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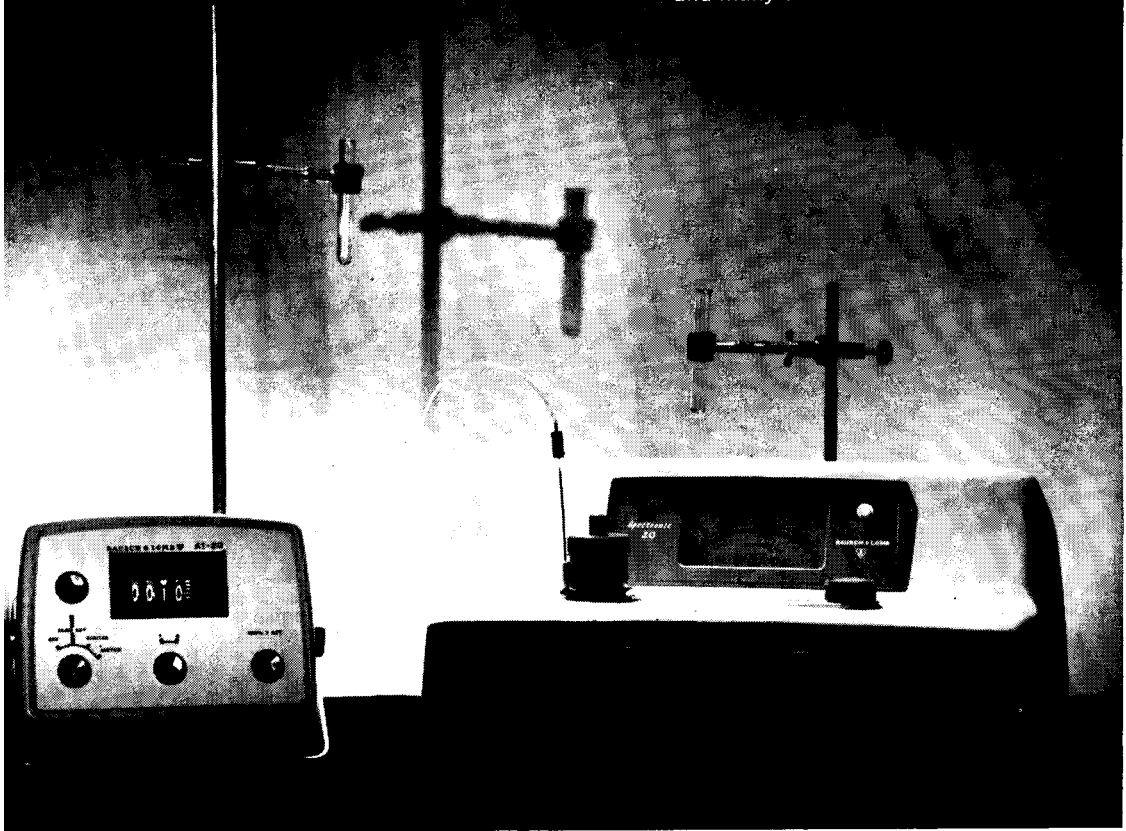
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SUMMARIES OF PAPERS PUBLISHED IN
ANALYTICA CHIMICA ACTA
Vol. 39, No. 3, November 1967

A STUDY OF Ag/Ag₂S AND Ag/AgSCN ELECTRODES: COULOMETRIC PRODUCTION OF SULPHIDE AND THIOCYANATE IONS

The electrochemical behaviour of Ag/Ag₂S and Ag/AgSCN electrodes was studied. The efficiency of generation of sulphide and thiocyanate ions was tested in the pH range 1-9; the error was always less than 1%. The best conditions for preparing the generating electrodes were also determined.

M. FIORANI AND F. MAGNO,
Anal. Chim. Acta, 39 (1967) 285-291

THE ATOMIC ABSORPTION SPECTROSCOPY OF TELLURIUM

Tellurium can be determined by atomic absorption spectroscopy at 2143, 2259, and 2386 Å. The sensitivities for these lines are in the ratio of 1:9.9:187. With aqueous solutions, a Beckman triple-burner (air-hydrogen) and a 5-pass optical system, the line 2143 Å has a sensitivity of 0.23 p.p.m., and a detection limit of 0.076 p.p.m. The sensitivities for this line in aqueous and organic solvents, and in air-hydrogen and air-acetylene flames were studied and the optimum conditions determined. Where necessary, preconcentration of tellurium by coprecipitation with elemental arsenic, or by extraction of K₂TeI₆ or tellurium diethyldithiocarbamate with MIBK can be applied; the latter gives a two-fold enhancement in sensitivity compared with aqueous solutions.

C. L. CHAKRABARTI,
Anal. Chim. Acta, 39 (1967) 293-299

ON A GENERAL SPECTROCHEMICAL METHOD FOR THE DIRECT ARCING OF LIQUID-LIQUID EXTRACTION RESIDUES IN A D.C. ARC

A considerable reduction in volume of the enriched sample is combined with the high absolute sensitivity of a mixed cathode layer-cathode excitation, which is applied directly to organic extraction residues in a 1:1 mixture with an alumina-graphite base. An oxygen protective atmosphere is used to increase the arc temperature, stabilize the column, and reduce cyanogen band interference. The method eliminates the need for subsequent mineralization or burning. Its application is discussed with reference to liquid-liquid extraction systems.

B. NEBESAR,
Anal. Chim. Acta, 39 (1967) 301-307

D.C. ARC SPECTROCHEMICAL DETERMINATION OF RHENIUM IN MOLYBDENITE ORES

Rhenium is isolated as tetraphenylarsonium perrhenate from solutions of molybdenite ores. It is excited in a mixture with an alumina/graphite buffer directly on the cathode in an oxygen atmosphere. Oxygen acts as a protective atmosphere and as a carrier to sweep into the discharge the highly refractory rhenium in the form of easily volatilized oxides. Intensity ratios of Re 3464.73, 3460.46, 3451.88 and 3399.30 Å lines with Co 3453.50 Å internal standard line cover the range 0.1-3.2 µg of rhenium on the electrode. The relative deviation of the method, computed by a routine regression analysis program, is +16-14% for the best analytical line. The detection limit is 6·10⁻⁸ g of rhenium. Several Canadian and other molybdenites with a rhenium content from 8 to 250 p.p.m. have been analysed.

B. NEBESAR,
Anal. Chim. Acta, 39 (1967) 309-319

THE SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM IN ILMENITE

A new diphenylcarbazide procedure free from iron interference is described for the determination of chromium in low-chrome ilmenite. After fusion of the sample, chromium is oxidised with permanganate and most of the iron is eliminated by extraction of chromium(VI) with MIBK. Residual iron causes fading of the final colour; this can be avoided by using a phosphoric acid medium at temperatures below 15°. When iron levels are less than 200 µg, temperature control (10°) suffices to prevent iron interference if the concentration of the usual sulphuric acid medium is increased to 0.2 *M*. However, the phosphoric acid-low temperature method gives wider tolerance to acidity variations and maximum stability with time.

E. S. PILKINGTON AND P. R. SMITH,
Anal. Chim. Acta, 39 (1967) 321-328

A DIRECT READ-OUT SYSTEM FOR FAST NEUTRON ACTIVATION ANALYSIS FOR OXYGEN IN STEELS

Fast neutron activation is useful for rapid determinations of oxygen in iron and steel, but the conventional calculations are tedious. A direct read-out system is described so that results are immediately available.

I. FUJII AND H. MUTO,
Anal. Chim. Acta, 39 (1967) 329-333

POTENTIOMETRIC DETERMINATION OF SILVER WITH DITHIOOXAMIDE

Potentiometric titration with dithiooxamide solution can be used to determine silver in the 0.0100-50.0 p.p.m. range with an average accuracy of *ca.* 0.5% and a relative standard deviation ranging from 1.26% to 0.03%. The metals commonly associated with silver can be masked with fluoride and EDTA. The advantages of the method over other potentiometric and common spectrophotometric methods are outlined.

L. H. KALBUS AND G. E. KALBUS,
Anal. Chim. Acta, 39 (1967) 335-340

THERMOMETRIC STUDIES OF COMPLEX FORMATION WITH IRON(III), ALUMINIUM AND GALLIUM

PART II. TARTRATES AND CITRATES

(*in French*)

Thermometric measurements make it possible to detect all tartrate and citrate complexes of iron(III), aluminium and gallium on only one enthalpogram. A suitable gradient of pH must be chosen in order to allow the successive formation of the complexes.

J.-P. GALLET AND R. A. PÂRIS,
Anal. Chim. Acta, 39 (1967) 341-348

OXIDATION OF CERIUM(III) TO CERIUM(IV) USING A MIXTURE OF HOT CONCENTRATED PERCHLORIC AND SULFURIC ACIDS

The oxidation of cerium(III) to cerium(IV) using a hot concentrated mixture of perchloric and sulfuric acids is shown to be quantitative. Optimum conditions for the oxidation are described. Complete removal of chlorine, an interfering decomposition product of boiling perchloric acid, is achieved by purging the concentrated acid solution with nitrogen *before* dilution with water. The presence of sulfuric acid is essential, the chief role of sulfuric acid apparently being to stabilize the cerium(IV) as a sulfatocerate complex.

L. A. KNECHT,
Anal. Chim. Acta, 39 (1967) 349-355

QUINOXALINES AS ANALYTICAL REAGENTS

PART I. DERIVATIVES CONTAINING THE COPPER(I)-SPECIFIC GROUPING

2,3-Bis(2-pyridyl)quinoxaline and 25 substituted derivatives were prepared and assessed as spectrophotometric reagents for copper. The compounds contain the copper(I)-specific "cuproine" grouping, but are much more readily prepared than most cuproine-type reagents. The possible formulations of the copper(I) chelates present under various conditions, and the effect of substituents are discussed. 2,3-Bis[2-(6-methyl)pyridyl]quinoxaline showed the greatest sensitivity for copper and was evaluated quantitatively with respect to ligand: copper ratio, pH effects, interfering ions and Beer's law dependence.

W. I. STEPHEN AND P. C. UDEN,
Anal. Chim. Acta, 39 (1967) 357-368

OXIMIDOBENZOTETRONIC ACID AS A REAGENT FOR THE SEPARATION AND GRAVIMETRIC DETERMINATION OF PALLADIUM AND COBALT

Oximidobenzotetronic acid is recommended for the separation and gravimetric determination of palladium and cobalt. An ethanolic solution of the reagent quantitatively precipitates palladium(II) from solutions which are 0.75 *N* in acid up to pH 5.1; the complex is weighed as Pd(C₉H₅NO₄)₂. Cobalt(II) can be determined in the filtrate after the precipitation of palladium. With 0.5 *N* acid solutions, no interference was found from Pt(IV), Ir(IV), Rh(III), Ru(III), Os(IV), Au(III), Ag(I), Cu(II), Fe(III), Ni(II), Hg(II), Pb(II), Bi(III), Cd(II), As(V), Se(VI), Te(IV), Mo(VI), Sb(III), Al(III), Cr(III), Zn(II), Ti(IV), Zr(IV), acetate, oxalate, citrate, tartrate, phosphate and fluoride.

G. S. MANKU, A. N. BHAT AND B. D. JAIN,
Anal. Chim. Acta, 39 (1967) 369-374

DETERMINATION OF SULPHUR AND SULPHATE BY TITRATION WITH BARIUM PERCHLORATE

COMPARISON OF VARIOUS COLOUR INDICATORS

Thorin, carboxyarsenazo, sulphonazo III, dinitrosulphoazo III, dimethylsulphonazo III and dibromosulphonazo III were compared as indicators for the precipitation titration of sulphate with barium perchlorate solution. Dimethylsulphonazo III was found to be best, and was tested further in determinations of inorganic and organic sulphur.

B. BUDĚŠÍNSKÝ AND L. KRUMLOVÁ,
Anal. Chim. Acta, 39 (1967) 375-381

EVALUATION OF EFFICIENCIES OF NORMAL FREEZING,
COLUMN CRYSTALLIZATION AND ZONE MELTING

The *n*-hexadecane/*n*-tetradecane solid-liquid phase diagram was determined for low concentrations of tetradecane. It was shown that in the 0.5-7% tetradecane region, the partition coefficient for tetradecane in hexadecane is linearly dependent on the concentration. The results can be applied to the evaluation of separating efficiencies of apparatus for normal freezing, zone melting, and column crystallization.

T. H. GOUW AND R. E. JENTOFT,
Anal. Chim. Acta, 39 (1967) 383-391

A SIMPLE SPECTROPHOTOMETRIC METHOD FOR THE
DETERMINATION OF COPPER BASED ON THE FORMATION
OF MOLYBDENUM BLUE

(Short Communication)

S. K. TOBIA, Y. A. GAWARGIOUS AND M. F. EL-SHAHAT,
Anal. Chim. Acta, 39 (1967) 392-393

INFLUENCE OF ACID CONCENTRATION IN THE ATOMIC
FLUORESCENCE OF CADMIUM

(Short communication)

M. P. BRATZEL, JR., J. M. MANSFIELD, JR. AND J. D. WINEFORDNER,
Anal. Chim. Acta, 39 (1967) 394

DETERMINATION OF SMALL AMOUNTS OF
PERYLENETETRACARBOXYLIC 3,4,9,10-DIANHYDRIDE IN
PIGMENTS BY SPECTROFLUORIMETRY

(Short Communication)

J. F. MCKELLAR AND G. T. PORTEUS,
Anal. Chim. Acta, 39 (1967) 395-397

THE STABILITY OF SOME LANTHANIDE COMPLEXES WITH
1,3,4,5-TETRAHYDROXYCYCLOHEXANECARBOXYLATE

(Short Communication)

W. OOGHE, H. THUN AND F. VERBEEK,
Anal. Chim. Acta, 39 (1967) 397-400

SPECTROPHOTOMETRIC END-POINT DETECTION FOR
DETERMINATION OF MAGNESIUM IN THE PRESENCE OF
CALCIUM AND PHOSPHATE BY TITRATION WITH CDTA

(Short Communication)

D. E. JORDAN AND D. E. MONN,
Anal. Chim. Acta, 39 (1967) 401-404

SPECTROPHOTOMETRIC DETERMINATION OF TIN IN
METALS AND ALLOYS

(Short Communication)

C. L. LUKE,
Anal. Chim. Acta, 39 (1967) 404-406

A STUDY OF Ag/Ag₂S AND Ag/AgSCN ELECTRODES: COULOMETRIC PRODUCTION OF SULPHIDE AND THIOCYANATE IONS

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(Received April 25th, 1967)

It is well known that second-order electrodes such as Ag/AgCl¹, Ag/AgBr and Ag/AgI^{1,2}, Ag/AgSCN², Ag/Ag₂S and Ag/AgCN³ can be successfully used in potentiometric and amperometric determination of the anions involved. In the present paper, the electrochemical behaviour of silver sulphide and silver thiocyanate electrodes is described and their ability to generate sulphide and thiocyanate ions, respectively, when they are employed as cathodes is discussed. Preliminary results have been reported elsewhere⁴.

EXPERIMENTAL

Materials

All chemicals were reagent grade (C. Erba, Milan). Twice-distilled water was used in the preparation of solutions. Nitrogen (99.99%) was purified from oxygen by passing it through a chromium(II) solution in sulphuric acid⁵.

Apparatus

The cell used to obtain the polarization curves was essentially the same as that described in a previous paper⁶. For the measurements of anodic and cathodic stripping and for the coulometric titrations, the head of the cell was replaced by another ground-glass connection with an appropriate number of ground-glass joints in order to introduce the electrodes and the salt bridge. The electrical apparatus consisted of a constant-current electronic generator (the stability of which is greater than 0.1%), a Leeds and Northrup Model K-3 Potentiometer, a standard 1000-Ohm Siemens Resistor, a Sefram Verispot Galvanometer, a Solartron Mod. LM 1420 Electrometer, a Varian Mod. A/4023 Recorder and a 100-Ohm Metrohm Potentiometer.

Procedures

Polarization curves. In order to obtain the polarization curves, a rotating platinum disc electrode made from a platinum cylinder of 0.4-mm diameter fitted in a teflon jacket, was first covered with silver by electrolysis from a Ag(CN)₂⁻ solution and then the appropriate salt was formed by anodizing it in a solution of either 10⁻² F sodium sulphide or 10⁻² F sodium thiocyanate with a current of 0.5 mA for 10 min. These experimental conditions must be strictly adhered to in the preparation of the Ag/AgSCN electrode.

