenient for direct titrations.

COMPLEXONES, in particular ethylenediaminetetra-acetic acid (EDTA) and its salts, have been widely applied to the titrimetric determination of yttrium and the lanthanons using visual internal indicators. Methods which have been recommended can be divided into two groups, depending on whether the metal ion in solution is titrated directly with EDTA, or whether a back-titration procedure is used. The direct titration has obvious advantages but the accuracy attainable in such procedures is not always appreciated and back-titration methods are sometimes recommended or used when they need not be. Further, direct methods have not been reviewed critically, and adequate grounds for making a satisfactory choice of method for a particular purpose are often lacking. An attempt, described here, has been made to compare a number of indicators and buffer systems previously recommended by different authors for such titrations. Relevant information pertaining to these systems is collected and summarised in Table I.

With the exception of Naphthyl Azoxine S, [7-(6-sulpho-2-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid], and SNAZOXS, [7-(4-sulpho-1-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid], all of the indicators referred to in the table were examined. From the account in the original papers, these indicators are used and behave in exactly the same way as does Naphthyl Azoxine, [7-(1-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid], which was therefore selected to represent methods 5, 6 and 7 in the investigation.

Preliminary titrimetric work showed that Arsenazo, [3-(2-arsenophenylazo)-4,5-dihydroxy-2,7-naphthalene disulphonic acid, trisodium salt] and Bromopyrogallol Red, [dibromopyrogallolsulphonephthalein] were decidedly less satisfactory as indicators than the others referred to in Table I. Arsenazo was found to be very pH sensitive, end-points were somewhat erratic at constant pH, and the colour change left much to be desired. With Bromopyrogallol Red the colour contrast

was rather poor, and end-points were somewhat unpredictable and sluggish, particularly at metal ion concentrations greater than about $5 \times 10^{-4}M$. End-points were sluggish irrespective of whether titrations were performed into hot or cold solutions. The relatively poor performance of this indicator has previously been commented upon by Asensi Mora,¹² who suggested Pyrocatechol Green (3,6-dihydroxy-9-*o*-sulphophenylfluorene-4,5-quinone) instead. [Because of the considerable errors quoted (*ca.* 1%) for light lanthanon determinations using the latter indicator, no attempt was made here to compare it with other indicators].

Cerium, yttrium and ytterbium were selected to represent the main groups of rare earths (excluding scandium), and a study was made of the indicator colour change

TABLE I.—SUMMARY OF METHODS PREVIOUSLY RECOMMENDED FOR THE DIRECT TITRATION OF YTTRIUM AND THE LANTHANONS

Indicator	Titration conditions	Colour change	Refs.
1. Alizarin Red S (C.I. 1034) screened with Methylene Blue	pH 4, CH ₃ COONH ₄ buffer in hot soln.	red → grey → green	1, 2
2. Arsenazo	pH 5.0–6.5, pyridine buffer in hot soln.	violet → orange-red	3
3. Bromopyrogallol Red	CH ₃ COONH ₄ buffer in the cold	blue → red	4
4. Eriochrome Black T (Solochrome Black T; C.I. 203)	(a) pH 8–9 in boiling tartrate or citrate soln. (b) TEA at pH 7	red → blue	5 5, 6
5. Naphthyl Azoxine	pH 5.5–6.5 with Cu present; CH ₃ COONH ₄ or pyridine buffer	yellow → red	7
6. Naphthyl Azoxine S	As for 5	as for 5	8
7. SNAZOXS	pH 6 with Cu present; pyridine buffer	yellow → red	9
8. Xylenol Orange ^α	(a) Acetate buffer pH 5 + 1 drop pyridine (b) pH 4.5–6 with hexamine buffer	red → yellow	10 11

^α 3,3'-bis-[*N,N*-di(carboxymethyl)-aminomethyl]-*o*-cresolsulphonophthalein.

at the end-point, precision, accuracy, buffering and working pH range applicable to each of the remaining methods (1, 4, 5 and 8) in Table I.

EXPERIMENTAL

Standard solutions

Cerium^{III}: A 0.05M solution was prepared by dissolving 27.4 g of analytical-grade ammonium nitratocerate IV in water, reducing with hydroxylamine hydrochloride and diluting to 1 litre with water and a little nitric acid. It was standardised by precipitating as cerium^{III} oxalate, igniting and weighing as CeO₂.¹³

Yttrium and ytterbium: 0.05000M solutions were prepared by dissolving 5.646 and 9.852 g of their respective trioxides (from L. Light and Co., England, 99.9% pure) in separate 20-ml portions of concentrated hydrochloric acid and diluting each to 1 litre with water.

Standard 0.01M solutions of cerium^{III}, yttrium and ytterbium were prepared by dilution of the above solution.

Zinc: A 0.1M solution was prepared from a weighed quantity of analytical-grade granulated zinc dissolved in a slight excess of dilute hydrochloric acid. Before weighing, the zinc was stirred with very dilute hydrochloric acid to remove surface oxide, washed well with water, alcohol and ether and dried at 50°.

Copper^{II}: A 0.005M copper nitrate solution was prepared from analytical-grade hydrated copper^{II} nitrate in water.

EDTA: A 0.1M solution was prepared by dissolving about 37 g of analytical-grade $C_{10}H_{14}O_8N_2Na_2 \cdot 2H_2O$ in 1 litre of water. It was shown to be 0.1005M by standardising against the 0.1M zinc solution using Zincon, (2-carboxy-2'-hydroxy-5'-sulphoformazybenzene), as indicator.¹⁴ 0.01M EDTA solutions used in the titrimetric work were prepared by diluting this stock solution with water.

Buffer solutions

For pH values within the range 4.5–6.5, 0.2M acetic acid and 0.2M sodium acetate solutions were mixed in the calculated ratios. For values within the range 6.5–8.0 a 10% solution of hexamethylenetetramine was added in the appropriate amount to the solution to be titrated. In titrations with Eriochrome Black T, triethanolamine (TEA) was used to raise the pH initially, and ammonium acetate was added for additional buffering as required. Buffer pH 10 was made from 570 ml of aqueous ammonia (sp. gr. 0.88) and 70 g of ammonium chloride made up to 1 litre with water.

Indicators

Chemical indicators were obtained either from British Drug Houses, England (B.D.H.) or Hopkin and Williams, England (H.W.) and were used as supplied.

Alizarin Red S screened with Methylene Blue (H.W.): 45 ml of 0.5% ammonium alizarin sulphionate were mixed with 15 ml of 0.1% methylene blue in water.

Arsenazo (B.D.H.): 0.5% in water.

Bromopyrogallol Red (B.D.H.): 0.05% in 1:1 (v/v) ethanol-water mixture.

Eriochrome Black T (B.D.H.): (a) 1% in 1:1 (v/v) ethanol-triethanolamine mixture, or (b) 0.5 g of indicator and 4.5 g of hydroxylamine hydrochloride made up to 100 ml in ethanol.

Naphthyl Azoxine (H.W.): 1% in dimethylformamide.

Xylenol Orange (B.D.H.): 0.1% in 1:1 (v/v) ethanol-water mixture.

Zincon (H.W.): 0.13 g of indicator dissolved in 2 ml of 0.1M sodium hydroxide and diluted to 100 ml with water.

Selection of optimum titration conditions

Five-ml samples of the standard 0.01M rare earth solutions, under varying buffer conditions and in a final volume of about 50 ml were titrated with 0.01M EDTA. Approximate upper and lower pH limits within which the indicator could be expected to function were determined by taking a titrated metal-containing sample and with the aid of a pH meter noting the values when the indicator showed a significant pH response on raising or lowering the pH. pH values of solutions to be titrated were set with the appropriate buffers around the crude limits thus obtained, and titrations were performed, end-points and colour changes being noted. In this way pH ranges were established within which the titration could be carried out with little uncertainty about the end-point, although colour changes might not be the best attainable with the indicator. Optimum conditions of pH were then determined by performing titrations within this range. All pH measurements were made at 20 to 25°.