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To prepare the polarization curves, in a $10^{-1} M$ potassium nitrate solution, sulphide or thiocyanate ions were generated coulometrically (see below) up to the desired concentration; 80 ml of solution were introduced into the cell. The auxiliary electrode with a surface of about 6 cm^2 was $\text{Hg}/\text{Hg}_2\text{SO}_4$. The potential was varied in 20-mV steps and waiting time after each potential variation was 2 min. In order to avoid possible modifications to the electrode surface, the potential at the extremes of the curves was limited so that current values were lower than $25 \mu\text{A}$. In Figs. 1 and 2 the polarization curves of Ag_2S and AgSCN respectively are plotted.

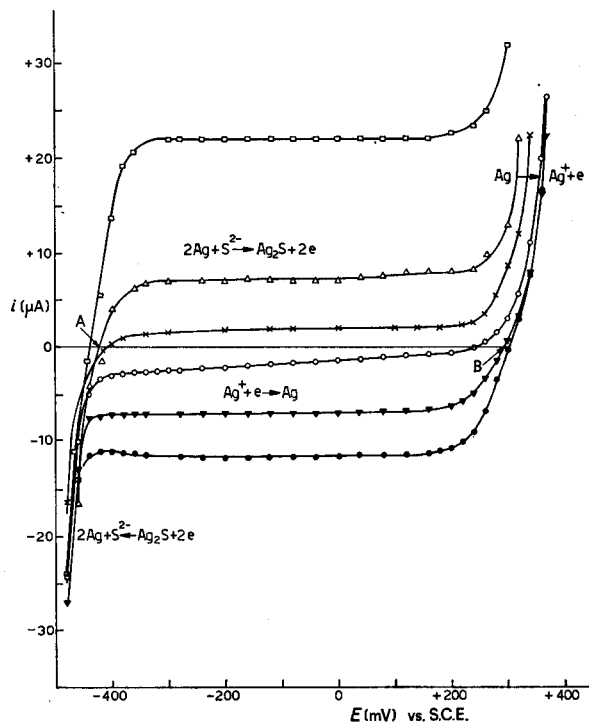


Fig. 1. Polarization curves for the $\text{Ag}/\text{Ag}_2\text{S}$ electrode in $10^{-1} M$ potassium nitrate. \square $2.4 \cdot 10^{-4}$ eq/l S^{2-} ; \triangle $8.1 \cdot 10^{-5}$ eq/l S^{2-} ; \times $3.1 \cdot 10^{-5}$ eq/l S^{2-} ; \circ $1.0 \cdot 10^{-5}$ eq/l Ag^+ ; \blacktriangledown $3.9 \cdot 10^{-5}$ eq/l Ag^+ ; \bullet $6.0 \cdot 10^{-5}$ eq/l Ag^+ .

Chronopotentiometric experiments. In the chronopotentiometric measurements, the working electrode was a silver spiral. The auxiliary electrode, separated by a sintered glass disc, was a piece of platinum foil. The calomel electrode was connected by means of a salt bridge. In Figs. 3 and 4 sulphide and thiocyanate chronopotentiograms are reported. The anodic electrolysis time (t_+) was arbitrarily long. The cathodic one (t_-) was found by measuring the time required to obtain a rapid linear voltage increase which is due to reduction of the solvent as discussed by LAITINEN AND LIN⁷.

Coulometric efficiency. The coulometric production of sulphide and thiocyanate ions was tested in the pH range of 1–9. The two species were titrated with coulometric-

ally produced silver, the end-point being detected by the potentiometric technique; biamperometric end-points were successfully used in the thiocyanate titrations, but only in acidic media. The indicator electrodes were Ag/Ag₂S and Ag/AgSCN in the potentiometric titrations and two silver wires in the biamperometric ones.

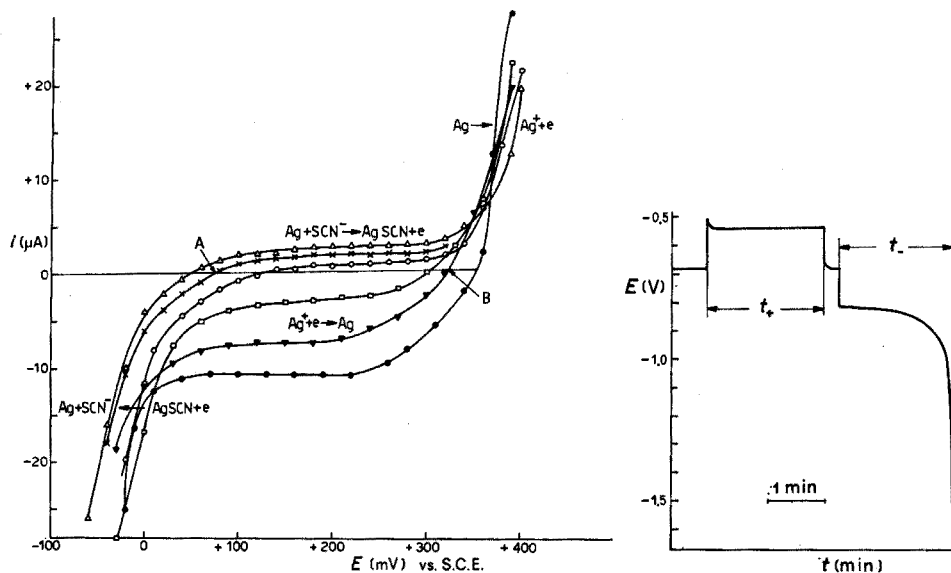


Fig. 2. Polarization curves for Ag/AgSCN electrode in $10^{-1} M$ potassium nitrate. \square $1.5 \cdot 10^{-6}$ eq/l Ag⁺; \circ $2.5 \cdot 10^{-6}$ eq/l SCN⁻; \blacktriangledown $3.0 \cdot 10^{-3}$ eq/l Ag⁺; \times $5.0 \cdot 10^{-5}$ eq/l SCN⁻; \bullet $9.0 \cdot 10^{-6}$ eq/l Ag⁺; \triangle $1.0 \cdot 10^{-4}$ eq/l SCN⁻.

Fig. 3. Chronopotentiogram in $10^{-1} F$ sodium sulphide. $i = 2$ mA.

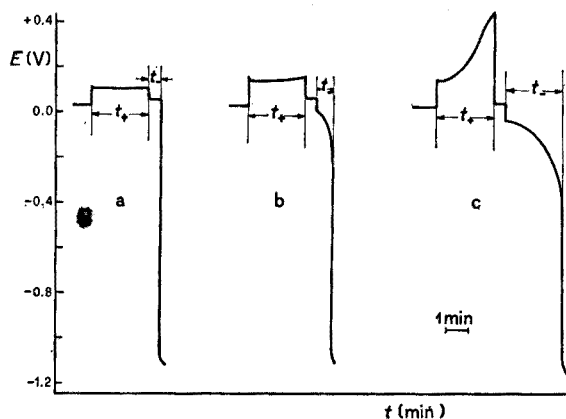


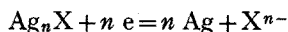
Fig. 4. Chronopotentiograms in $10^{-1} F$ sodium thiocyanate. (a) $i = 0.5$ mA; (b) $i = 2$ mA; (c) $i = 5$ mA.

RESULTS AND DISCUSSION

The shape of the polarization curves agrees with the values of the solubility products (K_{s0}) of silver sulphide and silver thiocyanate (10^{-49} and 10^{-12} , respectively).

This can be tested by comparing the potential values at $i=0$ for the curves, regarding free silver(I) and X^{n-} (sulphide or thiocyanate) as the ions in solution. In fact, in Fig. 1 from point A one obtains (all the potentials are referred to the N.H.E.) $E_{Ag/Ag_2S} = -0.20$ V and from point B: $E_{Ag/Ag^+} = +0.79$ V. From these values, taking into account the actual concentration of free S^{2-} ions in solution, one deduces $K_{so(Ag_2S)} = 10^{-41}$. On the other hand, in the case of Fig. 2, one has for A: $E_{Ag/AgSCN} = +0.32$ V and for B: $E_{Ag/Ag^+} = +0.83$ V and thus $K_{so(AgSCN)} = 10^{-12.8}$.

It is evident that in the coulometric production of X^{n-} , the interesting part of the polarization curve is that where the process:



takes place. At a potential of about -100 mV vs. S.C.E. in buffered solutions at pH

TABLE I

t_-/t_+ VALUES FOR CONSTANT-CURRENT EXPERIMENTS IN SULPHIDE SOLUTIONS

(Unstirred solution during the cathodic time)

i (mA)	$10^{-3}F Na_2S$ $10^{-1}M KNO_3$	$10^{-2}F Na_2S$ $10^{-1}M KNO_3$	$10^{-1}F Na_2S$	$1 F Na_2S$
0.5	1.07	1.08	1.14	1.14
1.0	1.10	1.01	1.05	1.06
2.0	1.00	1.00	1.02	1.03
3.0	1.00	1.00	1.02	1.03
4.0	1.00	1.00	1.00	1.00
5.0	1.00	1.00	1.00	1.00

TABLE II

t_-/t_+ VALUES FOR CONSTANT-CURRENT EXPERIMENTS IN THIOCYANATE SOLUTIONS

(Stirred solutions during the cathodic time)

i (mA)	$10^{-3}F NaSCN$ $10^{-1}M KNO_3$	$10^{-2}F NaSCN$ $10^{-1}M KNO_3$	$10^{-1}F NaSCN$ pH 7	$10^{-2}F NaSCN$ pH 1	$10^{-1}F NaSCN$ pH 1
0.5	0.98	1.00	0.98	0.98	1.00
1.0	0.97	1.00	1.00	0.98	1.00
2.0	—	0.99	0.99	0.99	1.00
3.0	—	1.00	1.01	1.00	1.00
4.0	—	—	—	0.99	1.00

TABLE III

t_-/t_+ VALUES FOR CONSTANT-CURRENT EXPERIMENTS IN THIOCYANATE SOLUTIONS

(Unstirred solution during the cathodic time)

i (mA)	pH 7			pH 1		
	$10^{-3}F NaSCN$ $10^{-1}M KNO_3$	$10^{-2}F NaSCN$ $10^{-1}M KNO_3$	$10^{-1}F NaSCN$	$10^{-3}F NaSCN$ $10^{-1}M KNO_3$	$10^{-2}F NaSCN$ $10^{-1}M KNO_3$	$10^{-1}F NaSCN$
0.5	0.95	0.92	0.00	1.12	0.87	0.00
1.0	0.95	0.97	0.37	1.05	0.97	0.00
2.0	1.04	0.99	0.56	0.99	1.00	0.17
3.0	1.00	0.98	0.77	1.05	1.00	0.41
4.0	0.97	1.00	—	0.98	0.99	0.68
5.0	—	—	1.00	0.80	—	0.74

9.2 ($10^{-2}M$ borax), a direct proportionality in the plateau range between the current and the concentration was observed in the range of $2 \cdot 10^{-6}$ – $10^{-4}M$ only for the sulphide ion. This finding will be utilized for a kinetic study of sulphide oxidation analogous to the iodide study⁶. Similar results were not obtained with the Ag/AgSCN electrode probably because of the high resistance of the silver thiocyanate layer. In Table I the results of constant-current experiments on sulphide solutions are reported, while in Tables II and III those for thiocyanate are given; in Figs. 3 and 4 two examples of these experiments are shown. With regard to the sulphide experiments, the t^-/t^+ ratio was almost always 1; this result agrees with the hypothesis that neither soluble complex formation nor silver sulphide formation takes place in the bulk of solution, for such reactions would be evidenced by a cathodic time lower than the anodic one. It is remarkable that the t^-/t^+ ratio was not modified in the sulphide chronopotentiogram by variable stirring conditions during the cathodic time. On the contrary in the thiocyanate experiments the ratio was strongly dependent on the stirring, owing to the possibility of reduction of silver complexes, which were formed during the anodic time. The data reported in Table III were obtained without stirring during the cathodic time; in this way, it was ensured that the current reduced only the silver thiocyanate layer on the electrode. It can be seen that the greater the concentration, the greater the current must be in order to obtain a t^-/t^+ ratio of 1. The silver thiocyanate layer on the electrode, which is indicated by a definite cathodic time, must be a poor conductor as can be seen from the increase in electrode potential (see Fig. 4). It is worth noting that at pH 1 in $10^{-1}F$ sodium thiocyanate without stirring, t^-/t^+ values of less than 1 and also less than those in neutral media were obtained. Further work is needed in order to establish if the above findings are related to different precipitation processes under the experimental conditions used. The t^-/t^+ ratio greater than 1 found in the case of sulphide for small currents can be ascribed to the spontaneous oxidation of silver by traces of oxygen present in the cell. This was confirmed by the high value of the t^-/t^+ ratio when nitrogen which had not been purified by the method mentioned above was used intentionally. In Tables IV and V the results of potentiometric and biamperometric titrations of sulphide and thiocyanate ions in the pH range 1–9 with coulometrically generated silver(I) are reported. It is

TABLE IV

POTENTIOMETRIC TITRATIONS OF SULPHIDE ION

pH	Coulombs for S ²⁻ production	Coulombs for Ag ⁺ production	Error %
9.2	1.242	1.236	-0.48
	1.242	1.236	-0.48
	1.249	1.245	-0.32
4.7	1.251	1.245	-0.48
	1.256	1.248	-0.64
1.0	1.258	1.250	-0.64

obvious that the greater the pH of the solution, the greater is the potential variation in the sulphide titration. The error was always much lower than 1%. The concentration of the titrated solutions was about $10^{-4}F$.

In the case of sulphide direct titration was possible even at pH 9, but in the case of thiocyanate it was necessary to acidify the solution after production of thiocyanate

TABLE V

POTENTIOMETRIC AND BIAMPEROMETRIC TITRATIONS OF THIOCYANATE ION

<i>pH</i>	<i>Coulombs for SCN⁻ production</i>	<i>Coulombs for Ag⁺ production</i>	<i>Error %</i>
9.2	3.710	3.700	-0.27
	3.720	3.740	+0.54
7.0	3.564	3.578	+0.39
	3.564	3.578	+0.39
1.0	0.686	0.689	+0.44 ^a
	0.686	0.688	+0.29 ^a

^a Biamperometric titrations.

in order to avoid the simultaneous precipitation of silver(I) oxide. The production of sulphide ion can be utilized for lead determination in the concentration range $4 \cdot 10^{-4}$ – $9 \cdot 10^{-5}M$; the solvent is an acetone–water mixture (50%, v/v) containing $10^{-2}M$ perchloric acid and the error was found to be less than 2%, its actual value depending on the strength of the solutions.

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SUMMARY

The electrochemical behaviour of Ag/Ag₂S and Ag/AgSCN electrodes was studied. The efficiency of generation of sulphide and thiocyanate ions was tested in the pH range 1–9; the error was always less than 1%. The best conditions for preparing the generating electrodes were also determined.

RÉSUMÉ

On a examiné le comportement des électrodes Ag/Ag₂S et de Ag/AgSCN. On a évalué le rendement de formation des ions sulfures et thiocyanates aux pH 1 à 9. L'erreur est toujours inférieure à 1%. Les conditions les meilleures pour la préparation de ces électrodes sont données.

ZUSAMMENFASSUNG

Das elektrochemische Verhalten von Ag/Ag₂S- und Ag/AgSCN-Elektroden

wurde untersucht und dabei die Wirksamkeit der Bildung von Sulfid- und Thiocyanat-Ionen beim pH 1-9 geprüft. Der Fehler lag immer unter 1%. Die besten Bedingungen zur Herstellung der Elektroden wurden bestimmt.

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THE ATOMIC ABSORPTION SPECTROSCOPY OF TELLURIUM*

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There is little information in the literature on the atomic absorption spectroscopy of tellurium. ALLAN¹ has mentioned only the sensitivity and the detection limit for the tellurium 2143 Å line, while SPRAGUE *et al.*² have dealt with the determination of tellurium in copper. In the present paper, the determination of tellurium in aqueous solutions and also after extraction into organic solvents is described.