Tests on the precision and accuracy of the various methods were made by carrying out replicate titrations (10 for each method with each metal ion) on 25-ml portions of 0.01M metal solutions in a total volume of 250 ml under optimum pH conditions. As a measure of the dispersion of titre values about the mean for each series, the standard deviation was determined. The mean titres were compared with the required calculated titres. The same burette and pipette (both grade A) were used throughout in these titrations. Dilutions of stock rare earth and EDTA solutions were made with the pipette mentioned, and with two standard flasks, all three of which were intercalibrated.

In all titrations involving cerium, a reducing agent was present. Hydroxylamine hydrochloride and ascorbic acid were equally satisfactory for this purpose.

RESULTS AND DISCUSSION

Working and optimum pH ranges are recorded in Table II for each of the three metal ions, with each of the four indicators and buffering systems compared. The pH ranges applicable to a particular indicator do not vary greatly from metal to metal titrated, a fact of use in determining mixed rare earths, excluding scandium. Table III permits comparison between required and experimental titres, and of standard deviations. It will be seen that all of the four methods are, in general, capable of giving quite precise and accurate results.

Alizarin S screened with methylene blue is quite satisfactory for light and middle lanthanon fractions, as recommended in the original paper,¹ but the results presented here suggest that it would give slightly early end-points in the titration of heavy rare earths. The titration is best performed in near boiling solution, otherwise the end-point approach is quite slow.

Eriochrome Black T should be suitable for titrating the lanthanons and yttrium in the pH range indicated in Table II with reliable results (*cf.* references 5 and 6). If desired, the pH can be adjusted by adding 1 drop of 1% methyl red indicator to the metal solution and raising the pH to the colour change with TEA before adding the metal indicator. Ammonium acetate may be added for additional buffering.

TABLE II.—WORKING AND "OPTIMUM" (IN PARENTHESIS) pH RANGES FOR TITRATIONS

Indicator	pH range		
	Ce ^{III}	Y	Yb
Screened Alizarin Red S	4.5-5.5 (4.7-5.3)	4.6-5.5 (4.7-5.3)	4.6-5.5 (4.7-5.4)
Eriochrome Black T	6.5-7.5 (6.7-7.2)	6.5-7.5 (6.7-7.2)	6.5-7.5 (6.7-7.2)
Naphthyl Azoxine	5.4-7.6 (5.5-6.0)	5.3-7.6 (5.5-6.0)	5.4-7.6 (5.5-6.0)
Xylenol Orange	5.0-6.5 (5.8-6.4)	5.1-6.5 (5.8-6.4)	5.1-6.6 (5.8-6.4)

The colour change is then from red to greenish-blue. There is no advantage in performing titrations in hot rather than cold solution. Indeed, evidence was obtained indicating that the end-point came early in titrating ytterbium in hot solution. The end-point reading should be taken when all reddishness has just permanently disappeared from the solution.

Although Eriochrome Black T can be used up to about pH 9.3, end-points are attained only very slowly above pH 8 in hot solution with TEA, citrate or tartrate being present to prevent hydrolysis of the metal ions. For this reason, titrations in the presence of citrate or tartrate at pH 8-9 (Table I) are not recommended.

In titrations with Naphthyl Azoxine, end-point detection results from indicator-copper-EDTA interaction. The standard deviation is caused by a combination of the dispersions in the lanthanon + copper titre and the copper titre alone. The necessity for a blank titration on the copper alone makes this method little more attractive than a back-titration. However, an advantage is that titrations are performed in the cold. The indicator is quite sensitive, but, because the colour contrast is not all that might be desired, for best results it is useful to have a flask containing a titrated solution standing near for colour comparison. Better end-points are also obtained by adding the copper towards the end of the titration rather than just before the beginning.

As is seen from Table III, Xylenol Orange gives accurate, and also very precise, titres. Of the indicators examined for the direct titration it is, in our opinion, the most satisfactory. The titration can be performed in the cold, but the end-point can be approached more quickly in warm solution. Preliminary pH adjustment of

acid solutions can be made by adding 1 drop of 0.1% Thymol Blue indicator, then aqueous ammonia until the indicator is about to change to yellow. Addition of buffer then gives optimum titrating conditions. Care is needed when hexamethylenetetramine is used as buffering agent, because addition of too much will raise the pH above the titration range. It may also be noted that there is a discrepancy between the previously recommended pH range for this titration (Table I) and the range found to be satisfactory in this work (Table II).

TABLE III.—“REQUIRED” AND MEAN TITRES OBTAINED UNDER “OPTIMUM” pH CONDITIONS ON TITRATING 25 ml OF STANDARD 0.01M METAL ION WITH 0.01005M EDTA (STANDARD DEVIATIONS IN PARENTHESES)

Indicator	Titre, ml of 0.01005M EDTA					
	Ce ^{III}		Y		Yb	
	Required	Found	Required	Found	Required	Found
Screened Alizarin Red S	24.82	24.82 (0.02)	24.88	24.88 (0.02)	24.88	24.83 (0.02)
Eriochrome Black T	24.82	24.83 (0.02)	24.88	24.91 (0.02)	24.88	24.86 (0.03)
Naphthyl Azoxine	24.82	24.83 (0.02)	24.88	24.89 (0.02)	24.88	24.87 (0.03)
Xylenol Orange	24.82	24.82 (0.01)	24.88	24.90 (0.01)	24.88	24.87 (0.01)

Of the commoner anions, chloride, nitrate, perchlorate and sulphate (at least up to 1M) do not interfere in these methods, but acetate interferes in concentrations above 1M, and solutions containing oxalate cannot be titrated satisfactorily by direct methods.

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Zusammenfassung—Eine Anzahl früher für die Bestimmung von Yttrium und den Lanthaniden publizierter direkter komplexometrischer Titrationsmethoden wurden verglichen. Die besten pH-Arbeitsbereiche für die wahrscheinlich besten Indikatoren, Alizarin S mit Methylenblau, Eriochromschwarz T, Cu-Naphthylazoxin und Xylenolorange wurden aufgesucht. Genauigkeit und Richtigkeit der Methode wurden mit mehreren Titrationen an Standardlösungen von Cer(III), Yttrium und Ytterbium ermittelt. Die Ergebnisse sprechen zusammen mit weiteren Beobachtungen über das Verhalten von Indikatoren bei den verschiedenen Methoden dafür, daß Xylenolorange bei pH 5,8 bis 6,4 in direkten Titrationen am zufriedenstellendsten und bequemsten arbeitet.

Résumé—On fait la comparaison des titrations complexométriques directes pour le dosage de l'yttrium et de les lanthanons. On décrit aussi les meilleures conditions pour l'emploi des indicateurs choisis.

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COMPLEXOMETRIC TITRATION OF YTTRIUM AND THE LANTHANONS—II*

METHODS FOR THEIR DETERMINATION IN OXALATES

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Summary—Complexometric methods for the determination of yttrium and the lanthanons in oxalate precipitates are investigated. In the method recommended, excess EDTA is added to a suspension of the oxalate, and solution is effected at pH 10 with ammonia-ammonium chloride buffer. The excess EDTA is titrated with standard zinc solution to the blue to red colour change of Eriochrome Black T indicator. It is more convenient, and generally more satisfactory, than the method previously suggested, in which magnesium is the back-titrant at pH 10.2 to 10.5. Both of these methods are superior to the back-titration with lanthanum using Arsenazo as indicator at pH 8 to 9 in the presence of oxalate, and more convenient than methods in which the oxalate is removed by wet oxidation before titrating directly with EDTA. The zinc titration method is particularly suitable for chemical-yield measurement in radiometric determinations of yttrium and lanthanons precipitated as oxalates for "counting" purposes.

OXALIC acid is commonly used to precipitate yttrium and the lanthanons (including lanthanum) from acid solution, and separations from other metal ions can frequently be made in this way.¹ Because of the variable composition of the product, it is usual in classical quantitative analysis to ignite the resulting precipitate to the metal oxide^{1,2} or to determine the metal indirectly by permanganate titration of the oxalate.^{1,2} The former method is slow, and the latter depends on being able to obtain a constant and known ratio of metal to oxalate in the precipitate; in any case, it cannot be used satisfactorily for cerium without prior separation of the metal.³

For isotope-dilution analysis, particularly of fission-product yttrium and lanthanons, using an end-window proportional or Geiger-Müller counter, Ballou⁴ showed that chemical yields could be measured to within a few per cent by direct weighing of the metal oxalate, precipitated and dried under carefully controlled conditions. However, with demands for improved accuracy, and accumulation of information on the thermal instability⁵ of the hydrates of these metal oxalates, it is more recent practice to ignite the oxalate to the oxide, and from this to prepare a solid radioactive "source" for counting.^{6,7} The last-mentioned operation is not without its difficulties if a uniform "source" of moderate thickness, reproducible geometry and known composition is to be obtained from the oxide. Probably the most convenient general method of preparing a solid "source" for radiometric work is to precipitate a stoichiometric chemical compound containing the radioactive isotope,

* Part I: see reference 15.

collect by filtration on a filter-disc of well defined geometry, and dry. Oxalate is the most frequently used precipitant for yttrium and the lanthanons and, by such a procedure, gives a deposit which, apart from its composition, is satisfactory. (For example, 8-hydroxyquinoline gives gelatinous deposits which shrink and crack excessively during the drying process). It is not expected that the variation in composition (amounting to perhaps 5% in terms of metal present) encountered in these oxalate precipitates will affect corrections for self-absorption of radioactivity, but in order to measure chemical yields a simple and reliable method is desirable for determining the metal content directly. Such a "direct" method would also have advantages in determining rare earth contents of oxalate precipitates generally.

Complexometric titration offers considerable scope for performing such analyses. Because oxalate interferes in the direct titration of yttrium and the lanthanons with EDTA, it must be destroyed or otherwise removed before the titration. This can be done by wet-oxidation methods; or by decomposition with alkali⁸ and separation by filtration; the latter is a process too slow to merit serious consideration for routine purposes. An alternative method is that described by Misumi and Taketatsu,⁹ in which the precipitate is dissolved in an excess of EDTA and the excess is back-titrated with magnesium at pH 10.2–10.5. In the work to be described, both approaches have been used; and in addition the use of zinc in place of magnesium in the back-titration is investigated. Another back-titration method, previously used¹⁰ in the absence of oxalate, in which the excess EDTA is back-titrated at pH 8–9 with lanthanum and Arsenazo indicator, has been examined for determinations in the presence of oxalate. Some oxalates have been prepared, and the metal contents have been determined.

EXPERIMENTAL

Reagents

Magnesium: A 0.01M solution was prepared from analytical-grade $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and was standardised with EDTA using Eriochrome Black T indicator.¹¹

Lanthanum: A 0.01M solution was prepared from reagent-grade hydrated lanthanum chloride (British Drug Houses, England), and was standardised with EDTA, using Xylenol Orange indicator.

Praseodymium: A 0.01M solution was prepared by weighing out an appropriate quantity of the trioxide (L. Light & Co., England, 99.9% pure) and dissolving in a minimum of hydrochloric acid.

Eriochrome Black T Indicator was prepared by method (b).¹⁵

All other reagent solutions were prepared as described previously.¹⁵

Titration of yttrium and lanthanum oxalates without prior removal of oxalate

To a 5-ml portion of each metal in solution a measured excess of standard EDTA (10 ml) was added, and the excess was determined by titrating in a total volume of 50 ml with either 0.01M magnesium or 0.01M zinc solution to a colour change from blue to red with Eriochrome Black T indicator. The titrations were repeated with the addition of an amount of oxalate calculated to be sufficient for precipitation of all of the metal ion. As recommended in the original procedure for magnesium, the solution to be titrated was buffered between pH 10.2 and 10.5, using buffer pH 10 and aqueous ammonia, and with the assistance of a pH meter. Buffer pH 10 provides adequate buffering and control of pH for titrations with zinc.

When lanthanum was used as back-titrant in conjunction with Arsenazo as indicator, the pH was adjusted using ammonium chloride and buffer pH 10, with the aid of a pH meter or phenolphthalein indicator as recommended by Wolfsberg.¹⁰ The solution, total volume about 50 ml, is brought almost to boiling and titrated with lanthanum until the indicator changes from pink to violet.

For freshly prepared oxalate precipitates addition of buffer and the excess EDTA is sufficient to cause rapid solution. However, precipitates filtered off, dried by the method described by Ballou or above 100°, and kept for some time, are somewhat more resistant to dissolution. Such "aged" precipitates are conveniently dissolved by first treating with a little dilute perchloric or hydrochloric acid, adding the EDTA, neutralising with aqueous ammonia, then buffering as required.

Analysis of weighed oxalate samples

Using Ballou's method⁴ suitably scaled up, batches of about 50 mg of each rare earth studied were precipitated as oxalate. The precipitate was split up into portions having weights ranging from about 5–65 mg, and each portion was collected on a glass-fibre disc (Whatman GF/A, 2.1 cm. diameter) in a demountable filter stick, washed with water, ethanol and finally ether, and was then dried to constant weight in a vacuum desiccator (without desiccant) connected to a water-pump.

For wet oxidation, the weighed oxalate sample, together with the glass-fibre support, was transferred to a 250-ml conical flask and treated with 5 ml of 72% perchloric acid. The temperature was maintained at the decomposition point of the acid for 10–15 min, depending on the sample size. (The time required for oxidation of different sample weights is determined in trial runs by the method suggested by Smith.¹²) The flask was cooled, the contents were diluted to about 25 ml and the acid was neutralised with ammonia to the yellow colour change of Thymol Blue. After buffering at pH 6 and addition of water to a final volume of about 150 ml, the contents of the flask were titrated with EDTA, using Xylenol Orange indicator.

Batches of metal oxalate prepared as described above were also analysed for metal content by the back-titration method without removal of oxalate, using zinc as titrant. About 5–10 ml of 0.01M EDTA in excess of that required to complex the metal ion was added before each titration.

RESULTS AND DISCUSSION

Table I records results obtained on titrating known amounts of yttrium and various lanthanons by the methods which do not require removal of oxalate ion. They may be compared with results obtained by titrating directly with EDTA the same amounts of metal ion, in the absence of oxalate, using Xylenol Orange indicator (column 2, Table I). It will be seen that both magnesium and zinc as back-

TABLE I.—DETERMINATION OF YTTRIUM AND SOME LANTHANONS BY VARIOUS TITRATION PROCEDURES^a

Element	Amount present, ^b mg	Amount found by back-titration, mg		Back-titrant
		Oxalate absent	Oxalate present	
La	6.95	—	6.96 ± 0.02	Zn
Ce	6.94	6.95 ± 0.02	6.97 ± 0.02	Mg
		6.96 ± 0.02	6.96 ± 0.02	Zn
Pr	4.86	—	4.86 ± 0.02	Zn
Y	4.43	4.41 ± 0.02	4.39 ± 0.02	Mg
		4.43 ± 0.01	4.43 ± 0.01	Zn
Yb	8.65	8.63 ± 0.02	8.62 ± 0.02	Mg
		8.65 ± 0.01	8.64 ± 0.01	Zn
		—	8.58 ± 0.02	La

^a In each case the mean value and standard deviation of 5 determinations.

^b Determined by titration using Xylenol Orange at pH 6 in the absence of oxalate.

titrants give highly satisfactory results. On the other hand, the colour contrast with Arsenazo in back-titrations with lanthanum in the presence of oxalate is rather poor, and the end-point is sluggish and drawn out, making the true equivalence point somewhat difficult to determine. In addition, the titration is performed in very hot solution, whereas titration with magnesium or zinc is carried out in the cold using Eriochrome Black T indicator. Of the two last mentioned titrants, zinc is preferred, because it can be used over a wide pH range (9 to 11) and the colour change is appreciably sharper. Although the relative stability constants¹³ of the EDTA complexes of lanthanum and zinc are such that the former is a little less stable than

the latter, results for lanthanum determination using zinc as titrant are not affected (Table I).