EXPERIMENTAL

Apparatus

Two different atomic absorption spectrophotometers were used. One was a Jarrell-Ash atomic absorption flame spectrometer, fitted with a multipass optical system, a Beckman "total-consumption" triple-burner (air-hydrogen) system, and a R-106 photomultiplier, sensitive at low wavelengths. The other was a Techtron Model AA3 atomic absorption spectrophotometer, fitted with a 10-cm long-path premix burner (air-acetylene or air-hydrogen) giving a laminar flow, and a R-106 photomultiplier. A Westinghouse tellurium hollow-cathode tube (standard) was used with both instruments.

Readout systems. A meter readout and a Brown chart-recorder were used with the Jarrell-Ash instrument, and a meter readout and a Sergeant recorder with the Techtron instrument.

Analytical absorption lines

Three tellurium lines 2143 Å, 2259 Å, and 2386 Å, were examined for their maximum sensitivities with the Jarrell-Ash spectrometer. The results are shown in Table I. It can be seen that the Te 2142.75 line (henceforth the 2143 line) is the most sensitive, hence all of the work described below was concentrated on this line. The sensitivity of the 2143 line is too high to be suitable for high concentrations of tellurium, but either of the other two lines could be used.

Multiple optical passes

The sensitivity and the detection limit obtained with the Jarrell-Ash spectrometer fitted with a 5-pass optical system are shown in Table II; the other conditions

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TABLE I

RELATIVE SENSITIVITIES OF ABSORPTION LINES

(3 optical passes; lamp current 10 mA; H₂ 17.5 psi; air 40 psi; tellurium in aqueous 10% (v/v) nitric acid solution)

State	Energy levels (K)	Absorption line (λ)	Sensitivity (p.p.m. for 1% absorption)
3P ₂	0-46653	2142.75	0.36
3P ₂	0-44253	2259.04	3.54
3P ₁	4751-46653	2385.76	66.7

TABLE II

SENSITIVITY AND DETECTION LIMITS OF TELLURIUM IN AQUEOUS SOLUTION

Line	3-pass system			5-pass system		
	Sensitivity (p.p.m. per 1% absorption)	Noise as % of I ₀ ^a	Detection limit (p.p.m.)	Sensitivity (p.p.m. per 1% absorption)	Noise as % of I ₀	Detection limit ^b (p.p.m.)
Te 2143	0.36	0.5	0.12	0.23	0.5	0.076

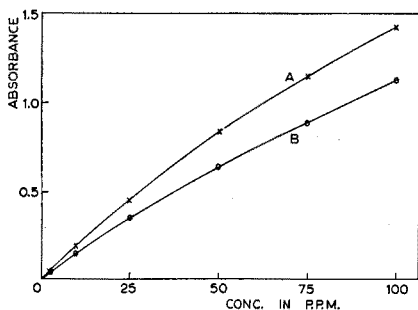
^a Noise; peak-to-peak noise as % of incident radiation.^b Concentration in p.p.m. for $\frac{2}{3}$ of peak-to-peak noise.

Fig. 1. Calibration curves for tellurium using multiple traversal of an air-hydrogen flame. Jarrell-Ash. Conditions as for Table I. Te 2143 line. (A) 5-pass. (B) 3-pass.

were the same as for the results in Table I. Figure 1 shows the calibration curves obtained with three- and five-optical passes.

Absorption by flames and as a function of lamp current

The Te 2143 line is not appreciably absorbed by an air-hydrogen flame, but is considerably absorbed by an air-acetylene flame, and the absorption by an air-acetylene flame becomes very intense with high flow rates of acetylene (see Figs. 2 and 3). Net absorbance means the absorbance corrected for blank absorbance including flame absorbance. The optimum flow rates of hydrogen are about 1.4-1.8 l/min and those of acetylene are about 1.5-2.2 l/min; the air flow rate in both cases is kept constant at 4.3 l/min. It can be seen from the ratio of fuel to air in both cases that the maximum sensitivity is obtained with strongly reducing flames. The steeply in-

creasing absorption by the flame gases above the flow rate of 2.2 l/min of acetylene makes this flow rate the upper limit.

Figure 4 (obtained with the Techtron AA₃ instrument) shows the sensitivity of the Te 2143 line as a function of lamp current. The decrease of absorption with

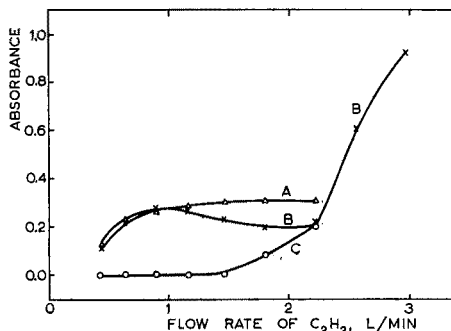
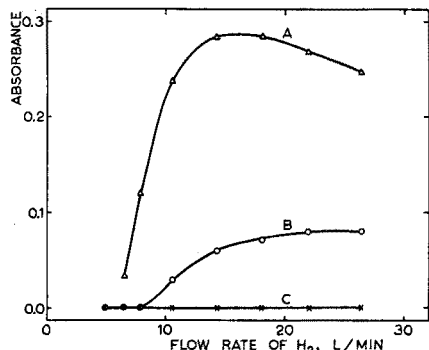


Fig. 2. Absorption of Te 2143 line by an air-hydrogen flame as a function of hydrogen flow rate. Techtron AA₃; 10 cm laminar flow burner; air flow rate 4.3 l/min; lamp current 7 mA; spectral band pass 9.9 Å. (A) Net absorbance by 40 p.p.m. Te in aqueous 10% (v/v) nitric acid solution. (B) Air-hydrogen flame + distilled water aspirated into the flame. (C) Air-hydrogen flame alone.

Fig. 3. Absorption of Te 2143 line by an air-acetylene flame as a function of acetylene flow rate. Conditions as for Fig. 2. (A) Net absorbance by 40 p.p.m. Te in aqueous 10% (v/v) nitric acid solution. (B) Air-acetylene flame alone. (C) Air-acetylene flame + distilled water aspirated into the flame.

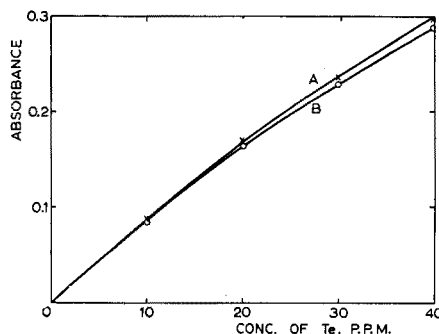
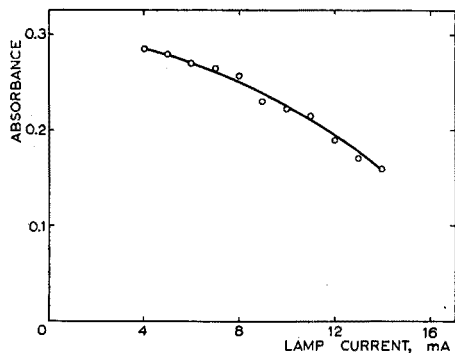


Fig. 4. Sensitivity of Te 2143 line as a function of lamp current. Techtron AA₃; air-hydrogen flame; Te 40 p.p.m. in aqueous 10% (v/v) nitric acid solution; spectral band pass 9.9 Å.

Fig. 5. Calibration curves for tellurium with air-hydrogen and air-acetylene flames. Techtron AA₃; Te 2143 line; lamp current 7 mA; spectral band pass 9.9 Å. (A) Air-acetylene flame. (B) Air-hydrogen flame.

increasing lamp current is due to increasing Doppler-broadening, and also to self-absorption broadening of the emission line. Higher lamp currents generate higher temperatures in the hollow-cathode lamp and thereby increase the Doppler width of the emission line; they also cause more sputtering of atoms from the hollow cathode, which results in self-absorption broadening of the emission line.

Calibration curves in aqueous solution

Figure 5 shows calibration curves for tellurium in 10% (v/v) nitric acid media with air-hydrogen and air-acetylene flames. The air-acetylene flame is slightly more sensitive than the air-hydrogen flame.

Determination of tellurium at the p.p.m. level in aqueous samples

Tellurium in some aqueous samples from metallurgical processes cannot be determined satisfactorily by means of the calibration curves obtained with aqueous solutions of tellurium. For example, solutions containing very high concentrations of ions such as copper, nitrates, and free nitric acid, cannot be accurately determined from the calibration curve obtained with aqueous solution of tellurium (see Fig. 6). This interference can be removed by making the samples simulate the standards in physical, and also, as far as possible, in chemical, characteristics. This can be done either by preparing suitably compensated standards, or by diluting the sample solutions with water until they simulate the aqueous standards, provided that the

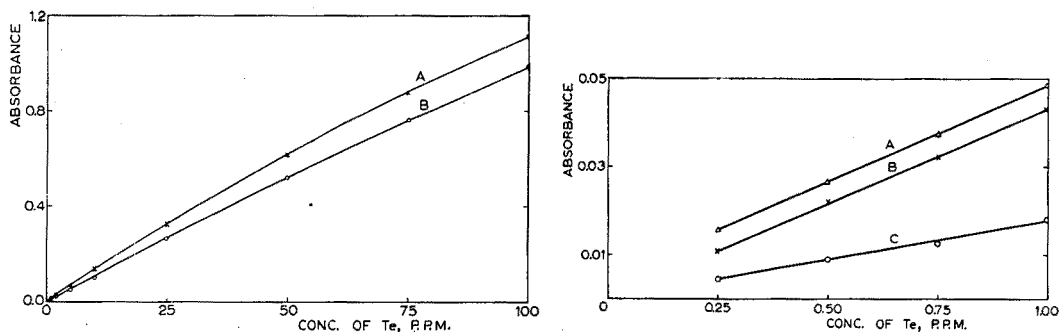


Fig. 6. Calibration curves for tellurium. Jarrell-Ash; air-hydrogen flame; lamp current 10 mA; triple pass. Te standards in: (A) distilled water, (B) 2% Cu-20% HNO₃.

Fig. 7. Calibration curves for tellurium. Techtron AA₃; Te 2143 line; lamp current 7 mA; spectral band pass 9.9 Å; air-hydrogen flame. (A) Tellurium as K₂TeI₆ in MIBK. (B) Tellurium as Te(DDTC)₄ in MIBK. (C) Tellurium in aqueous 10% (v/v) nitric acid solution.

concentration of tellurium is not decreased below the detection limit. Some results are shown in Table III. Tests were also made with a Se-Te composite, solutions of which were prepared to contain 2% Cu + 8% HNO₃ + 10% HCl; the solutions were analyzed using a calibration curve prepared with standards containing 2% Cu + 20% HNO₃. On three separate solutions the results obtained were 10.8, 10.7 and 10.4 p.p.m. Te (certified value 10.5 p.p.m.). It is thus clear that the partial substitution of hydrochloric acid for nitric acid in the final samples did not affect the accuracy of the method. The interference of high electrolyte concentrations is predominantly due to the difference in physical characteristics (viscosity, surface tension, solid contents, etc.) between the sample and the standards, but partly to molecular absorption^{3,4}. Table IV shows the effect of these interferences. For example, tellurium in synthetic samples of zinc electrolyte could not be determined by aspirating the aqueous samples (without elaborate sample preparation) into the flame. Even more serious interferences were observed with other tellurium lines, Te 2259.04, and Te 2385.76, when they were used to analyze such synthetic samples of zinc electrolyte.

TABLE III

RECOVERY OF TELLURIUM

(2% copper + 20% nitric acid used as base stock for preparing standards and samples. Jarrell-Ash spectrometer with Beckman triple-burner (air-H₂). Te 2143 line)

Sample no.	Te (p.p.m.)		Recovery (%)
	Added	Found	
1	20.0	19.3	96.5
2	40.0	39.5	98.8
3	50.0	50.0	100.0
4	75.0	76.0	101.3

TABLE IV

EFFECT OF INTERFERENCES

(Jarrell-Ash spectrometer with Beckman triple-burner (air-H₂). Te 2143 line)

Aqueous solutions containing	% decrease of incident radiation
Cu 2% (20,000 p.p.m.)	6.2
Na, 10,000 p.p.m.	3.0
Zn, 1,000 p.p.m.	0.8
Zn, 80,000 p.p.m.	25.5
Ca, 440 p.p.m.	1.0

TABLE V

TELLURIUM IN p.p.b. LEVEL IN ZINC ELECTROLYTE SAMPLES

(Jarrell-Ash spectrometer with Beckman triple-burner (air-H₂). Te 2143 line)

Sample no.	Te (p.p.b.) found by	
	Atomic-absorption spectroscopy	Spectrography
1	23	20
2	6	8
3	2	3

The synthetic samples of zinc electrolyte contained besides zinc as zinc sulphate also 17.4% (v/v) of sulphuric acid (s.g. 1.84).

Determination of tellurium at the p.p.b. level in aqueous samples

As can be seen from Table I, the sensitivity of even the Te 2143 line is not high enough for determination of tellurium at the p.p.b. level, so that concentration to the p.p.m. level is necessary. Such concentration can be achieved either by coprecipitation of tellurium with elemental arsenic or by extracting tellurium as a complex into an organic solvent.

In the arsenic coprecipitation method, tellurium present at the p.p.b. level can be isolated from its matrix and concentrated by the procedure described by LUKE⁵. Recoveries of tellurium by this method followed by atomic absorption

spectrophotometry were 98–100% for 2–10 p.p.m. Te in the original solution (the arsenic coprecipitation step was omitted in the case of the standards). Table V shows the results of determination of tellurium at the p.p.b. level in unknown samples of zinc electrolyte. The arsenic coprecipitation method finally yields tellurium as nitrate and nitrate solution was therefore used in preparing the standards. The concentration of tellurium by this method is time-consuming, but the procedure is more practical than solvent extraction when large volumes of sample, say over 500 ml, have to be handled to determine very low concentrations of tellurium.

With solutions containing 25 p.p.b. or more of tellurium, solvent extraction has advantages of speed and simplicity over coprecipitation. Tellurium can be extracted with methyl isobutyl ketone (MIBK) from an aqueous solution containing 5% (v/v) hydrochloric acid by forming potassium hexaiodotellurate, K_2TeI_6 , with excess of potassium iodide, which is used as a freshly prepared saturated aqueous solution. Alternatively, tellurium can be extracted with MIBK from a nearly neutral aqueous solution by forming tellurium diethyldithiocarbamate, $Te(DDTC)_4$, with a freshly prepared aqueous 2% (v/v) solution of sodium diethyldithiocarbamate. If the pH of the aqueous solution is not rigidly controlled at 8.5–8.8, other elements may be co-extracted into MIBK but no such interferences were found in the present work. Figure 7 shows the optimal calibration curves for the two systems, and also for tellurium in aqueous solution containing 10% (v/v) nitric acid. The sensitivities (p.p.m. for 1% absorption) of these systems, as obtained under the optimal conditions for each case with the Jarrell-Ash instrument with a 5-pass optical system at the Te 2143 line, were found to be 0.12 for the K_2TeI_6 complex in MIBK and 0.09 for the $Te(DDTC)_4$ complex in MIBK.

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SUMMARY

Tellurium can be determined by atomic absorption spectroscopy at 2143, 2259, and 2386 Å. The sensitivities for these lines are in the ratio of 1:9.9:187. With aqueous solutions, a Beckman triple-burner (air–hydrogen) and a 5-pass optical system, the line 2143 Å has a sensitivity of 0.23 p.p.m., and a detection limit of 0.076 p.p.m. The sensitivities for this line in aqueous and organic solvents, and in air–hydrogen and air–acetylene flames were studied and the optimum conditions determined. Where necessary, preconcentration of tellurium by coprecipitation with elemental arsenic, or by extraction of K_2TeI_6 or tellurium diethyldithiocarbamate with MIBK can be applied; the latter gives a two-fold enhancement in sensitivity compared with aqueous solutions.

RÉSUMÉ

Le tellure peut être dosé par spectroscopie par absorption atomique à 2143, 2259 et 2386 Å. Les sensibilités pour ces lignes sont dans le rapport 1:9.9:187. En solution aqueuse, avec triple brûleur Beckman (air–hydrogène), à 2143 Å, la sensibilité

est de 0.23 p.p.m. et la limite de détection 0.076 p.p.m. Si nécessaire, il y a possibilité de préconcentration du tellure par coprécipitation à l'aide d'arsenic élémentaire ou par extraction de K_2TeI_6 ou de diéthylthiocarbamate de tellure dans un solvant.

ZUSAMMENFASSUNG

Tellur kann mit der Flammenabsorptions-Spektralanalyse bei 2143, 2259 und 2386 Å bestimmt werden. Die Empfindlichkeiten dieser Linien haben das Verhältnis 1:9.9:187. Mit wässrigen Lösungen, einem Beckman-Dreifachbrenner (Luft-Wasserstoff) und einem 5-wegigen optischen System ergibt sich mit der Linie 2143 Å eine Empfindlichkeit von 0.23 p.p.m. und eine Nachweisgrenze von 0.076 p.p.m. Die Empfindlichkeiten dieser Linien in wässrigen und organischen Lösungsmitteln und in Luft-Wasserstoff- und Luft-Acetylen-Flammen wurden untersucht und die optimalen Bedingungen bestimmt. Weitere Möglichkeiten zur Empfindlichkeitssteigerung durch vorhergehende Konzentration des Tellurs durch Mitfällung oder Extraktion werden angegeben.

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ON A GENERAL SPECTROCHEMICAL METHOD FOR THE DIRECT ARCING OF LIQUID-LIQUID EXTRACTION RESIDUES IN A D.C. ARC

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The theoretical and practical advantages of the liquid-liquid extraction separation technique make it most attractive for spectrochemical enrichment work¹⁻³. However, the direct arcing of organic extraction residues seems to have received little attention, probably because of inherent practical difficulties. Such an approach, however, has been shown to be suitable for elements possibly lost on charring, *e.g.* rhenium⁴, and has some generally useful features.

Liquid-liquid extraction methods can be divided into two groups: those methods which yield almost no organic residue, and other methods which yield considerable organic matter after the evaporation of the organic solvent. (Methods using the aqueous phase are not considered here.) Residues from the first group can be arced directly^{5,6}, while those from the second group usually must be charred, burned or mineralized.

This paper describes the principles and the techniques of a general spectrochemical enrichment method that allows direct arcing of metal-organic residues under controlled conditions, with advantages in handling, reference standards, and spectrography.

EXPERIMENTAL

The apparatus employed and the general spectrographic conditions were the same as in the application of this method to determination of rhenium⁴. The following additional reagents were also used: cupferron and benzoic acid (J. T. Baker Chemical Co.), 8-hydroxyquinoline (Eastman Organic Chemicals), potassium sulphate and lithium and calcium carbonates (all Specpure, Johnson, Matthey and Co.).

Preparation of metal-organic standards

Prepare the liquid standards by dissolving weighed quantities of well-defined metal-organic or inorganic compounds in appropriate organic solvents and adjust to volume.

For the preparation of dry metal-organic standards, weigh aluminum oxide, the organic reagent used for extraction, and graphite in the required proportion (total weight exactly 1 or 2 g) into a 25-ml porcelain casserole. Dissolve the organic reagent in the appropriate solvent and add the required volumes of the element and/or internal standard solutions by means of micropipettes or microburettes. Homogenize the suspension well and evaporate to dryness under a heat lamp, a hot

plate, and the controlled draft from a small fan. Dry the residue in an oven for *ca.* 1 h at a temperature below the decomposition temperature of all compounds involved, cool in a desiccator and grind to a homogeneous powder.

Preparation of the electrode charge

By preliminary testing, establish the weight of the reagent recovered by extraction and evaporation under the analytical conditions. Choose a suitable ratio of organic matter to spectroscopic buffer, and also the final weight of the mixture, but do not exceed a limit of 50% of organic matter. At a ratio of 1:1, 0.0400 g of the mixture—containing 0.0200 g of the buffer—is adequate for charging duplicate electrodes. To the extract, in a 25-ml porcelain casserole, add the internal standard solution if required. Homogenize and evaporate to dryness. With a small amount of solvent, transfer the dry and still warm organic residue into a tared 2- or 5-ml porcelain crucible or Teflon vial, containing the weighed spectroscopic buffer. Evaporate again. Rinse the walls of the vessel with solvent to collect most of the matter at the bottom. Evaporate the solvent and then dry in an oven for about 15 min. Cool in a desiccator. Adjust to the final weight (to within ± 0.0002 g) with the powdered organic reagent. Homogenize the residue well with a graphite rod, which should have a diameter slightly smaller than the cavity. Tap the inverted electrode (held in a holder) into this mixture, pressing it firmly with the rod into the cavity (not less than 4–5 times for a cavity with a depth of 4 mm). Fill the electrode completely, clean the edges with paper tissue and make a vent into the centre of the charge with a needle mounted in a pin-vise (L. S. Starrett Co., Athol, Mass., size A).

RESULTS AND DISCUSSION

Chemical considerations

Relatively few separation techniques can be used in general spectrochemical procedures. Classical methods based on precipitation or coprecipitation with inorganic or organic reagents are still often employed. However, the necessity of exceeding the solubility product of the compounds involved has been pointed out² as a serious theoretical drawback inherent in the principle of such methods.

Ion exchange and liquid–liquid extraction have been suggested as the best separation and enrichment methods, and of these extraction is preferred in spectrochemical work because of its greater speed.

In a well-known aqueous solution technique^{7,8}, the sample is dissolved (with the advantage of homogenizing it), followed by the addition of the internal standard and matrix material, then evaporated, with final recovery of the sample in a powdered form. It was thought that a similar procedure could be devised for organic liquids and reagents, where the extraction would be the first step, provided that suitable arcing conditions could be found.

The prospective chemical system has to meet several requirements. First, a quantitative extraction and separation method for the elements in question must be available. Separation factors as low as 100 are still useful². Group reagents are particularly suitable and are often employed. Solvents denser than water are preferred if separatory funnels are used. Secondly, the organic material and the isolated metal-organic compound must be stable at the temperatures required for complete evapora-

tion of the solvent. After the isolation step, water does not appear further in the process. Good solubility of organic reagents in solvents and their good miscibility help to homogenize the material. Chlorinated, aromatic, and polar organic solvents, usually employed for liquid-liquid extraction work, satisfy these conditions. By means of the forced draft, a rapid low-temperature evaporation is achieved.

Thirdly, if excess of the reagent is co-extracted (under controlled conditions this usually occurs in a reproducible manner), the total weight of the reagent must not exceed a few tens of milligrams because otherwise excessive quantities of organic material would appear in the final charge and the advantages of the extreme volume reduction would be lost.

Some considerations which were incorporated into the technical manipulations were the following: a minimum number of transfers, nonadherence of samples to vessel surfaces, easy cleaning of utensils, easy weighing and stability of weight, no necessity to attend evaporation (as in several other similar procedures), simple and generally available laboratory equipment. The use of porcelain-ware satisfied most of the above requirements. Weighings were easily maintained to within ± 0.2 mg, affording a precision of at least $\pm 1\%$ for weighing operations.

Spectrographic considerations

Since enrichment methods are usually applied to trace elements which cannot directly be determined in the original sample, their sensitivity and freedom from matrix effects are likely to be of greatest interest. Theoretical investigations of the conditions in the discharge column⁹ have indicated that short excitation times, extreme reduction in volume of the sample charge, and an effective transport of the specimen vapor into a stabilized discharge column can lead to a considerable increase in analytical sensitivity. Several principles and techniques, satisfying the above requirements, were applied in the present method.

Electrodes and their charge. A small-diameter electrode, generally accepted as the best for the cathode layer technique, was adopted. A thin-wall, small-diameter electrode of the length required is not available commercially; 6-mm crater electrodes do not allow a complete burn (with the instrumentation available), while 3-mm electrodes hold less charge⁴.

Apart from discharge conditions, the successful direct arcing of organic matter depends on the composition of the electrode charge. Relatively few inorganic compounds could be considered for use as a diluant to prevent the ejection of the charge on striking the arc. Because of the liquid-liquid extraction considerations (if excess reagent is co-extracted), and because of the desirable bulk-volume reduction, a proportion of 50–66% of organic matter in the charge seemed most suitable. Previously, but not in extraction work, the proportion of organic material was much lower¹⁰. Aluminum oxide with graphite, which has been successfully used for cathode layer excitation in the past¹¹, and also other salts that have been used in buffers for anode excitation, were investigated. Detailed tests showed that not much more than 50% of the charge can be either organically-bound carbon or graphite. Graphite makes the electrode charge electrically conducting and helps to trace white residues in white vessels. Table I shows the results of arcing mixtures of various organic reagents with inorganic compounds. All charges, containing aluminum oxide and up

TABLE I

DIRECT ARCING OF MIXTURES CONTAINING VARIOUS ORGANIC REAGENTS^a

Electrode charge (%)					Behaviour in 1.0-sec arcing under analytical conditions
Inorganic component	Organic component		Graphite		
K ₂ SO ₄	40	TPAsCl ^b	50	10	Remains in electrode ^c
Li ₂ CO ₃	40	TPAsCl	50	10	Ejected
CaCO ₃	40	TPAsCl	50	10	Ejected
Al ₂ O ₃	40	TPAsCl	50	10	Remains in electrode
Al ₂ O ₃	26.6	TPAsCl	66.7	6.7	Remains in electrode, vigorous ignition
Al ₂ O ₃	40	Benzoic acid	50	10	Remains in electrode
Al ₂ O ₃	50	Cupferron	37.5	12.5	Remains in electrode
Al ₂ O ₃	40	8-Hydroxy-quinoline	50	10	Remains in electrode

^a Duplicates of standard electrode charge.^b Tetraphenylarsonium chloride.^c Triggers the overload switch in about half of the 22-sec test.

to at least 50% organic matter (regardless of its origin) were also successfully arced in a normal 22-sec analytical test⁴.

Charging of electrodes as described above was investigated by weighing 16 identical electrodes. At an average weight of 14.6 mg, a precision of $\pm 2.3\%$ was obtained for a 1:1 mixture of tetraphenylarsonium chloride with the spectroscopic base (4 Al₂O₃/1 graphite). Charging by volume was therefore precise enough to eliminate another weighing and was conveniently accomplished directly from the crucible. Mixing of the electrode charges with a commercial mixer (Wig-L-Bug, Spex Industries, Inc., Metuchen, N.J.) was tried (with Teflon vials because of the action of chlorinated solvents on polystyrene), but much of the material remained on the ball and walls of the vial, so that only one electrode could be charged from a 40-mg mixture. The very fine powder, moreover, was not loaded as easily as the more plastic residues obtained by hand mixing and was also carried by oxygen in the arc.

Light source. The initiator of the unit available could not start the arc under the analytical conditions required. A step-wise switching out of a higher resistance, employed for starting, is suggested by the manufacturer in order to obtain high currents. This, as well as the rod-shortening or electrode short-circuiting techniques could not be used because of the criticality of timing, geometry, and excitation conditions. A wire short-circuiting technique—an idea borrowed from the pedestal-type electrodes—made arcing feasible under the required analytical conditions.

Because the available arc stand and the protective atmosphere device did not allow a continuous monitoring of the 10-mm arc gap, the excitation used was really a combination of two distinct and different excitation techniques: the cathode layer technique and cathode excitation of the sample. As the arc burns, the cathode tip volatilized from a position 1 mm above the optical axis to a position 3 mm below it, and moreover, disappeared below the edge of the ceramic shield.

Oxygen has been shown to decrease effectively the cyanogen band interference. The sensitivity and precision of determination is increased particularly for refractory elements¹². While in the present work, an argon/oxygen (75/25) mixture

hardly volatilized 1 mm of the cathode charge, pure oxygen allowed considerable shortening of the times for cathode-type excitation. They are otherwise 2 to 3 times longer than for anode excitation. Because of the intense heat in the oxygen stream, the anode is consumed more rapidly, the final gap after 22 sec being about 20 mm. The oxygen serves in a multiple capacity: it stabilizes the arc column mechanically and thermally, it reduces the cyanogen band interference, increases the temperature of the arc, and may even take part in the reactions in the arc⁴.

The combination of the 3 techniques: cathode layer excitation, application of oxygen as protective atmosphere, and direct arcing of organic matter gives a light source with unusual characteristics. In Fig. 1 the arc is shown in operation. A reproducible and sharply defined volatilization of the cathode and sample is achieved.

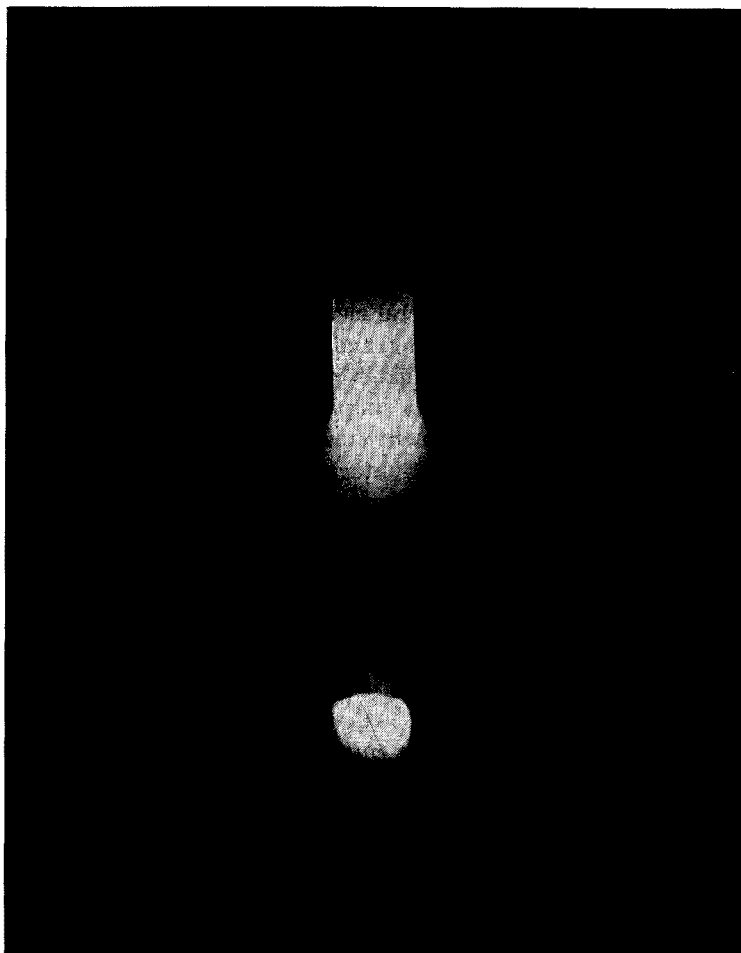


Fig. 1. D.C. arc in operation.

For identical electrodes and charges (1:1 ratio of organic matter to spectroscopic buffer), arced according to analytical conditions, the loss of graphite from electrode for 3 runs was 0.0561 g with a precision of $\pm 1\%$. The light streaks in Fig. 1 are

caused by glowing graphite particles that are also observed when arcing is performed with only solid electrodes.

The critical part of the arcing cycle is its first second. The easily volatilized matter from the top layers of the charge is almost instantaneously burned in the intense heat of the arc. The micro-quantities of elements to be analysed are gradually evaporated, starting in the first second and transported from the alumina skeleton into the arc. After completion of the arcing cycle a small bead of alumina (1-2 mg) remains, representing about 15-30% of the original quantity. If excited for a second time, the alumina hardly changes weight. There is a possibility that the aluminum oxide, requiring reduction by carbon for its effective volatilization, is only partially volatilized because of the oxidizing atmosphere. While this technique has been successfully applied to the determination of rhenium⁴, a very refractory element, the possibility of the formation of refractory compounds with alumina must not be overlooked.

CONCLUSIONS

While many elements in solutions of organic solvents can be determined directly by other spectroscopic techniques, the proposed technique offers several advantages. Some of these advantages are great sensitivity, the use of conventional spectroscopic apparatus, the application of existing liquid-liquid extraction procedures, the simultaneous determination of several elements, the possibility of high concentration, the elimination of separate charring, and therefore, of losses of volatile elements, speed (*e.g.* aqueous ion-exchange eluates require much more time for evaporation), a minimum number of transfers, simplicity in operation, and easy preparation of accurate, economic and permanent standards in powder form from available, well-defined compounds. The disadvantages of the technique are the usual contamination problems of all enrichment methods, the disparity in concentration levels for various elements extracted, the change of concentration of liquid standards by evaporation, instability of the organic reagent and variations in its co-extraction. There is also an additional step involved in weighing but this is more than compensated by the elimination of charring.