In Table II, the percentage metal found in oxalate samples of different weights varies over a range of 2–3% for some batches of precipitate. This variation is probably largely associated with the washing, which is done on separate portions of the batch, and with the final drying. However, in rare earth oxalate precipitation many factors contribute to variable composition,^{2,14} and hence to the various hydrates reported by different investigators.^{4,5,8} The desirability of determining the metal

TABLE II.—ANALYSIS^a OF WEIGHED OXALATE SAMPLES FOR METAL CONTENT^b

1. Wt. of sample, mg	Y found, %	2. Wt. of sample, mg	Ce found, %
14.41	29.4	10.91	39.5
14.60	29.8	11.32	39.7
17.63	29.8	23.24	39.4
26.28	29.7	25.41	38.1
32.42	29.7	27.20	38.3
Mean	29.7	Mean	39.0

3. Wt. of sample, mg	Ce found, %	4. Wt. of sample, mg	Yb found, %
4.53	38.2	14.73	51.3
7.11	38.9	29.81	49.0
9.71	38.4	30.30	49.5
15.16	38.3	47.32	48.4
21.93	39.0	63.66	50.0
Mean	38.6	Mean	49.6

^a Batches 1 and 2 were analysed by wet oxidation of the oxalate followed by direct titration with EDTA, 3 and 4 by adding excess EDTA and back-titrating with zinc.

^b $Y_2(C_2O_4)_3 \cdot 9H_2O$ requires 29.44% of Y.

$Ce_2(C_2O_4)_3 \cdot 10H_2O$ requires 38.68% of Ce.

$Yb_2(C_2O_4)_3 \cdot 5H_2O$ requires 49.42% of Yb.

content of an oxalate, rather than assuming a formula and calculating the content from the sample weight for the purpose of determining radiochemical yields, is thus obvious, because there may easily be a 5 or 6% variation in the amount of metal in the compound.

Both methods for which results are presented in Table II are satisfactory for the determination of yttrium and lanthanons in oxalate precipitates in the range 2–30 mg of metal; and with suitable scaling up they can be used equally satisfactorily on larger samples. However, oxidation of oxalate with perchloric acid requires nearly 20 min in all to complete a determination, compared to 3–5 min for the back-titration with zinc, all solutions and reagents being to hand. Other oxidants (nitric acid, *aqua regia* and alkaline hypochlorite or hypobromite) are somewhat less effective and slower than perchloric acid. Sulphuric acid could, however, probably replace the last mentioned oxidant without adding to the time required for complete oxidation. Addition of excess EDTA, and back-titration of the sample with zinc solution in the presence of oxalate ion, therefore has an appreciable advantage over complexometric titration methods requiring removal of oxalate.

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Zusammenfassung—Komplexometrische Methoden für die Bestimmung von Yttrium und den Lanthaniden in Oxalatniederschlägen wurden untersucht. In der empfohlenen Methode wird überschüssige EDTA zu einer Suspension des Oxalats gegeben und die Lösung Ammoniak-Ammonchloridpuffer auf p_H 10 gebracht. Die überschüssige EDTA wird mit eingestellter Zinklösung bis zum Farbumschlag blau/rot von Eriochromschwarz T titriert. Die Methode ist bequemer und um allgemeiner zufriedenstellender als die früher vorgeschlagene⁹, in der Magnesium bei p_H 10,2 bis 10,5 zur Rücktitration verwendet wird. Beide Methoden sind der Rücktitration bei p_H 8 bis 9 in Gegenwart von Oxalat mit Lanthan und Arsenazo als Indikator überlegen und bequemer als Methoden, in denen Oxalat vor der direkten Titration mit EDTA durch nasse Oxydation entfernt wird. Die Zinktitrationmethode ist besonders geeignet für die Messung der chemischen Ausbeute zu Zählzwecken bei radiometrischer Bestimmung von als Oxalat gefällten Lanthaniden und Yttrium.

Résumé—On décrit les meilleures conditions pour le dosage de l'yttrium et de les lanthanons au moyen de l'oxalate. Deux méthodes choisies sont supérieures aux les méthodes déjà décrites où l'on emploie l'arsenazo.

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PRECIPITATION FROM HOMOGENEOUS SOLUTION OF PALLADIUM USING INDANE-1,2-DIOXIME

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Summary—The preparation of indane-1,2-dioxime and its use for the precipitation of palladium from homogeneous solution is described. The complex $\text{PdC}_{13}\text{H}_{14}\text{O}_4\text{N}_4$ has a complex:metal weight ratio greater than those with reagents normally used for the gravimetric determination of palladium. The effect of foreign ions on the precipitation is investigated and the optimum analytical conditions are established.

THE analytical applications of various vic-dioximes have been reviewed by Diehl¹ and Banks.² Palladium and nickel have been determined by vic-dioximes obtained from straight-chain ketones and from several alicyclic diketones, such as 1,2-cyclohexanedione, 1,2-cycloheptanedione and 1,2-cyclodecanedione. 4-Alkylcyclohexanedione dioximes³ and 1,2-cycloheptanedione dioxime^{4,5} are particularly recommended for the gravimetric determination of palladium.

From a consideration of steric models of compounds containing 5-, 6-, 7- and 8-membered carbon ring systems and the dioxime group, the present authors concluded that because the N—N separation in the dioxime is greater in a 5-membered ring system than in the other systems (in all of which it is approximately equal), this system should favour the formation of complexes with the palladium ion rather than with the smaller nickel ion.

Banks⁶ has reported that 1,2-cyclopentanedione dioxime was difficult to prepare, precipitated nickel only between pH 6.0 and 8.6, in non-quantitative amounts, and concluded that the material, although giving a precipitate with palladium and nickel, was of no analytical significance for either.

The present authors considered that dioximes of the indane 5-membered ring system might prove to be more useful and accordingly the simplest member, indane-1:2-dioxime, was prepared for investigation as an analytical reagent.

Two methods of precipitation of the palladium indane-1,2-dioximate were attempted, *viz.* conventional precipitation, and precipitation from homogeneous solution (PFHS).

Whilst with the conventional precipitation technique the dioxime gave the expected precipitate with palladium and the precipitation was quantitative under suitable conditions, the complex could only be filtered with difficulty, and prolonged washing was necessary to remove excess precipitant.

Generally, oximates obtained by PFHS give a much improved precipitate with respect to the ease of filtration when compared to that obtained by the conventional method.^{12,13} Gordon *et al.*⁷ reported that this is not so with palladium dimethylglyoximate. This was confirmed by the present authors, who also found that palladium

1,2-cyclohexanedione dioximate prepared by PFHS had no advantages over normal precipitation. However, precipitation of palladium indane-1,2-dioximate from homogeneous solution, using indane-1-one-2-oxime and hydroxylamine with palladium^{II} chloride, was attempted.

It was considered that using indane-1-one-2-oxime in acid solution, two simultaneous reactions are possible:

(i) Hydrolysis back to the monoxime of any dioxime formed, establishing an equilibrium system with only a small amount of dioxime present in solution.

(ii) Immediate reaction of any dioxime with the palladium present, to form the metal complex.

If the metal complex has an exceptionally high stability constant under the reaction conditions, the second reaction will predominate until all of the metal has been removed as complex. Reaction (i) will prevent formation of excess of reagent, and thus gross contamination of the precipitate with precipitant is avoided. Interference from foreign ions is also restricted to substances either forming complexes with the dioxime of equal or greater stability than does the palladium, or forming a precipitate with one of the reactants.

On precipitation of the palladium complex of indane-1:2-dioxime from homogeneous solution an easily-filtered precipitate, free from contamination with excess precipitant, was obtained. The effect of foreign ions on the precipitation was investigated, and the optimum analytical conditions were determined.

EXPERIMENTAL

Preparation of indane-1-one-2-oxime

β -Phenylpropionic acid is cyclised by heating with 10 times its weight of polyphosphoric acid at 100° for 1 hr. The reaction mixture is poured into a large volume of ice-cold water and the organic product is filtered and washed successively with water and sodium bicarbonate solution. The crude indane-1-one is extracted with ether, then oximated by a modification of the method of Perkin and Robinson.⁸ The solid indane-1-one (1 mole) dissolved in methanol is treated with freshly distilled amyl nitrite (1 mole) and a small amount of concentrated hydrochloric acid. The temperature of the reaction mixture is regulated at 50° for 30 min. On cooling, the monoxime separates as a pale yellow solid. This is washed with, and recrystallised from, aqueous ethanol, then dried in an air oven at 60–90° [m.p. 218–220° (with decomposition)].