SUMMARY

A considerable reduction in volume of the enriched sample is combined with the high absolute sensitivity of a mixed cathode layer-cathode excitation, which is applied directly to organic extraction residues in a 1:1 mixture with an alumina-graphite base. An oxygen protective atmosphere is used to increase the arc temperature, stabilize the column, and reduce cyanogen band interference. The method eliminates the need for subsequent mineralization or burning. Its application is discussed with reference to liquid-liquid extraction systems.

RÉSUMÉ

Dans la méthode proposée, on combine une réduction considérable de volume de l'échantillon enrichi avec la grande sensibilité d'une excitation "cathode layer-

cathode" combinée, à l'aide de l'arc continu. Les résidus organiques, après extraction, sont mélangés dans un rapport 1/1 avec un tampon oxyde d'aluminium-graphite, et sont excités directement. On utilise une atmosphère protectrice d'oxygène pour augmenter la température de l'arc, pour stabiliser la décharge et pour réduire les bandes de cyanogène. Ce procédé permet d'éviter de minéraliser et de brûler le résidu. L'auteur traite de l'application de la méthode aux systèmes d'extraction liquide-liquide.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen, in der eine stark angereicherte Probe mit einer Bogenentladung (die durch Kombination von Glimmschichtverfahren und Kathodenentladung eine hohe absolute Empfindlichkeit aufweist) angeregt wird. Die organischen Extraktionsrückstände werden in einer 1:1 Mischung mit einem Aluminiumoxyd-Graphit-Puffer direkt angeregt. Es wird eine Sauerstoffatmosphäre zur Erhöhung der Bogentemperatur und -stabilität, als auch zur Erniedrigung der Cyangas-Interferenz gebraucht. Die Methode ist auf Standardlösungen und -pulver metallorganischer Verbindungen aufgebaut. Eine nachträgliche Mineralisation oder Veraschung ist nicht notwendig. Die generelle Anwendung der Methode für Extraktions-Systeme wird diskutiert.

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D.C. ARC SPECTROCHEMICAL DETERMINATION OF RHENIUM IN MOLYBDENITE ORES

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The recently discovered element rhenium is already extensively applied in technology; its increasing importance commands a steady interest in related analytical problems. Complete surveys of classical and modern methods of analysis have been published¹⁻⁴ and are being supplemented by methods applying advanced instrumentation or reagents. Because of the extremely low terrestrial abundance of rhenium an enrichment separation with removal of interfering elements must usually precede any determination.

Spectrophotometry still remains the most widely used technique⁵⁻¹¹ and usually relies on liquid-liquid extraction isolation of rhenium compounds or removal of interfering elements. Ion-exchange separations¹²⁻¹⁵ represent the alternative universal enrichment procedure, followed generally by spectrophotometric determination of the separated rhenium. A combination of these techniques is usually incorporated in the neutron activation and radiochemical analysis^{4,16,17}, to date the most sensitive technique for rhenium.

Recent efforts to improve the analytical methods for isolated rhenium have included little optical emission spectroscopy. It is used, however, extensively for direct determination of this element in natural materials¹⁸. A distillation method for quantitative spectrographic determination of rhenium in concentrations from 5 to 200 p.p.m. in products of non-ferrous metallurgy was recently reported¹⁹. It requires special instrumentation. Enrichment of rhenium has been followed by a spectrographic technique in a qualitative way for separation by ion-exchange¹⁵, and by liquid-liquid extraction²⁰.

After the completion of the experimental work, two methods for spectrochemical determination of rhenium in molybdenite came to our attention^{21,22}. Liquid-liquid extraction is also used in both of them but all other features differ considerably from the present method. This paper is a specific application of the general principle and method of arcing dry liquid-liquid extraction residues in oxygen²³.

EXPERIMENTAL

Reagents and solutions

Rhenium standards. A stock solution of 1000 p.p.m. of rhenium in water was

TABLE I

SPECTROGRAPHIC APPARATUS AND CONDITIONS

Spectrograph:	Bausch and Lomb, 2-mm dual grating			
	Grating A		Grating B	
	Rulings	1200	grooves per mm	600
	Blaze	3000	Å	6000
	Order	1st		2nd
	Reciprocal linear dispersion	4	Å/mm	4
	Wavelength	2650-3600	Å	5300-7200 (1st order)
	Slit width	20	μ	20
	Slit length	4.5	mm	4.5
	Filter	100/33	neutral density(%T)	12.5 + 100/33
Excitation source:	Direct current arc (Applied Research Laboratories, Multisource Model 5700-21-1); peak voltage: 300 V; current: 12 A continuous.			
Arc stand:	Applied Research Laboratories Model 7400.			
Optical system:	The light source was located 74 cm from the slit. On the optical bench were a cylindrical quartz condenser, axis vertical, located 12 cm from the slit, a biprism at 41.5 cm, with neutral filters for one of the two gratings, and a relay lens at 58 cm, all relative from the slit. A 3.0 mm portion of the analytical gap at the cathode was observed by the spectrograph.			
Microphotometer:	Projection Comparator-densitometer (Applied Research Laboratories Model 2250); effective slit: 20 μ wide, 0.7 mm high.			
Electrode assembly:				
Upper electrode (anode):	3.05-mm diam. graphite rod.			
Lower electrode (cathode):	3.05-mm diam. graphite cupped electrode, I.D. 2.2 mm (drill #44). Side wall height of the cup 4.0 mm, overall electrode length 20 mm, contains 14.5 mg of the analysis mixture.			
Analytical gap:	10 mm, not maintained. Short-circuited, at start with a bare #36 AWG tinned copper wire, glued on by means of a conductive graphite-collodion lacquer ²⁷ .			
Atmosphere:	Oxygen 4.3 l/min at 1.0 atm.			
Flowmeter:	The Matheson Co., Inc., Oxygen tube No. 603.			
Controlled atmosphere chamber:	Angstrom, Inc. (Chicago), Model 1200 Atmosphere controller with ceramic flow tube, not allowing independent electrode movement.			
Exposure timing:	Prearc: none; exposure: 22 sec.			
Photographic photography:				
Emulsion:	Eastman Kodak SA-1; emulsion calibration: two-step filter, a preliminary curve method, using two exposures of a silver-manganese arc ^{27,34} on each plate. The Mn multiplet between 3441.98 and 3497.53 Å was used.			
Photographic processing:	Developer: D-19, using an Applied Research Laboratories developing machine; time: 3.0 min; temperature: 20 ± 0.5° adjusted manually before development.			

TABLE I (continued)

Background corrections:	For all lines, using Spex Industries, Inc., Metuchen, N.J., preliminary curve and relative exposure charts.			
Exposure index:	Transmittance of the Co 3453.50 Å internal standard line varies with each arcing.			
Analytical lines:				
Analytical line (Å)	Grating	Internal standard line (Å)	Concentration index (µg/40 mg)	Concentration range (µg/40 mg)
Re 3464.73	A	Co 3453.50	1.35	0.24-2.4
Re 3464.73	B	Co 3453.50	1.4	0.4-4.0
Re 3460.46	A	Co 3453.50	0.84	0.24-1.6
Re 3460.46	B	Co 3453.50	0.92	0.24-4.0
Re 3451.88	A	Co 3453.50	2.9	0.4-8.0
Re 3451.88	B	Co 3453.50	2.75	0.6-8.0
Re 3399.30	A	Co 3453.50	Not attainable	0.8-8.0
Re 3399.30	B	Co 3453.50		1.2-8.0

prepared from ammonium perrhenate (Specpure, Johnson, Matthey and Co.). Tetraphenylarsonium perrhenate was precipitated as described by WILLARD AND SMITH²⁴ with a recovery within $\pm 0.3\%$ of theory. It was used for preparing a stock solution of 100 p.p.m. of rhenium in chloroform. Tetraphenyl arsonium chloride was obtained from K and K Laboratories, Plainview, N.Y..

Cobalt standards. Electrolytic cobalt metal (99.35%, obtained from the Physical Metallurgy Division (PMD) of this Branch) or cobalt(II) chloride (Baker and Adamson Co.) was used to prepare a stock solution of 500 p.p.m., and the internal standard solution of 0.25 p.p.m. of cobalt in isopropanol (by direct dissolution of cobalt chloride and stepwise dilution just before use).

Manganese. Electrolytic manganese metal 99.98% (PMD).

Molybdenum and sulphur. Rhenium-free molybdenum oxide "Baker analyzed" (J. T. Baker Chemical Co.) and special high-purity sulphur (99.999%, American Smelting and Refining Co.) were mixed in a ratio 2:3 (*i.e.* MoS₂). Molybdenum sulphide (99%, City Service Co., N. Y.) and molybdenite (laboratory reagent grade, E. H. Sargent Co.) were also used.

Spectroscopic base. Aluminum oxide (Specpure, Johnson, Matthey and Co.), and spectroscopic graphite powder UCP-2 (Ultra Carbon Co.) were mixed (by grinding) in a ratio 4 Al₂O₃/1 C.

Dry metal-organic standards. Powders with various contents of rhenium and cobalt were prepared as described in another paper²³.

All other common reagents were of the highest available grade.

Procedure

Fuse 1.00 g of sample with sodium peroxide in a zirconium crucible and dissolve the melt in water. After decomposing the excess peroxide by boiling, adjust the pH to 8-9 (thymol blue indicator) with 1:1 sulphuric acid. Add 10 ml of aqueous sodium chloride solution (35.06 g/l), filter, and adjust to 200 ml. Pipet 20.0 ml of the solution into a 60-ml separatory funnel. Other aliquots can be used but they should be adjusted in volume and chloride ion concentration. Add 0.50 ml of the aqueous

2% (w/v) tetraphenylarsonium chloride solution, shake, and extract for 2 min with 10 ml of chloroform. Drain through an absorbent cotton plug in a funnel into a 25-ml porcelain casserole. Rinse the separatory funnel and stem from the top with chloroform. Add reagent again and repeat the extraction. Wash-extract the aqueous solution with about 3 ml more of chloroform, draining as previously. To the extract add 1.00 ml of the internal standard cobalt solution and complete the preparation of the electrode charge according to the general technique²³.

For each point on the calibration curve fuse 1.3 g of molybdenum oxide-sulphur mixture in place of the sample. Before dissolving the melt add from a microburette the appropriate volumes of an aqueous 1.0 or 10.0-p.p.m. rhenium standard solution. In other respects the general procedure is followed.

A series of 14 solutions containing from 2.4 to 250 μg of rhenium per 200 ml was prepared. From 2 to 6 electrodes for each calibration point, originating from at least 2 independent extractions, were arced and the spectra recorded on separate plates. Not less than 6 points (with one exception) were used for each calibration curve. The spectrographic conditions and apparatus are listed in Table I.

RESULTS AND DISCUSSION

Decomposition of sample

As in most recent methods for rhenium, sodium peroxide fusion was used. Sulphides decrease the time required for peroxide fusion and react almost instantaneously. The unpleasant foaming and the two-step fusion in mixed sodium hydroxide-peroxide procedure⁵ is eliminated. The much lower reactivity of standard mixtures of molybdenum oxide with sulphur, however, considerably lengthened the fusion time, and for this reason the Parr-bomb decomposition procedure had to be abandoned. In addition the perchlorate accelerator was not sufficiently reduced and interfered in the subsequent use of tetraphenylarsonium chloride.

Isolation and enrichment

Of all the separation methods for rhenium the direct extraction-separation by tetraphenylarsonium chloride is still considered one of the best and most universal^{7,10}. Rhenium from large volumes of ion-exchange eluates has, in any event, to be concentrated by evaporation, liquid-liquid extraction, or precipitation¹⁴. The conditions governing the extraction have been thoroughly investigated²⁵. Since with the present decomposition method only sulphates are formed, chlorides are added to yield a 0.03 *M* solution. The separation factor is still several hundred, while the recovery of the excess reagent is of the order of 75% under the conditions given. Reproducibility is good (for $n = 12$, precision is $\pm 3.1\%$).

Preparation of the electrode charge

Charring of the organic extraction residues as well as ashing in oxygen may lead to losses of the easily oxidized rhenium. Wet mineralization requires additional handling, but has been used for rhenium after isolation as the thiocyanate complex²⁶. However, in the case of the tetraphenylarsonium chloride method, considerable excess of the reagent is co-extracted, reacting explosively with the perrhenate present when heated with nitric acid. The dry metal-organic electrode charge was, therefore,

arced directly^{23,27}. Rhenium as the tetraphenylarsonium salt and cobalt as the chloride, plus a large excess of tetraphenylarsonium chloride were deposited from chloroform–alcohol solutions on to the spectroscopic buffer.

The composition of the final analysis mixture is adjusted to one part of the organic compound to one part of the inorganic spectroscopic buffer. All the compounds involved including the tetraphenylarsonium perrhenate²⁸ are stable at 150°—the drying temperature.

Dry metal-organic standards

The concentrations ranged from 20 to 200 μg Re/g, and from 7.5 to 75 μg Co/g of the standard. The quantity on the electrode then corresponded to *ca.* 1/66.7th of these values. Such standards were used, *e.g.*, for instrument precision test, volatilization (Fig. 1), and excitation time studies (Fig. 2) as a matrix for element interference checking, for protective atmosphere experiments, spectroscopic buffer tests, and in general, for instrument control.

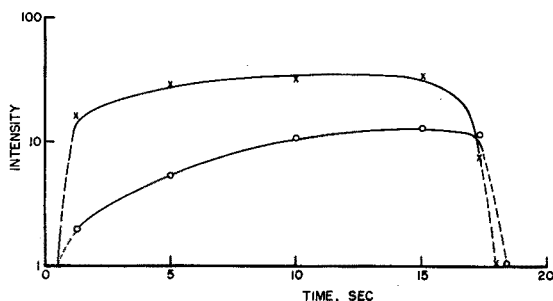


Fig. 1. Moving plate study for rhenium and cobalt. (○) Re 3464.73; (×) Co 3453.50. 1:1 Ph_4AsCl -buffer. Re, 3.0 μg ; Co, 1.125 μg . Time 25.0 sec.

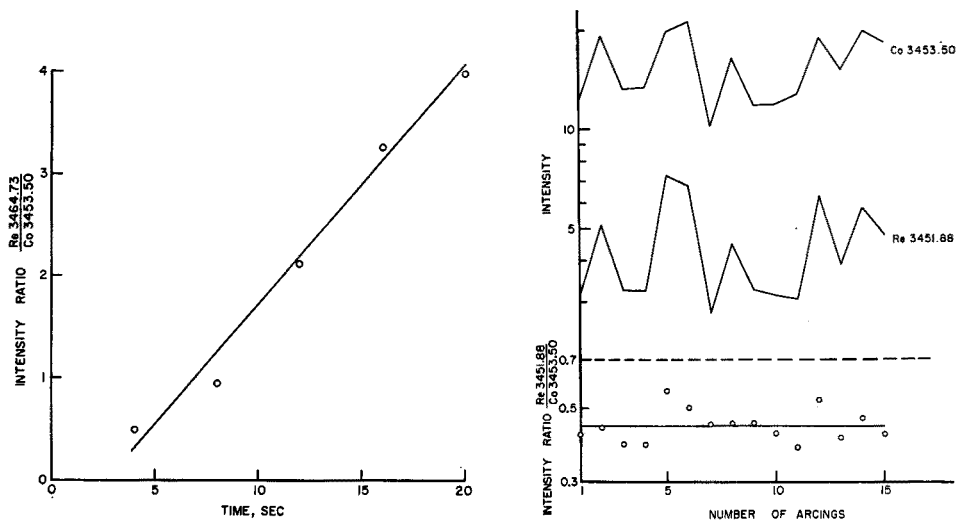


Fig. 2. Arcing time study. Re, 0.375 μg ; Co, 0.187 μg . 1:1 Ph_4AsCl -buffer. 6-mm crater electrode.

Fig. 3. Suitability of internal standard. Re, 3.0 μg ; Co, 1.125 μg . 1:1 Ph_4AsCl -buffer. Coefficient of variation $\pm 13.4\%$. Numbers 6 and 12 repeated ignition.

Spectrographic detection limit, excitation type and protective atmosphere

The detection limit for d.c. -arc anode or cathode layer excitation is known to be 500 ng of rhenium on the electrode in 70% Ar/30% O₂ atmosphere. In air this limit is increased to 2 μ g in both cases. For the copper spark method, 200 ng²⁹, or 0.1 μ g³⁰ detection limits have been quoted. This technique requires, however, special apparatus and was not considered in the present work. The technique of direct arcing of the liquid-liquid extraction residues²³ was therefore chosen. Oxygen served not only as a protective atmosphere, but had several other important effects for the determination of rhenium.

For the lowest calibration point (0.24 μ g of Re) on the Re 3460/Co 3453 B calibration curve, a relative error of +34, -25% is indicated. This represents a detection limit of 6.10⁻⁸g according to ASTM definition³¹.

Internal standard

Cobalt was used for this purpose. The excitation potential of its 3453.505 Å line and its ionization potentials are similar to those of rhenium, and the proximity in wavelength is good; Fig. 3 shows the dependence of the intensity ratio on number of arcings for a synthetic standard and demonstrates the compensation. A continuous moving plate study for both elements under analytical conditions is shown in Fig. 1. Cobalt is volatilized somewhat faster but the agreement is surprisingly good for a "refractory" element. Rhenium behaves here as an element of moderate volatility.

Time

The moving plate study (Fig. 1) also provided data for excitation timing. Since the ignition of the arc, the start of the plate travel, and the shutter opening were synchronized, a relatively exact measurement was possible from distances. Table II contains the results for arcing of 3.0 μ g of rhenium and 1.125 μ g of cobalt.

A similar experiment with 25 μ g of rhenium showed its presence still in the 24th second. The 20-sec arcing time was adequate for complete charge consumption apart from the residual alumina bead. The additional two seconds are a safety margin. Longer times could not be considered because of instrument limitations.

The calibration results are in excellent agreement with these data. The amounts of rhenium which could be volatilized quantitatively, exceeded only by a small margin those for "8 μ g Re/40 mg" point. The linear portion of the curves ends with 3.2 μ g of rhenium (ca. 40% of 8.0 μ g) on the electrode.

Interferences

Only a few of the possible chemical interferences of the tetraphenylarsonium chloride method²⁴ need be considered, since additional spectral separation is available. A composite synthetic sample, containing as well as 92% of molybdenite, 1% of cobalt, manganese, nickel and 5% of bismuth as oxides (bismuth is present in Quebec ores), was analysed according to the procedure. A qualitative spectrographic test failed to reveal any lines interfering with analytical lines; 100 μ g of cobalt was not extracted if present in aqueous solution.

From a spectral interference aspect (after isolation) molybdenum was completely absent. Rhenium lines at 3453.28 and 3452.50 Å, which could possibly interfere with the cobalt 3453.50 line have extremely low intensities because of their high

TABLE II
VOLATILIZATION CONDITIONS IN THE DISCHARGE COLUMN

<i>Time*</i> (sec)	<i>Observation</i>
0.0	Start of the arc and of the plate travel, practically instantaneous appearance of CN bands on plate, giving zero point in agreement with that obtained from rack position
0.5	Co 3453 appears
0.8	Re 3460 appears
0.9	Re 3464 appears
1.2	First possibility of transmittance measurement for Re 3464 and Co 3453
2.9	Re 3451 appears
8.0	Re 3399 appears (extremely weak)
16.8	Re 3399 disappears
17.3	Last possibility of transmittance measurement for Re 3464 and Co 3453
18.0	Co 3453 disappears
18.2	Re 3451 disappears
18.4	Re 3464 disappears
18.7	Re 3460 disappears
19.0	No Re and Co lines observable. Al 3082 still very strong
20.0	Al 3082 less strong
23.5	Al 3082 still present
25.0	End of arcing.

* Estimated error max. ± 0.2 – 0.3 sec. 1.66 mm on plate corresponds to a distance of 32 mm on ARL densitometer and a time of 1.0 sec.

excitation energies. Their influence was not apparent in the straight portion of the calibration curves. The precision even at high concentrations remained good; but the deviation from linearity, probably a multiple influence of self-absorption, incomplete volatilization, and spectral interference, precluded their analytical use.

Reactions in the arc

The intensity I of a line of an element i has been expressed³² by the relation

$$I_i = (k - Bp_i)(h - E_i),$$

where I_i is the intensity of a line of element i , Bp_i is the boiling point of the element i , in $^\circ$, E_i is the excitation potential (in eV) of element i , h is a constant of the source, being a measure of its capacity to excite atoms, and k is a constant representing the temperature of the arc. The use of pure oxygen in connection with a 12-A d.c. arc between 3.05-mm graphite electrodes considerably increases the constant k in the first factor. Since this factor represents the ability of the arc to vaporize the sample, the boiling point (360.3°) of rhenium oxide formed easily by direct oxidation, has to be considered instead of the boiling point (5630°) of the element itself². The first factor in the above equation and the intensity of the element line should, therefore, be substantially increased—in excellent agreement with the experimental data.

The ease of oxidation of rhenium is characteristic of the element. Moreover rhenium carbide, if formed at all, is not stable at moderately elevated temperatures², differing in this respect from tungsten and molybdenum carbides. Once the rhenium oxide is in the arc column, it is easily decomposed and the atoms can be excited. The dissociation pressure of Re_2O_7 is 10 atm at 1620°K ³³. The oxygen acts, therefore, also as a carrier to sweep the rhenium out of the electrode charge.

Precision

The precision of the determination was evaluated by a routinely available CDC 3100 computer program. Table III contains the results and Figs. 4 and 5 show the 95% confidence limits for individual predictions.

TABLE III

PRECISION AND CALIBRATION DATA

Analytical line (<i>A</i>)	Total degrees of freedom ^a	No. of calibr. points	Regression coeff. (<i>b</i>)	Proportion of variation (%) ^c	Constant term <i>a</i> ^d	Standard error in terms of		Relative error ^e (%)
						<i>Y</i> units ^a	<i>X</i> units ^a	
3464 A ^b	24	7	1.082	89.27	0.741	0.154	0.142	+ 39 - 27
3464 B ^b	20	7	0.965	94.14	0.726	0.080	0.083	+ 21 - 17
3460 A	23	6	1.209	85.98	1.262	0.159	0.132	+ 36 - 26
3460 B	28	8	1.082	90.79	1.086	0.137	0.126	+ 34 - 25
3451 A	25	8	0.890	93.83	0.392	0.128	0.144	+ 39 - 28
3451 B	16	7	0.974	97.44	0.373	0.064	0.065	+ 16 - 14
3399 A	12	6	0.745	95.51	0.151	0.136	0.182	+ 52 - 34
3399 B	7	4	0.811	97.93	0.136	0.077	0.095	+ 25 - 20

^a Number of arcings — 1.

^b Grating.

^c Due to the independent variable.

^d Log transformation.

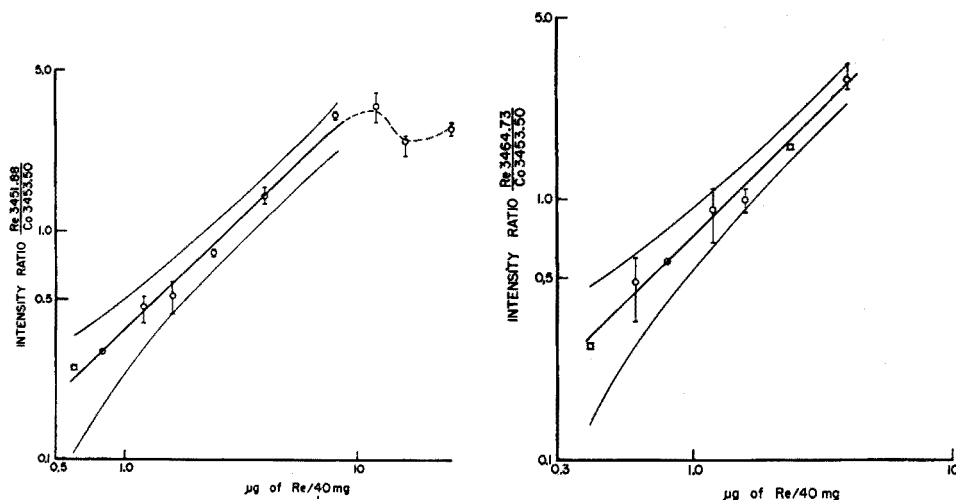
^e Scatter in concentration along the regression line.

The results of an independent replication test for a molybdenite sample solution with the lowest available concentration of rhenium ($n=6$ for extractions, $n=11$ for arcings) are shown in Table IV. They show that the scatter along the regression line is a much more realistic assessment of the precision of an analytical method than the simple replication.

This compares with a replication test (Fig. 3) on a standard powder where a coefficient of variation of $\pm 13.4\%$ was obtained. The limiting factor for the precision is thus the instrument response and not the preliminary treatment.

Originally it was hoped that both gratings could be used simultaneously for a maximum concentration coverage. The results show that this is not possible. While the filtration on grating B markedly improves the precision, the range is not materially altered.

The slopes of the calibration curves are in the best examples close to unity, with the best analytical line Re 3451 B closely followed by Re 3464 B. In the former case a slightly delayed excitation (Table II), after the initial stabilization of the discharge column has been achieved, is probably most responsible for the improvement. Calibration curves for the two best analytical rhenium lines are shown in Figs. 4 and 5. Unless otherwise stated, the precision was calculated from range.



Figs. 4-5. Calibration curve and 95% confidence limits for (4) Re 3451.88 Å, (5) Re 3464.73 Å and Grating B.

TABLE IV
PRECISION COMPARISON

Analytical line (Å)	Grating	Rhenium found (µg)	Relative error (%) from regression curves	Coefficient of variation (%) from replication test ^b
Re 3464	A ^a	0.86	+39 -27	±14.9
Re 3451	A ^a	0.77	+39 -28	±15.5

^a Grating A used only.

^b Eleven spectra on one plate.

TABLE V
RHENIUM CONTENT IN MOLYBDENITES

Calibration curve Re line (Å)	Grating	Rhenium found (µg) in sample						
		City Service Co. N.Y. 99 ^a	Quebec I composite head	Quebec I/138I 94.2 ^{a,c}	Quebec I/1388 91.6 ^a	Canada I concentrate B	E. H. Sargent lab. reagent 99 ^a	Ontario I comp. head non-processed
3464	A	0.8 ₆	3.0 ₄	—	2.9 ₈	—	—	0.7 ₄
3464	B	—	3.0 ₆	7.4	2.9 ₀	5.6	6.6	0.8 ₆
3460	A	0.7 ₈	3.0 ₈	—	—	—	—	0.7 ₄
3460	B	0.7 ₇	—	—	2.8 ₇	—	—	0.7 ₅
3451	A	0.7 ₉	3.2 ₁	—	2.9 ₁	6.2	—	0.7 ₄
3451	B	—	2.9 ₈	7.0	3.0	5.6	6.2	—
3399	A	—	—	6.2	—	6.4	6.0	—
3399	B	—	3.0	7.1	—	5.4	6.2	—
p.p.m. Re ^b		7.7	29	35	30	56	248	8.6

^a % MoS₂.

^b Best available analytical line used.

^c Aliquot 20/100 ml.

Accuracy

No samples of known rhenium content were available. The rhenium-free molybdenum oxide was spiked with known rhenium amounts and used for calibration by applying the complete analytical procedure. Therefore, the calibration results are also a measure of the accuracy attainable. Several Canadian and other molybdenite samples have been analysed routinely by the method proposed. The results are shown in Table V.

The author thanks Dr. A. H. GILLIESON, of this Branch, for suggesting the problem of spectrochemical determination of rhenium in ores by an enrichment method and for the critical reading of the manuscript. A discussion on statistical evaluation of the results with Dr. V. SESHADRI, McGill University, Montreal, Quebec, is gratefully acknowledged while Messrs. H. SOMERS and G. D. CAMERON of the Departmental Computing Centre, are thanked for their modification of the existing computer program.

SUMMARY

Rhenium is isolated as tetraphenylarsonium perrhenate from solutions of molybdenite ores. It is excited in a mixture with an alumina/graphite buffer directly on the cathode in an oxygen atmosphere. Oxygen acts as a protective atmosphere and as a carrier to sweep into the discharge the highly refractory rhenium in the form of easily volatilized oxides. Intensity ratios of Re 3464.73, 3460.46, 3451.88 and 3399.30 Å lines with Co 3453.50 Å internal standard line cover the range 0.1–3.2 µg of rhenium on the electrode. The relative deviation of the method, computed by a routine regression analysis program, is +16––14% for the best analytical line. The detection limit is $6 \cdot 10^{-8}$ g of rhenium. Several Canadian and other molybdenites with a rhenium content from 8 to 250 p.p.m. have been analysed.

RÉSUMÉ

On propose une séparation du rhénium sous forme de perrhéate de tétra-phénylarsonium, dans le cas de solutions de molybdénites. On procède ensuite à une excitation sur cathode, dans une atmosphère protectrice d'oxygène, avec mélange oxyde d'aluminium-graphite. L'oxygène permet de volatiliser le rhénium réfractaire dans la décharge (sous forme de ses oxydes volatils). Les rapports d'intensité des raies Re 3464.73, 3460.46, 3451.88 et 3399.30 Å à celle du cobalt (étalon interne) 3453.50 Å couvrent les concentrations d'environ 0.1 à 3.2 µg, sur l'électrode. Limite de détection: $6 \cdot 10^{-8}$ g Re.

ZUSAMMENFASSUNG

Rhenium wird aus Lösungen von Molybdänit-Erzen als Tetraphenyl-arsonium-perrhenat isoliert. Es wird in Mischung mit einem Aluminiumoxyd-Graphit-Puffer in einer Sauerstoffatmosphäre direkt an der Kathode angeregt. Sauerstoff wirkt als eine Schutzatmosphäre und als ein Träger, um das hochsiedende Rhenium in Form der leicht flüchtigen Oxyde in den Bogen zu tragen. Die Intensitätsverhältnisse der

3464.73, 3460.46, 3451.88 und 3399.30 Å Linien des Rheniums mit der 3453.50 Å Linie des Cobalts (Bezugselement) werden zur Bestimmung von 0.1 bis 3.2 µg Rhenium an der Elektrode verwandt. Der relative Fehler wird mittels eines Computers und eines Regressionsanalysen-Programms kalkuliert und beträgt +16, -14% für die beste analytische Linie. Die Empfindlichkeitsgrenze beträgt $6 \cdot 10^{-8}$ g Rhenium. Einige kanadische und andere Molybdänite mit einem Rhenium-Gehalt von 8 bis 250 p.p.m. wurden analysiert.

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THE SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM IN ILMENITE

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In the evaluation of ilmenite concentrates as a source of titanium, the chromium content is of particular significance owing to its effect on the colour of pigment-grade titanium dioxide¹. Several spectrophotometric procedures for the determination of chromium are available, the most sensitive and most frequently employed being the diphenylcarbazide method² but few of these procedures have been concerned with materials containing relatively large amounts of both iron and titanium as well as vanadium at a similar level to chromium.

Iron causes serious interference in the diphenylcarbazide-chromium(VI) reaction and is reported variously as giving both high and low results²⁻⁵. One common procedure to avoid iron interference is to oxidise the chromium to chromium(VI) in a nitrate or peroxide alkaline fusion and filter the iron oxide residue from the aqueous leach to collect the chromium in an iron-free filtrate. This approach has a number of disadvantages. Removal of chromium from the oxide residue may not be absolutely complete⁵⁻⁹; a portion of the iron can remain dispersed in the alkaline filtrate¹⁰; peroxide or nitrite from the fluxing materials can cause reduction of chromium(VI) when the solution is acidified, and vanadium, which also interferes in the diphenylcarbazide procedure^{2,10}, is not separated from chromium.

These possible sources of interference can be avoided if chromium in an acidified solution is firstly oxidised to chromium(VI) and extracted in a 1 *M* hydrochloric acid medium with a suitable solvent. Iron and vanadium remain substantially in the aqueous raffinate and extracted chromium may then be stripped to an aqueous phase to obtain a relatively pure system for the diphenylcarbazide reaction. This general approach was chosen therefore as a basis for development.

Preliminary considerations

Oxidation of chromium to the hexavalent state before the extraction can be achieved by various techniques³ although for small amounts of chromium few of these are satisfactory as reaction by-products can cause subsequent chromium reduction^{7,11}. In preliminary experiments it was confirmed that potassium permanganate was a completely satisfactory chromium oxidant but only if no attempt was made to remove the excess with a selective reductant, *e.g.* sodium azide, which was found to reduce a small fraction of the chromium under certain conditions. One of the advantages of the solvent extraction approach is that excess of permanganate is not co-extracted with chromium(VI).