The material has been kept in the solid form in contact with air and in ethanolic solution for 2 years without noticeable deterioration.

Precipitation of palladium complex of indane-1,2-dioxime from homogeneous solution

Palladium^{II} chloride solution (25 ml containing about 5 mg of palladium) and 10 ml of aqueous 20%W/V hydroxylamine hydrochloride solution are treated with an ethanolic solution of the monoxime. The mixture is diluted with water to about 100 ml and the pH is adjusted to the desired value using a pH meter. After standing for a measured time at a controlled temperature, the orange-yellow palladium complex is filtered on a No. 4 sintered glass crucible, washed with a small volume of water or 0.1M hydrochloric acid and dried.

Investigation of suitable drying conditions for the complex

A weighed amount of the complex was heated for four successive 3-hr periods at 110° and for further 3-hr periods at 125° and 145°. No change in weight was observed. With the amounts of precipitate obtaining in this work, drying for 2 hr at 110° was usually sufficient to reach constant weight. Thermal analysis of a sample showed that the complex decomposed at 220–225°. Differential thermal analysis, in a nitrogen atmosphere, showed that this decomposition was a highly exothermic reaction. Visual inspection of the product indicated charring.

Determination of purity of complex

A known amount of the complex was dry-ashed by heating at 900–1000° for 30 min and the palladium metal remaining was weighed. The complex contained 23.33% of palladium (calculated for PdC₁₈H₁₄O₄N₄: 23.29% of palladium).

Determination of pH for precipitation

Using the above method, with a 10% excess of the monoxime, a series of solutions was adjusted with dilute hydrochloric acid to different pH values, then maintained at $23^\circ \pm 1^\circ$ for successive 12-hr periods until a maximum weight of washed precipitate was obtained (see Table I).

TABLE I

pH of solution	0.6	0.9	1.3	2.23	2.23	2.7	3.1	3.5
Pd taken, mg	6.09	6.09	6.09	6.09	6.09	4.88	4.88	4.88
Pd recovered, mg	5.93	6.08	5.93	6.04	6.00	4.90	4.88	4.94
Time, hr	72	72	72	72	72	48	48	48

In practice a pH of 2.0–2.5 is considered convenient and suitable for determinations. All results subsequently quoted in this paper were, in fact, obtained at pH 2.0–2.1.

Effect of temperature on precipitation

Using the above method, with a 10% excess of the monoxime and a pH of 2.0–2.1, precipitations were carried out at different temperatures (see Table II).

TABLE II^a

$23^\circ \pm 1^\circ$	Time, hr	15	20	24	48	72			
	Pd recovered, mg	3.60	4.07	4.26	4.71	4.89			
$50^\circ \pm 1^\circ$	Time, hr	1.0	1.5	2	3	4	5	6	7
	Pd recovered, mg	3.18	3.46	4.35	4.52	4.79	4.86	4.88	4.88
$60^\circ \pm 1^\circ$	Time, hr	3	5						
	Pd recovered, mg	4.69	4.88						
$65^\circ \pm 1^\circ$	Time, hr	1	2	2.5	3	3.5	24		
	Pd recovered, mg	4.16	4.70	4.88	4.89	4.88	4.88		

^a 4.88 mg of Pd taken in all cases.

At temperatures above 65° precipitation is too rapid and the advantages of PFHS are progressively lost. Therefore precipitation by heating at 65° for 2.5–3 hr is recommended.

Effect of increasing the amount of monoxime used

Using the above method at pH 2.0–2.1 the results shown in Table III were obtained.

TABLE III^a

	Time, hr		2	3	4	5	6
$60^\circ \pm 1^\circ$	Pd recovered, mg	10% monoxime excess		4.69		4.87	
		20% monoxime excess	4.70		4.87		4.87
$65^\circ \pm 1^\circ$ ^b	Monoxime excess, %	20	100	400			
	Pd recovered, mg	4.71	4.88	4.92			

^a 4.88 mg of Pd taken in all cases.

^b Heating for 2 hr.

It is apparent that an excess of up to 400% of the monoxime does not have any deleterious effect on the weight of the precipitate obtained.

To test the validity of the supposition that excess dioxime, if formed at this pH, would be hydrolysed and hence not coprecipitate, a duplicate determination was made using the recommended conditions but adding *ca.* a 20% excess of the dioxime* in ethanol. The mixture was allowed to stand 15–30 min, then filtered, washed, dried and weighed. There was no apparent alteration in the physical properties of the complex and the weights obtained (corresponding to 4.88 and 4.87 mg of palladium recovered; 4.88 mg of palladium taken), indicate that coprecipitation of the dioxime did not occur.

* The dioxime was prepared by reaction of the monoxime and hydroxylamine hydrochloride in sodium acetate solution, and purified by recrystallisation from aqueous ethanol.

Effect of foreign ions

The effect of foreign ions (Al^{III} , As^{III} , Au^{III} , Ag^{I} , Cd^{II} , Ce^{IV} , Co^{II} , Cu^{II} , Fe^{II} , Fe^{III} , Ni^{II} , Hg^{I} , Hg^{II} , Mn^{II} , Os^{VIII} , Pt^{IV} , Rh^{III} , Sn^{II} , Sn^{IV} , Tl^{I} , and Zn^{II}) on both the monoxime and dioxime was investigated by heating an appropriate salt solution with a solution of the oxime, in alkaline (ammine), neutral and acidic conditions. All solutions were heated at 100° for 30 min.

The colorations (pale yellow) and precipitates (orange, pale yellow, brown) obtained are given in Table IV.

TABLE IV^a

Alkaline (ammine) conditions	
Monoxime	Al (c), As (c), Au (p) ^b , Cd (c), Ce (c), Cu (c), Co (p), Fe ^{II} (c) ^c , Ni (p), Fe ^{III} (p) ^b Mn (p) ^b , Pt (c), Rh (p).
Dioxime	Au (p) ^b , Cd (p), Ce (p), Cu (p), Co (p), Fe ^{II} (c) ^c , Fe ^{III} (p) ^c , Ni (p), Mn (p), Os (c), Pt (c), Rh (c).
Neutral conditions	
Monoxime	As (c), Au (p) ^b , Co (c), Fe ^{II} (c), Pt (p), Rh (p).
Dioxime	Cu (p), Co (c), Fe ^{II} (c), Fe ^{III} (p) ^b , Ni (c), Hg ^I (p) ^b , Pt (p), Rh (c).
Acid conditions	
Monoxime	No colorations or precipitates
Dioxime	

^a (c) = coloration, (p) = precipitate.

^b Probably hydrated oxide or reduction product.

^c The coloration with Fe^{II} in alkaline condition was purple-red with both oximes.

In view of the results in Table IV and considering the elements normally found with palladium (in analysis), transition metals Mn, Co, Ni, Fe, Cu, Pt and Au were considered under the following reaction conditions:

(a) Foreign ion (in amount equivalent to 48.8 mg of palladium) + indane-1-one-2 oxime.

(b) As (a) + a large excess of hydroxylamine hydrochloride solution.

(c) As (b) + 4.88 mg of palladium (as palladium^{II} chloride solution).

The weight of complex was determined in each case and the apparent weight of palladium recovered (mg) calculated (see Table V).

TABLE V

Foreign ion	Mn ^{II}	Co ^{II}	Ni ^{II}	Fe ^{III}	Cu ^{II}	Pt ^{IV}	Au ^{III}
Condition (a)	NR	NR	NR	NR	NR	NR	NR
Condition (b)	NR	NR	NR	NR	NR	DGP	DBP
Condition (c)	4.88	4.95	4.92	4.97	4.86	5.53	—

NR = no apparent reaction, DGP = dark green precipitate, DBP = dark brown precipitate.

From Table V there is seen to be no interference from manganese, nickel or copper, but slightly high results were obtained in the presence of iron^{III} or cobalt. The solution *must* be free from both platinum and gold.