Conditions for quantitative recoveries of chromium by solvent extraction have been studied extensively using methyl isobutyl ketone (MIBK) as the sol-

vent^{3,4,12-17}. Investigations of the reported procedures confirmed that certain recommended experimental conditions, *e.g.* low extraction temperature, short extraction time and minimum delay between extraction and strip, were necessary for satisfactory recoveries of microgram amounts of chromium but they also revealed a variety of additional factors which can cause low results. With the high ratio of iron to chromium in low chrome ilmenites, for example, the 1 *M* hydrochloric acid medium for extraction of chromium still allows some iron to be extracted in an amount sufficient to decrease chromium diphenylcarbazide absorbances with currently accepted procedures. A further problem is that chromium(VI) is easily reduced by impurities in certain reagents, an aspect of increasing importance as the chromium content diminishes. The aim of the present studies therefore was to develop a relatively simple procedure to avoid low results arising both from possible iron interference and from reduction of chromium(VI).

Oxidation of chromium

It has been reported, following an examination of various oxidants, that ceric sulphate is preferable to potassium permanganate and certain other alternatives³. In the present work the presence of a high concentration of titanium required that the sulphuric acid concentration be increased to prevent separation of titanium oxy compounds during the boiling period for chromium oxidation. Under these conditions ceric sulphate was an unsatisfactory oxidant presumably through the formation of sulphate complexes. A comparison of oxidants in the presence of titanium and 1 *M* sulphuric acid, using 50- μ g amounts of chromium(III), gave only a 75% oxidation yield of chromium(VI) with ceric sulphate compared with 97% using permanganate. The latter was therefore adopted for the procedure, the slight excess being allowed to remain.

Loss of chromium(VI) by reduction

After oxidation, care is required to avoid reduction of chromium(VI) by traces of reducing materials present in reagents. Methyl isobutyl ketone requires several equilibration steps to remove traces of alcohols and phosphoric acid requires treatment with permanganate. It is not surprising also that distilled water blown by mouth from a wash bottle can almost invariably reduce a considerable fraction of the chromium(VI). Simple alternative techniques in dilutions or transfer procedures are readily available.

Reduction of chromium(VI) directly by MIBK is virtually prevented by operating at the specified low temperature provided that the analysis is completed without unnecessary standing periods once the extraction has been commenced.

Influences in the diphenylcarbazide reaction

Effect of iron. As the literature provides conflicting data on the effect of iron, this aspect was examined in detail. It has been claimed that an iron-diphenylcarbazide reaction yields a brown colour with measurable absorption at the chromium peak. Some standard procedures in fact suggest reading at a higher wavelength of 580 nm to diminish such absorption. The present studies showed, however, that this approach is misleading. At temperatures above 15°, positive absorbance readings due to iron are only obtained in the virtual absence of chromium; the more serious

effect in the presence of chromium is, in fact, a decrease in absorbance, as has been shown by several other workers^{3,5}. Expedients to counteract such fading by taking readings rapidly, as is sometimes recommended, were considered unsatisfactory.

As a preliminary to devising a method of iron control, the amount of iron normally co-extracted with chromium(VI) using MIBK in the 1 *M* hydrochloric acid medium was determined. From a simulated ilmenite sample solution an aliquot containing 15 mg of iron was taken through the extraction procedure. The final aqueous phase contained 300 μg of iron (2% of the original). By incorporating 0.5 ml of 1:1 phosphoric acid in the extraction this amount of iron contamination was diminished to 190 μg .

The effect on colour development of amounts of iron of this order is shown in Fig. 1A. An important but little recognised variable, the reaction temperature, was also incorporated in these tests since no data on temperature effect in the presence of iron could be located in the literature. The colours were developed from 50 μg of chromium and 2 ml of 0.25% diphenylcarbazide in a final volume of 50 ml for 10 min at a sulphuric acid concentration of 0.1 *M* as this medium has become widely accepted in published procedures. While the results in Fig. 1A emphasise the limited tolerance of a sulphuric acid system to iron, the effect of low temperature in eliminating the iron effect is seen to be highly significant.

Further control over iron interference can be obtained by substituting a phosphoric acid medium for sulphuric acid^{2,5,18,19}. The effect of the phosphoric acid system is shown in Fig. 1B for the same range of iron contents and temperature. These data confirm the benefits expected of the phosphoric medium and again indicate the advantages of lower temperatures (< 15°). As an adequate rate of colour development is obtained at 5°, this temperature may be adopted for the convenience of thermostatic bath operation at a single low temperature. As the amounts of iron remaining with chromium after solvent extraction are so low (> 200 μg) some latitude in temperature of colour development is permissible. For such low levels of iron, temperature control is only required during colour development and need not extend to the spectrophotometer cell compartment. Comparison of Figs. 1A and 1B shows that the accuracy obtainable with the new low temperature-phosphoric acid procedure provides a marked contrast, even when small amounts of iron are present, to the room temperature-sulphuric acid system when room temperatures are 20° or higher.

Effect of acid concentration and standing time. An acid concentration of 0.1 *M* sulphuric acid has been widely accepted as the optimum in respect of rate of colour formation and stability. The effect of varying the acidity for both sulphuric and phosphoric acids and taking 1-mg amounts of iron at 20° to enhance the limitations of sulphuric acid is shown in Fig. 2. While it is seen that doubling the acidity at 0.2 *M* sulphuric acid gives improved tolerance to iron, the superiority of the phosphoric acid medium again stands out; with the latter medium the acid concentration can cover an extremely wide range.

Other data confirm that 10 min is an adequate reaction time and stability with time is extended as temperature is lowered. At 10° with phosphoric acid, for example, in the presence of 1 mg of iron—a considerably greater amount than expected in the procedure—there was no decrease in absorbance with 50 μg of chromium after 1 h.

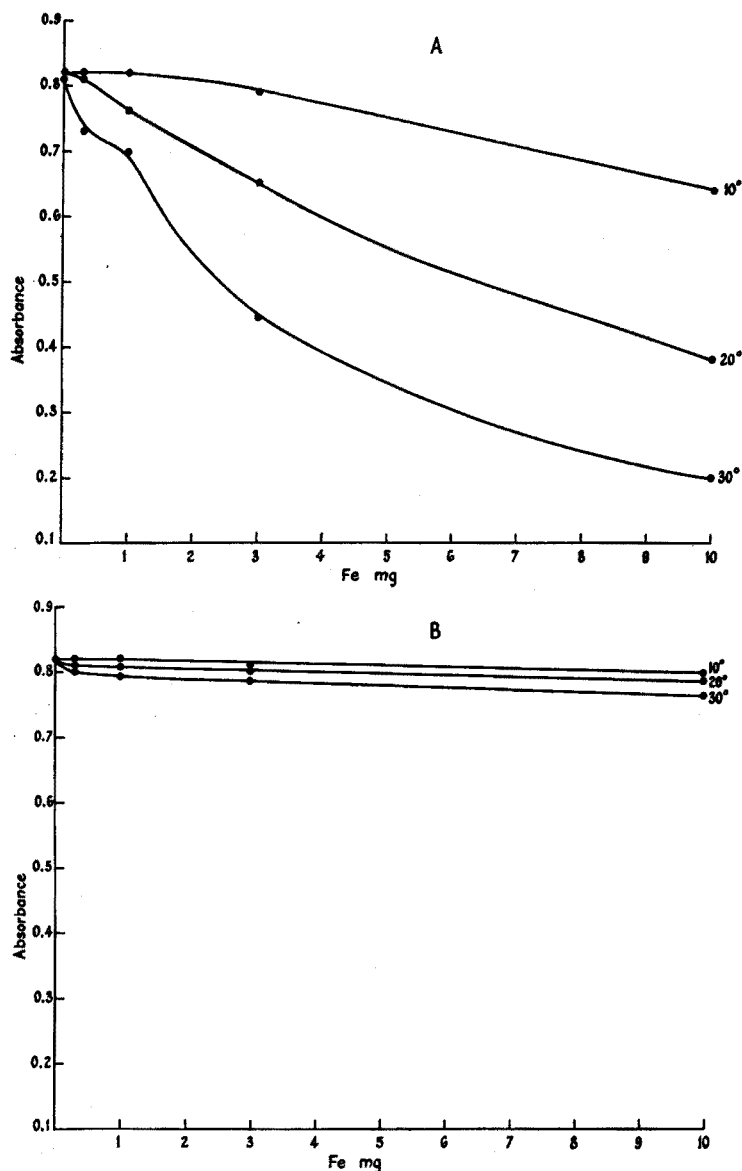


Fig. 1. Effect of iron on absorbance of the chromium diphenylcarbazide complex at various temperatures. (A) 0.1 *M* sulphuric acid medium; (B) 0.3 *M* phosphoric acid medium.

It will be observed from Figs. 1A and 1B that the disadvantages of sulphuric compared to phosphoric acid tend to disappear as the amount of iron is decreased to the level expected in the procedure. This factor may well make the choice of acid immaterial in such low iron situations, leaving control of iron to the low temperature only. Notwithstanding, substitution of phosphoric acid seems desirable in any diphenylcarbazide procedure for chromium, because temperature requirements then become less critical.

Diphenylcarbazide reagent quality. Commercially available reagents were observed to be of two types as previously noted by ALLEN²⁰. Most of them gave a molar absorptivity of $3.3 \cdot 10^4$ while AnalaR grade gave a value of $4.2 \cdot 10^4$. These values are in good agreement with those obtained by ALLEN who regarded the lower value as applying to a mixture of diphenylcarbazide and phenylsemicarbazide.

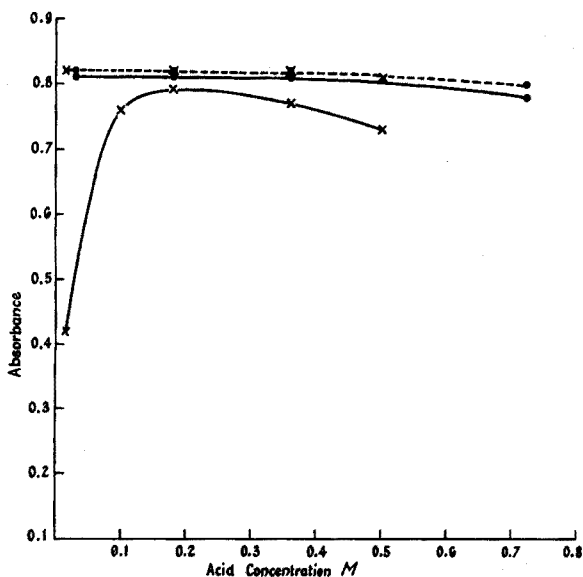


Fig. 2. Effect of acid concentration on absorbance of the chromium diphenylcarbazide complex at 20°. ● phosphoric acid medium; × sulphuric acid medium; --- Fe absent; — Fe, 1 mg present.

EXPERIMENTAL

Reagents

Methyl isobutyl ketone (commercial grade). Pre-equilibrate 3 times with equal volumes of 1 M hydrochloric acid at 5° and store at 5°. Prepare a batch fresh daily.

Hydrochloric acid, 5 M and 1 M. Dilute A.R. material with distilled water and store at 5°.

Diphenylcarbazide reagent. 0.25% solution of AnalaR grade in A.R. acetone. Prepare fresh daily.

Phosphoric acid 1:2, oxidised. Dilute 1 volume of phosphoric acid (A.R., s.g. 1.75) with 2 volumes of distilled water, warm to 60° and add 0.01 M potassium permanganate dropwise to a faint pink colour. Continue heating to discharge the colour.

Use glass-distilled water throughout.

Procedure

Fuse 15 g of A.R. sodium hydrogen sulphate in a 250-ml round-bottom quartz or Vycor flask, cool, and add 1.000 g of carefully sampled ilmenite (particle size < 200 mesh). Fuse until decomposition is complete, cool and, without undue

delay, dissolve in 50 ml of 2 *M* sulphuric acid heating gently as necessary. Add 30 ml of water, cool, and filter any residue into a 200-ml volumetric flask. Wash the residue well with 0.5 *M* sulphuric acid, ignite in a platinum crucible and volatilise any silica by hydrofluoric-sulphuric acid treatment. Fuse any remaining residue with 0.5 g of sodium hydrogen sulphate, leach with 2 *M* sulphuric acid and combine with the main portion (Note 1).

Dilute the filtrate or combined solutions to volume. Measure an aliquot (conveniently 10 ml) to contain not more than 50 μg of chromium, into a 50-ml beaker. Add 2 *M* sulphuric acid if necessary, to provide a total of approximately 15 mmol of this acid (Note 2). Dilute to 15 ml, add 1 ml of 0.01 *M* potassium permanganate dropwise to provide an excess. Add a small stirring rod, cover, boil gently for 5 min and cool to 5°. Prepare a degreased separating funnel (Note 3), cool to below 15° and lubricate the tap with distilled water. Transfer the solution to the funnel completing the transfer with 5 ml of 5 *M* hydrochloric acid and water in a small pipette. (Do not use water blown by mouth from a wash bottle or water from a polyethylene squeeze bottle.) The total volume in the funnel should not exceed 25 ml.

Add 0.5 ml of 1:2 oxidised phosphoric acid and 25 ml of pre-equilibrated MIBK at 5° and extract for 30–40 sec. Reject the aqueous phase as soon as separation is complete and scrub the solvent with 5 ml of 1 *M* hydrochloric acid at 5° for 30 sec, again rejecting the aqueous phase. Strip the chromium by extracting with 40 ml of water at 70° for 30 sec and separate and collect the aqueous phase in a 50-ml cylinder. Wash the solvent once with 5 ml of water at room temperature and combine with the first strip. Add 3 ml of 1:2 oxidised phosphoric acid and distilled water to a volume of 48 ml, mix and cool to 5–10°. Add 2 ml of 0.25% diphenylcarbazide reagent, mix immediately and stand for at least 10 min at 5–10°. Measure the absorbance at 546 nm against a water blank. Prepare a calibration graph by taking various amounts of chromium through the whole procedure; this corrects for the *ca.* 97% recovery. With A.R. diphenylcarbazide, 50 μg of chromium taken through the procedure gives an absorbance in a 1-cm cell of 0.785 (Note 4).

Notes

(1) Residue treatment is usually unnecessary as negligible chromium remains with the few milligrams of unattacked minerals, *e.g.* quartz and zircon.

(2) The additional acid prevents precipitation of titanium oxy compounds.

(3) Any grease should be removed with solvent and the funnel then cleaned with chromic acid solution. Thorough rinsing leaves no residue of chromium to vitiate the results and properly cleaned funnels rarely require further treatment.

(4) Other grades of diphenylcarbazide give markedly lower values but this does not necessarily detract from their usefulness.

RESULTS AND DISCUSSION

The two-fold effect of iron in the diphenylcarbazide reaction with chromium may account for its interference having been overlooked in some of the published procedures; with very low amounts of chromium, positive absorption values arising from iron are offset by the fading induced in the chromium colours. The present work has shown that over a normal working range of chromium levels, iron fading

is the more usual effect but in either event iron interference is effectively controlled by the combination of the phosphoric acid medium and low temperature for development.

Various quantities of chromium(III) covering the range 5–50 μg Cr were taken through the complete procedure. A linear relationship was obtained with recoveries not less than 95% at all levels. At 50 μg , recovery was 97%.

To establish the general reliability of the procedure recovery tests were conducted on synthetic standards representing a comprehensive typical ilmenite matrix. Solutions contained the flux and acid required by the procedure and Ti, Fe, Mn, V, Al, Ca, Mg and PO_4 at the maximum expected levels. Recoveries of chromium at several levels were identical with those obtained from pure solutions. As a further check, results obtained using the procedure on ilmenite samples of various chromium contents were compared with results obtained by an atomic absorption procedure (Table I).

TABLE I
COMPARISON OF RESULTS ON ILMENITE SAMPLES

Sample	% Cr_2O_3	
	Atomic absorption	This paper
1	0.041	0.038
2	0.113	0.114
3	0.153	0.150
4	0.246	0.243

An assessment of sensitivity showed that the chromium contents of ilmenite or upgraded ilmenite or rutile can be determined accurately to a convenient lower limit of 0.005% Cr_2O_3 . This level suffices for commercial low chrome titanium concentrates normally containing 0.01–0.3% Cr_2O_3 .