The amount of EDTA necessary to complex iron^{III} or cobalt was determined on a separate aliquot of solution (using copper-PAN as indicator at pH 3.5–4). Approximately twice this amount of EDTA was then added to a palladium sample before the monoxime and the determinations were repeated (see Table VI).

TABLE VI

Foreign ion	Fe ^{III}	Co ^{II}	Fe ^{III} + Co ^{II}	Pd alone
Pd recovered, mg	4.91	4.91	4.89	4.90

Thus EDTA will remove any possible interference from iron^{III} or cobalt and it does not affect the palladium complex.

DISCUSSION

The recommended method for the determination of palladium by indane-1,2-dioxime is: Use a solution containing approximately 5 mg of palladium per determination. After addition of 10 ml of 20% W/V hydroxylamine hydrochloride solution, a 20–50% excess of ethanolic monoxime and sufficient EDTA to complex any iron^{III} or cobalt present, adjust the volume to approximately 100 ml with water and the pH to 2.0–2.5 with dilute hydrochloric acid. Heat the solution for 2.5–3 hr at 65°. Allow to cool. Filter at the pump. Wash with water or 0.1M hydrochloric acid. Dry to constant weight at 110°.

The over-all time per determination compares favourably with that using conventional methods of precipitation and any of the 4-alkylcyclohexanedione dioximes, where prolonged washing is essential to remove excess precipitant absorbed on the precipitate.

Unlike many examples of products obtained by PFHS, and reported by Gordon *et al.*⁹ as adhering extensively to the sides of the containing vessel, this oximate does not adhere to the vessel, neither does it "creep" when wet with hydroxylamine hydrochloride solution.

It is not necessary to maintain continual stirring of the reaction mixture, to avoid supersaturation or contamination with excess precipitant, as is recommended in other cases.¹⁰

The nature of the platinum complex has not been completely elucidated, but interference by platinum^{IV} is to be expected, by analogy with the reaction of platinum^{IV} and dimethylglyoxime reported by previous workers.¹¹

Acknowledgement—The authors acknowledge the award of a studentship (to D. B.) by the D.S.I.R

Résumé—On peut employer la préparation de l'indane-1,2-dioxime dans le P.F.H.S. du palladium. Ce complexe $\text{PdC}_{18}\text{H}_{14}\text{O}_4\text{N}_4$ a un rapport de poids complexe/métal plus élevé que celui observé avec les réactifs habituellement utilisés. On décrit les conditions d'analyse.

Zusammenfassung—Die Darstellung von Indan-1,2-dioxim und sein Gebrauch zur Fällung von Palladium aus homogener Lösung wird beschrieben. Der Komplex $\text{PdC}_{18}\text{H}_{14}\text{O}_4\text{N}_4$ hat ein größeres Gewichtsverhältnis Komplex: Metall als die Komplexe mit normalerweise zur gravimetrischen Palladiumbestimmung verwendeten Reagentien. Der Einfluß von Fremdionen auf die Fällung wird untersucht und die optimalen analytischen Bedingungen ermittelt.

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SHORT COMMUNICATION

Use of masking agents in chelatometric titrations—III*:

β -Mercaptopropionic acid†

(Received 24 June 1963. Accepted 3 August 1963)

ALTHOUGH thioglycolic acid (TGA) has been well studied as a masking agent and titrant in chelatometric titrimetry,^{1,2} the chelating behaviour of β -mercaptopropionic acid (MPA) has been investigated only for selected metal ions.³ The only paper which has appeared on the use of MPA as a masking agent is that of Hara,⁴ who employed it to mask lead in the EDTA titration of zinc at pH 4.5 with dithizone as indicator.

The present investigation was undertaken to find any difference in masking properties between TGA and MPA.

EXPERIMENTAL

Reagents

β -Mercaptopropionic acid (MPA): Practical-grade material‡ was purified by distillation in vacuo and the fraction boiling at 115–120° (7 mm of mercury) was collected. Pure MPA can be stored for many months if it is kept in a well-stoppered bottle in a refrigerator. It was used either without dilution or as a 50% aqueous solution. Practical-grade MPA is not suitable for direct use because it sometimes turns pink in alkaline solution. [Reagent grade MPA is now available from Dojindo & Co. of Kumamoto.]

Solutions of cations and EDTA were prepared in 0.01M concentration from reagent-grade chemicals.

Metallochromic indicators included Erio T, Murexide, Pyrocatechol Violet and Thymolphthalein Complexone.

Procedure

To an acidic solution of cations, a suitable amount of MPA was added dropwise. This sometimes resulted in a coloration or a precipitation, depending upon the cations present. The pH of the solution was then adjusted to 10 with ammonia-ammonium chloride buffer and the solution diluted to about 100 ml. After adding a suitable indicator, the solution was titrated with 0.01M EDTA solution.

RESULTS AND DISCUSSION

Bismuth forms a stable, colourless, soluble complex with MPA, both in acid and in alkaline solutions, and it is masked against titration with EDTA. Iron forms a stable, colourless complex in acid solution, but it turns brown in alkaline solution and precipitates at high concentrations. The complex does not react with EDTA in alkaline solution and the coloration is not so intense as in the case of TGA. Zinc and cadmium form colourless complexes in alkaline solution, but they are not stable enough to be masked against titration with EDTA. This behaviour is different from that of TGA which masks zinc and cadmium against titration with EDTA. At pH 10, the apparent stability constant of the zinc-MPA complex appears to lie between those of the zinc-Erio T and zinc-EDTA complexes. Therefore, the red zinc-Erio T complex turns blue to form the zinc-MPA complex on addition of MPA, but the zinc-MPA complex still reacts with EDTA. The same is true for cadmium. Lead forms a white precipitate in acid solution, but it dissolves at pH 10, forming a colourless complex. However, the lead-MPA complex slowly reacts with EDTA both in acid and in alkaline solution. Nickel forms a brown complex in acid solution, but the colour fades to pale brown or almost colourless at pH 10 with an excess of buffer solution. Because the complex is not sufficiently stable, nickel is not masked by MPA against EDTA titration. Cobalt forms a yellow to brown complex at pH 10, and the cobalt-MPA complex does not react with EDTA at

* Part II: see *Talanta*, 1963, 10, 1041.

† Contribution No. 50 from Department of Organic Synthesis, Kyushu University, Japan.

‡ Dojindo and Co., Kumamoto, Japan.

this pH. Because the coloration of the cobalt complex is not very intense, it is possible to mask cobalt effectively with MPA. In the case of TGA, the brown coloration with cobalt is so intense that it is of little practical value as a masking agent for cobalt in the determination of nickel. Mercury forms a white precipitate in acid solution, but it dissolves at pH 10, forming a colourless stable complex which does not react with EDTA. Copper forms a yellow precipitate in acid solution, but this dissolves at pH 10, forming a colourless stable complex which does not react with EDTA. Alkaline earth metals and manganese do not form stable complexes with MPA, so they can be titrated with EDTA in the presence of MPA.

TABLE I.—DETERMINATION OF Ni, Ca, Mg AND Mn IN THE PRESENCE OF Co, Fe, Cu AND Hg AT pH 10 (NH₃-NH₄Cl)

Metal taken, ml of 0.01M soln.	Other metals added, ml of 0.01M soln.	MPA ^a added	Indicator ^b	Metal, mg			End-point colour change
				Calc.	Found	Difference	
Ni 10.00	Co 2.00	1 drop	PV	5.80	5.75	-0.05	green to red-brown
Ni 10.00	Fe 2.00	1 drop	MX	5.80	5.77	-0.03	yellow to red-orange
Ni 10.00	Fe 3.00	3 drops plus TEA 10 drops	MX	5.84	5.85	+0.01	yellow to pink
Ni 10.00	Cu 100.0	0.7 ml	PV	5.87	5.85	-0.02	blue-green to light brown
Ni 10.00	Hg 100.0	0.7 ml	PV	5.84	5.80	-0.04	blue-green to red violet
Mn 10.00	Cu 100.0	0.7 ml	Erio T ^d	4.80	4.84	+0.04	red to blue
Mn 10.00	Co 1.00	1 drop	Erio T ^d	4.80	4.81	+0.01	red to blue
Ca 5.00	Fe 2.00	1 drop	Erio T	4.04 ^c	3.95	-0.09	red to blue
Mg 5.00							
Ca 5.00	Co 2.00	1 drop	Erio T	4.04 ^c	4.03	-0.01	red to blue
Mg 5.00							
Ca 5.00	Cu 100.0	0.7 ml	Erio T	4.04 ^c	4.00	-0.04	red to blue
Mg 5.00							
Ca 5.00	Hg 100.0	0.7 ml	Erio T	4.01 ^c	4.00	-0.01	red to blue
Mg 5.00							
Ni 10.00	Fe 1.00	7 drops	MX	5.80	5.78	-0.02	yellow to red-orange
	Cu 10.0						
	Hg 10.0						

^a MPA was used without dilution.

^b PV = Pyrocatechol Violet; MX = Murexide.

^c Calculated as Ca.

^d Ascorbic acid added.

From the above observations it is possible to titrate calcium, magnesium, manganese^{II} and nickel^{II} in an alkaline medium selectively in the presence of the various other cations mentioned. The results of some of these titrations are summarised in Table I.

For the titration of nickel, Pyrocatechol Violet was used as indicator, except in the presence of iron when Murexide was employed. Thymolphthalein Complexone was used for the titration of calcium and for the titration of manganese, magnesium and a mixture of calcium and magnesium. Erio T was employed as indicator.

Because iron and cobalt form coloured complexes, the end-point colour change becomes indistinct with an increasing concentration of these cations. The upper limit of their concentration is $2 \times 10^{-4}M$ in the final solution. If triethanolamine is used together with MPA, the iron concentration can be increased to a level of $3 \times 10^{-4}M$. In the case of copper and mercury, a concentration of up to $10^{-2}M$ can be masked with MPA because these cations do not form coloured complexes.

As stated before, the apparent stability constant of the zinc-MPA complex at pH 10 appears to lie between those of the zinc-Erio T and zinc-EDTA complexes. The direct titration of zinc in the presence of MPA is, therefore, impossible because Erio T is already blue at the beginning of the titration. No

indicators other than Erio T were found to function properly under these conditions. Thus, if zinc is accompanied by other cations which are not masked by MPA, the total amount of these cations will be titrated. Although zinc might be back-titrated, in the presence of MPA, with nickel using Pyrocatechol Violet as indicator at pH 10, the end-point is not sharp.

Hara titrated zinc at pH 4.5 using dithizone as indicator while masking lead with MPA.⁴ However, when Xylenol Orange is used, no colour change is observed at the zinc end-point. This phenomenon may be understood from the rate of the reactions involved at the end-point. When the zinc end-point is reached, the lead-MPA complex will dissociate slightly to release free lead ion, which, in turn, will react with dithizone. However, the reaction of dithizone with lead is so slow that an apparent end-point can be located, although, the colour at the end-point goes back in a few min. On the other hand the rate of reaction with Xylenol Orange is so fast that the colour of the indicator goes back immediately at the zinc end-point and no clear end-point can be observed with this indicator.

Acknowledgement Thanks are expressed by the authors to the Japanese Ministry of Education for financial assistance and to Dojindo & Co. for a fellowship to one of them (K. Y.).

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KEIHEI UENO®

Summary— β -Mercaptopropionic acid has been investigated as a masking agent in EDTA titrations. With the use of this reagent at pH 10, it is possible to determine nickel^{II}, manganese^{II}, calcium^{II} and magnesium^{II} in the presence of bismuth^{III}, cobalt^{II}, iron^{III}, copper^{II} and mercury^{II}.

Zusammenfassung— β -Mercaptopropionsäure wurde auf Maskierungseigenschaften bei EDTA-Titrationen untersucht. Mit Hilfe dieses Reagens ist Bestimmung von Ni(II), Mn(II), Ca(II) und Mg(II) in Gegenwart von Bi(III), Co(II), Fe(III), Cu(II) und Hg(II) möglich.

Résumé—On peut, au moyen de l'acide β -mercaptopropionique, de doser Ni(II), Mn(II), Ca(II) et Mg(II), en présence de Bi(III), Co(II), Fe(III), Co(II) et Hg(II).

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LETTER TO THE EDITOR

Suggestions for reporting dynamic thermogravimetric data

SIR:

THE increasing use of dynamic thermogravimetry has emphasised the need for workers in this field to use methods of reporting that, while concise, still contain all of the data that are essential to a critical evaluation and possible future reinterpretation of the results by other investigators. We have read many articles that could have included important additional information at the cost of no more than two or three lines of type; indeed, the space devoted to thermograms in published articles is often largely wasted, because the supporting data are incomplete.

A thermogram produced by a reliable recording thermobalance often shows certain features that are deliberately or inadvertently ignored in the reported discussion of it, either because their significance is not readily apparent, or because they are not considered germane to the principal line of investigation. This is particularly true of complex thermograms, which cannot easily be interpreted in complete detail, and for thermograms showing small weight changes of uncertain significance.

It is important that the published thermogram be as faithful a reproduction as possible of the original recording, so that any additional information is available to other workers. A well-prepared photocopy of the original record often makes the best illustration because it can be critically evaluated, even at the reduced scale of the usual journal reproduction, provided the experimental conditions are given. When it is necessary to trace the original thermogram, care should be taken to avoid either losing important detail or introducing inflections and curvatures not in the original.

The following eight pieces of supporting information should be given for each thermogram:

1. Identification of the substance examined by a definitive name, or an empirical formula, or equivalent compositional data; and the source of the substance.
2. The sample weight, and a weight scale for the ordinate.
3. Furnace, heating rate.
4. Atmosphere.
5. Size, shape, and material of the container.
6. Methods used to identify intermediates and final products.
7. Identification of the thermobalance, including the location of the thermocouple used for temperature measurements.
8. Identification of the abscissa scale in terms of time, furnace temperature, or sample temperature.

The best way to report this information is a matter of taste, and depends upon the purpose for which the thermogram is being shown. Thermograms of precipitates of interest in gravimetric analysis are used mainly to show whether plateaus of constant weight exist for the precipitate, for any intermediates, and for the final product of pyrolysis. The weight scale is usually given either directly or as a bar (parallel to the ordinate) whose length represents a known weight. Thermograms of hydrates and similar co-ordination compounds are often shown with the number of co-ordinated molecules as ordinate. For comparative purposes, such as studies of varieties of commercial plastics, it may be desirable to use as ordinate the percentage weight change, or the weight fraction of sample remaining. If there is a reasonable doubt about the interpretation, the weight scale should be shown as the ordinate, and the suggested interpretation should be indicated by fiducial marks and a formula near the point of interest. An open grid of lines at the major scale divisions is also helpful, particularly near plateaus, in revealing gentle changes in slope.

ARTHUR E. NEWKIRK
EDWARD L. SIMONS

General Electric Research Laboratory
P.O. Box 1088
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21 August 1963

NOTICES

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

UNITED KINGDOM

Thursday 7 November 1963: Meeting on Gas Analysis: Society for Analytical Chemistry: Wellcome Building, Euston Road, London N.W.1: 3.00 p.m.

The programme is as follows:

<i>Some Recent Developments in Gas Chromatography and Infrared Gas Analysis.</i>	D. W. HILL
<i>Some Problems Associated with the Analysis of Town Gas by Means of Gas Chromatography.</i>	G. R. BOREHAM
<i>Some Methods for Moisture Determination in Gases. Use of the Electrolytic Hydrometer for Determination of Moisture in Gases.</i>	J. H. SCAWIN J. E. STILL
<i>Sonic Gas Analysers: Uses and Limitations.</i>	A. E. MARTIN
<i>Some Electrochemical Methods of Gas Analysis. Use of a Slow Injection Syringe for Calibration of Gas Mixtures in the v.p.m.</i>	J. H. GLOVER H. F. DOWNING
<i>Apparatus for Handling Gas Samples and for Preparation of Gas Mixtures of Known Composition.</i>	J. E. STILL
<i>Dispersive and Non-Dispersive Infrared Analysers for In-line Measurements.</i>	A. W. HOUGH-GRASSBY

Wednesday 4 December 1963: Meeting on Differential Thermal Analysis: Society for Analytical Chemistry: Burlington House, London W.1: 7.00 p.m.

Friday 6 December 1963: Analysis of Monoglyceride and Related Emulsifiers: G. F. LONGMAN: Society for Analytical Chemistry, North of England Section: Unilever Research Laboratory, Port Sunlight: 5.45 p.m.

Tuesday 10 December 1963: Sampling and Analysis of Coal: D. FLINT and J. SHACK: Society for Analytical Chemistry, Midlands Section: University, Edgbaston, Birmingham 15: 6.30 p.m.

Tuesday 10 December 1963: Annual General Meeting of Atomic Absorption Spectroscopy Discussion Panel of Physical Methods Group, Society for Analytical Chemistry: Burlington House, London W.1: 6.30 p.m.

Wednesday 11 December 1963: London Discussion Meeting: Society for Analytical Chemistry, Microchemistry Group: The Feathers, Tudor Street, London E.C.4: 6.30 p.m.

Thursday 12 December 1963: Annual General Meeting followed by Discussion Meeting on Methods for the Detection of Teratogenic Activity: Society for Analytical Chemistry, Biological Methods Group: The Feathers, Tudor Street, London E.C.4: 6.30 p.m.

Wednesday 17 December 1963: Relative Conductometry for Micro Determination of Carbon, Hydrogen, Oxygen and Sulphur: H. MALISSA: Society for Analytical Chemistry, Midlands Section: University, Edgbaston, Birmingham 15: 6.30 p.m.

Sunday-Saturday 19-25 July 1964: Third International Congress of Polarography: Polarographic Society: University of Southampton.

PROFESSOR I. M. KOLTHOFF has been elected President of the Congress and will deliver the Presidential Address on **Polarography in Organic Solvents**. A small number of plenary lectures will be given. Contributed papers will be presented and discussed under the following headings:

1. *Theoretical Studies (to include rate and mass transfer processes, etc.).*
2. *Instrumentation.*
3. *Non-aqueous Systems.*
4. *Analytical and Industrial Applications.*
5. *Organic and Biological Applications.*
6. *Miscellaneous Applications.*

Authors are asked to provide summaries of up to 500 words in any major language, but preferably in English. The abstract will be published before the Congress and will be used as the basis

for consideration of the paper by a Sub-Committee of Referees. If accepted, the full paper should be submitted in the same language as the abstract unless the author is advised otherwise by the Scientific Programme Committee: the full paper will then be published in a separate volume of proceedings of the Congress. Abstracts must be received by 31 January, 1964

Further information may be obtained from the Secretary of the Congress, Dr. D. A. PANTONY, Department of Metallurgy, Imperial College of Science and Technology, London S.W.7, England.

British Standards Institution has announced the following *New British Standard*:

B.S. 3630: Methods for the sampling and analysis of zinc alloys: Part 1: 1963: Sampling of ingot zinc alloy ingots. This describes the selection of ingots, preparation of surfaces, method of taking samples by drilling or sawing and precautionary measures against contamination of the drilling or sawings. (Price 3s.)

Part 4: 1963: Sampling of ingot zinc, zinc alloy ingots and zinc alloy diecastings for spectrographic analysis, etc. This describes the selection of ingots and diecastings, the preparation of surfaces prior to sawing, the cleansing of the sample pieces and the method of casting the rods for spectrographic analysis. (Price 3s.)

Part 5: 1963: Iron in ingot zinc and zinc alloys (photometric method). This describes the reagent required, recommended methods of sampling and test procedure for the determination of iron in ingot zinc and zinc alloys having an iron content in the range 0.001 to 0.1%. (Price 3s.)

PAPERS RECEIVED

Proportional thermoregulator using silicon-controlled rectifiers: GILLIS JOHANSSON. (26 August 1963).

Indirect determination of traces of uranium using 1-(2-pyridylazo)-2-naphthol: M. R. HAYES and J. S. WRIGHT. (28 August 1963).

A colorimetric determination of nickel with 2-mercaptobenzothiazole: E. G. WALLICZEK. (1 September 1963).

Pioniers der Elektroanalyse: F. SZABADVÁRY. (3 September 1963).

Amperometrische Bestimmung der Metalle unter der Anwendung von Thioacetamid—V: Untersuchungen über PbS-Bildungsgeschwindigkeit in ammoniakalischen Pb²⁺-Ionenlösungen mittels Thioacetamid: MARIA PRSZCZEWSKA. (3 September 1963).

Determination of gases in metals by an improved vacuum fusion method: TAKAYUKI SOMIYA, SHIZO HIRANO, HITOSHI KAMADA and ICHI OGAHARA. (10 September 1963).

Spectrophotometric methods for the determination of impurities in pure and analytical reagents—I: Proposed methods and algebraic formulae: ABRAHAM GLASNER and PINCHAS AVINUR. (11 September 1963).

Spectrophotometric methods for the determination of impurities in pure and analytical reagents—II: Some absorption spectra in concentrated chlorides and their application: ABRAHAM GLASNER and PINCHAS AVINUR. (11 September 1963).

Spectrophotometric methods for the determination of impurities in pure and analytical reagents—III: The determination of six ions in potassium chloride: ABRAHAM GLASNER and PINCHAS AVINUR. (11 September 1963).

Spectrophotometric determination of hydrogen peroxide in alkaline solution: FARHATAZ MIRZA and GHAZANFAR A. MIRZA. (11 September 1963).

The hydrolysis of uranium and plutonium carbides: I. R. MCGOWAN and D. W. OCKENDEN. (12 September 1963).

Liquid-liquid extraction of tungsten^{VI} with tributylphosphate: Application to alloy steels: ANIL K. DE and SYEDUR RAHAMAN. (12 September 1963).

Volumetric determinations of quinol: U. A. TH. BRINKMAN and H. A. M. SNELDERS. (13 September 1963).

Die Spurenanalyse und ihre praktische Durchführung—I: Definition und Durchführung: OTHMAR G. KOCH. (14 September 1963).

Application of cationic-sensitive glass electrodes to the study of alkali metal complexes—I: The sodium-malate system: G. A. RECHNITZ and J. BRAUNER. (21 September 1963).

The titration of anthranilic acid with electrolytically generated bromine: Application to the coulometric determination of copper: LARRY G. HARGIS and DAVID F. BOLTZ. (23 September 1963).

Stability constants and analytical applications of diethylaminodithioformates: ADAM HULANICKI. (23 September 1963).

Determination of submilligram amounts of cobalt by ferricyanide titration with photometric end-point detection: H. POPPE and G. DEN BOEF. (25 September 1963).

Stability constants of palladium, copper, nickel, zinc and manganese chelates of 3-hydroxy-1,3-di-phenyltriazene: D. N. PUROHIT and N. C. SOGANI. (26 September 1963).

An International Quarterly Journal

DISARMAMENT AND ARMS CONTROL

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DISARMAMENT AND ARMS CONTROL has been launched to provide an international forum for the discussion of disarmament, arms control and related topics as a means of reducing the manifest dangers in which mankind now stands. Such work has, in the past, been largely undertaken and published within the haven of the research worker's own country, and makes its greatest impact there. It is hoped that this new medium will encourage the exchange of ideas, insights and experience between workers in different countries. It seeks to establish the understandings through which voluntary limitation and elimination of armaments may be reached.

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First Step—Sealed Records Caches?, *John C. Polanyi*; The Role of the Neutrals in the Geneva Negotiations, *M. Samir Ahmed*; Violations of Disarmament Agreements, *Richard J. Barnet*; The International Control of Fissile Material Production, United Kingdom Atomic Energy Authority; A Proposal for an African and Near-Eastern Zone Free from Certain Weapons, *David H. Frisch*; Obituary: A. V. Topchiev, *C. F. Powell*; Note: Perjury before International Tribunals; Book Reviews; Current Literature and Research.

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