SUMMARY

A new diphenylcarbazide procedure free from iron interference is described for the determination of chromium in low-chrome ilmenite. After fusion of the sample, chromium is oxidised with permanganate and most of the iron is eliminated by extraction of chromium(VI) with MIBK. Residual iron causes fading of the final colour; this can be avoided by using a phosphoric acid medium at temperatures below 15°. When iron levels are less than 200 μg , temperature control (10°) suffices to prevent iron interference if the concentration of the usual sulphuric acid medium is increased to 0.2 *M*. However, the phosphoric acid–low temperature method gives wider tolerance to acidity variations and maximum stability with time.

RÉSUMÉ

On décrit un nouveau procédé pour le dosage du chrome dans l'ilménite, à l'aide de diphénylcarbazide. Après fusion de l'échantillon, le chrome est oxydé par le permanganate. Le fer est presque complètement éliminé par extraction du chrome

au moyen de MIBK. Le fer pouvant rester produit un affaiblissement de la coloration; ce qu'on peut éviter en milieu acide phosphorique, à une température inférieure à 15°. Lorsque la teneur en fer ne dépasse pas 200 µg, le contrôle de la température (10°) suffit pour empêcher le fer de gêner si la concentration de l'acide sulfurique est portée à 0.2 M. Cependant la méthode, à l'acide phosphorique—basse température, présente plus de latitude aux variations d'acidité et une stabilité maximum avec le temps.

ZUSAMMENFASSUNG

Zur Bestimmung von Chrom in Ilmenit mit niedrigen Chromgehalten wird ein neues Verfahren mit Diphenylcarbазид beschrieben, das frei von Störungen durch Eisen ist. Nach Aufschluss mit Disulfat wird das Chrom mit Permanganat oxidiert und der grösste Anteil des Eisens durch Extraktion des Chrom(VI) mit MIBK eliminiert. Durch Verwendung eines phosphorsauren Mediums bei Temperaturen unter 15° wird eine Störung restlichen Eisens auf die Farbbildung vermieden. Betragen die Eisengehalte weniger als 200 µg, so verhindern Temperaturen von 10° eine Störung durch Eisen, wenn die Konzentration des üblichen schwefelsauren Mediums auf 0.2 M gesteigert wird.

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A DIRECT READ-OUT SYSTEM FOR FAST NEUTRON ACTIVATION ANALYSIS FOR OXYGEN IN STEELS

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In the iron and steel industry, a rapid and precise method for the determination of oxygen has been in great demand for many years; if such a method were available, precise control of the Bessemer converter operation as well as that of the Siemens-Martin furnace could be achieved and this would result in lower production costs. Recently, new activation methods for the determination of oxygen have been developed¹⁻⁵ in order to overcome this problem, but the problems of a rapid sampling method and of a rapid calculation of analytical results have remained. In this paper, a direct read-out system in which essentially no time is required for calculation is discussed and applied to the analysis of iron and steels for oxygen.

Principle of the direct read-out system

A fast neutron activation unit⁶ was used in this work. The C-R neutron-monitoring system⁷ in this unit can automatically normalize the observed count value by a simple integrating circuit whose time constant is $1/\lambda$ (where λ is the decay constant of nitrogen-16 produced from the nuclear reaction $^{16}\text{O}(n, p)^{16}\text{N}$). It is possible to compare each observed count value without calculation under different neutron fluxes. Details of the apparatus have been reported previously⁷. Under the experimental conditions used, in which the analytical procedure is controlled entirely automatically by means of the C-R neutron-monitoring system, the oxygen content of the sample can be calculated as follows⁴:

$$\text{oxygen wt \%} = \frac{100k}{WT} (n_1 - n_2 - B) \quad (1)$$

where n_1 is the count value (0-30 sec), n_2 the count value (30-60 sec), k the sensitivity (mg of oxygen/count), B the blank count value, W the weight of sample (mg), and T the transmittance value = 0.879 for iron and steel.

In eqn. (1), W can be made constant for a specified sample, e.g. 8.750 g in the case of iron and steel; it is a general rule to keep the size of the sample constant in order to maintain constant geometry for the neutron bombardment when a particle accelerator is used as the activation source. T , the transmittance value⁴, is also constant for a defined type of sample, e.g. 0.879 for iron and steel with the sample sizes used (diam. 12 mm and length 10 mm). The sensitivity for oxygen, k , is made constant by the action of the C-R neutron-monitoring system. Therefore, the term $(100k/WT)$ in eqn. (1) is constant for a definite type of sample. Accordingly, if a counting system represented by the coefficients of the ascending powers of $(WT/100k \cdot$

10^m) is used in the first stage of a counting circuit in the measuring system for the activated sample while the ordinal decimal system is used in the next stage, the weight percentage of the oxygen to be analyzed can be directly indicated by the counting system. The term 10^m is introduced to furnish the decimal point to the analytical results and its value can be chosen suitably. The value of the term ($WT/100k$) itself is also variable for different sample types and may be adjusted to suitable values for various sensitivities.

Circuit of the direct read-out system developed

A block diagram of the system developed and a photograph of the control panel are shown in Figs. 1 and 2 respectively. The system consists of an input pulse shaping circuit, a multiplication circuit, a division circuit, a reversible decimal scaler

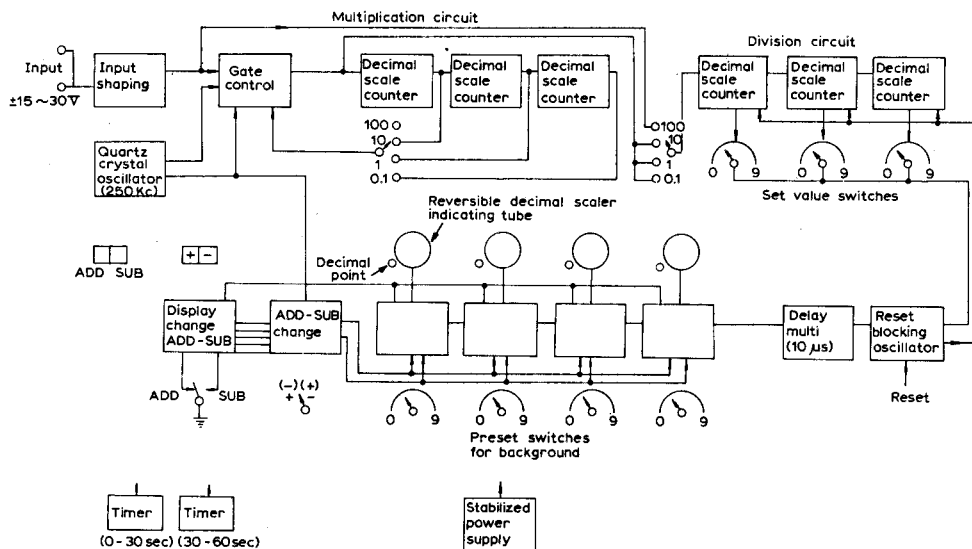


Fig. 1. A block diagram of the direct read-out system.

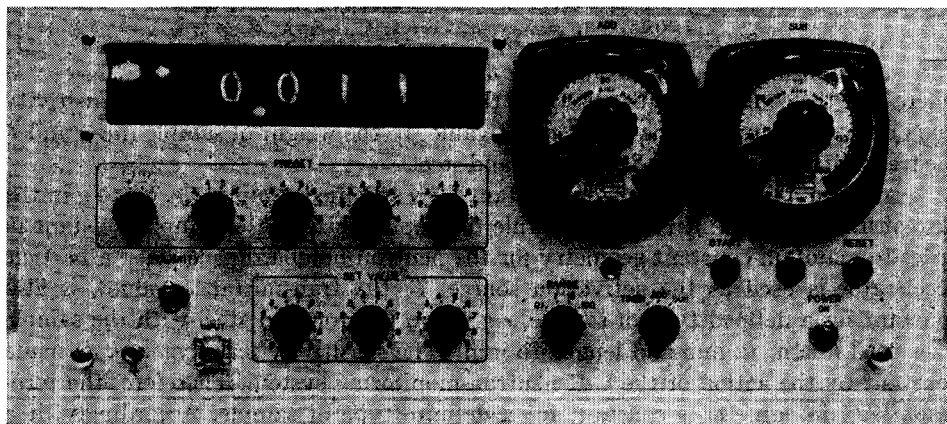


Fig. 2. The control panel of the direct read-out system.

and two timers for addition (0–30 sec) and subtraction (30–60 sec) of the number of pulses. The circuitry is transistorized.

Input shaping circuit. Input voltage 15–30 V, input impedance 1 M Ω polarity plus and minus.

Multiplication circuit. When the number of pulses from the pulse-height analyzer is smaller than the value of the term ($WT/100k$) which is set up for the next stage (division circuit), the analytical value in the indicating tube may be shown as zero. In order to prevent this phenomenon, a pulse from the pulse-height analyzer produces 1, 10, 100, or 1000 pulses from a quartz crystal oscillator in the multiplication circuit.

Division circuit. The division circuit consists of a 3-figure decimal-scale counter and three set-value switches. The circuit is operated as a counting system for numbers represented by the coefficient of the ascending powers of 1–1000. By means of the three set-value switches, the value of the term ($WT/100k$) can be preset. In this circuit, when the number of pulses from the multiplication circuit amounts to the preset value, all values are reset to zero and counting is continued once again. In this case, a shaped reset pulse is introduced to the next stage (reversible decimal scaler).

Reversible decimal scaler. The reversible decimal scaler consists of a 4-figure decimal-scale counter, 4 preset-value switches which allow the blank test result to be set up before analysis, and two timers with which the reset pulses are counted: 0–30 sec for addition and 30–60 sec for subtraction, respectively.

EXPERIMENTAL

Apparatus

A 14-MeV neutron activation analysis unit "Activac" constructed by Tokyo Shibaura Electric Co., was used. The neutron generator output in the unit (Cockcroft-Walton type, accelerating voltage 200 kV, ion current 1 mA) was $3 \cdot 10^{10}$ n/sec for oxygen analysis in iron and steels. All analytical procedures were controlled by the C-R neutron-monitoring system reported previously⁷. A $5 \times 5''$ well-type sodium iodide (Tl) crystal was used as the γ -ray detector.

Samples

In this work, various iron and steel samples containing oxygen between 0.2% and 0.0015% were used. The sample size was 12 mm in diameter and 10 mm long.

Procedure

Activation and measurement for a standard sample (iron containing 0.203% oxygen) are carried out. The multiplication circuit is adjusted so that a pulse from the pulse-height analyzer produces 10 pulses (this value is selected in proportion to the level of the induced activity of oxygen).

A definite value in the division circuit is chosen so that the analytical result of the standard in the indicating tubes is equal to the weight percentage of oxygen in the standard.

The blank test is then carried out and the result obtained on the indicating tubes is preset on the reversible decimal scaler. Finally, the unknown sample is activated and measured.

RESULTS

The results obtained for oxygen in iron and steel samples by the direct system developed and by the conventional calculation method are given in Table I. It can be seen that these results were in good agreement.

TABLE I
RESULTS FOR OXYGEN IN IRON AND STEELS

Sample	%O present ^a	%O obtained	
		Direct read-out	Conventional method
K-1	0.203	0.214, 0.208, 0.200 0.192, 0.205, 0.194	0.214, 0.209, 0.201 0.194, 0.205, 0.193
K-2	0.017	0.016, 0.016, 0.018 0.016, 0.015	0.016, 0.016, 0.018 0.017, 0.016
V-4	0.0015	0.0012, 0.0016 0.0010, 0.0011	0.0009, 0.0017 0.0011, 0.0013
H-8	0.0033	0.0030, 0.0032 0.0037, 0.0030	0.0032, 0.0039 0.0030, 0.0029
N-4	0.223	0.209, 0.224 0.212	0.212, 0.224 0.214
NBS 1040	0.033 ^b	0.033, 0.030, 0.029 0.030, 0.031	0.032, 0.030, 0.028 0.030, 0.031

^a Result obtained by the vacuum-fusion method.

^b Oxygen content for the core area 0.357" in diameter of NBS standard sample (NBS RP-976, 262, 1937).

DISCUSSION

In the conventional activation analysis unit (controlled by a C-R neutron-monitoring system) for oxygen, the numerical values indicating the intensity of the induced radioactivities, which are proportional to the number of oxygen atoms, are given on the scaler, and it is necessary to calculate the analytical results from these values. Because of the troublesome calculation, the total analysis thus requires considerable time and effort despite the rapidity of the actual analytical procedure. The development of the direct read-out system provides an activation apparatus which can immediately indicate the analytical results so that the speed of the activation method itself can be properly utilized. With the new instrumentation described here, the weight percentage of the oxygen is instantly obtained in a digital display. The remaining problem in rapid analysis for oxygen is the development of a rapid sampling method for high-temperature molten metal.

SUMMARY

Fast neutron activation is useful for rapid determinations of oxygen in iron and steel, but the conventional calculations are tedious. A direct read-out system is described so that results are immediately available.

RÉSUMÉ

L'activation avec neutrons rapides est utile pour le dosage rapide de l'oxygène dans le fer et l'acier, mais les calculs conventionnels sont fastidieux. Un système de lecture directe est décrit, permettant d'obtenir immédiatement les résultats.

ZUSAMMENFASSUNG

Die Aktivierung mit schnellen Neutronen ist nützlich für schnelle Bestimmungen von Sauerstoff in Eisen und Stählen. Jedoch sind die konventionellen Berechnungen zeitraubend. Es wird ein selbstanzeigendes Gerät beschrieben, mit dem die Ergebnisse sofort zur Verfügung stehen.

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POTENTIOMETRIC DETERMINATION OF SILVER WITH DITHIOOXAMIDE

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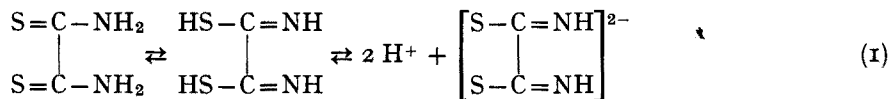
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Most methods for determining small amounts of silver suffer from one or more of the following disadvantages: (1) lengthy preliminary separations, (2) numerous interferences, (3) unstable reagents, (4) sensitivity to pH and salt concentration, etc., (5) the use of expensive instruments, (6) slow color development, (7) the need for simultaneous calibration curves, and (8) lack of suitable precision and/or accuracy¹⁻¹².

A potentiometric titration of copper with dithiooxamide (rubeanic acid) has already been described¹³; a tertiary electrode system with silver metal as the indicating electrode was found to produce a high degree of accuracy, precision, selectivity and speed. During that investigation it was found that silver could also be titrated under similar conditions and promising results were obtained¹⁴. In the present investigation, the method for silver was thoroughly examined and its accuracy and precision evaluated.

Dithiooxamide was first used as a precipitation reagent by RAY AND RAY¹⁵. It exists in solution in equilibrium with its tautomeric form¹⁶:



It reacts with metals such as zinc, copper, palladium, cobalt, and nickel to form 1:1 chelates which are stable at room temperature. The salts probably are polymeric compounds of dithiooxamide¹⁷. Iron(II), iron(III), ruthenium, silver, cadmium, and mercury ions form unstable compounds which rapidly decompose to yield sulfides¹⁸. By proper pH control and by complexation with fluoride and EDTA, the reagent can be made more selective.

EXPERIMENTAL

Standard solutions

Standard silver nitrate solution (0.200 mg Ag/ml). Weigh 315.0 mg of analytical-reagent silver nitrate (previously dried at 150° for 2 h), dissolve and dilute to 1 l with water.

Dithiooxamide solution. Heat 125.3 mg of dithiooxamide gently with 700 ml of deionized, distilled water, with continuous stirring until dissolution is complete.

Then cool and dilute to 1 l with water. The reagent appeared to be stable for at least one month.

Deionized distilled water was used throughout this work.

Instrument

A Beckman Zeromatic pH meter with a silver indicator electrode and glass reference electrode was employed in all titrations.

Procedure

To the sample solution in a 150-ml beaker, add 1.0 g of reagent-grade potassium acid phthalate, 0.5 g of reagent-grade sodium fluoride, and 0.10 g of reagent-grade disodium ethylenediaminetetraacetate; dilute to 100 ml with water. Titrate with the dithiooxamide solution, allowing the potential to come to equilibrium between additions; near the end point, wait for 4-5 min before recording the potential. The potential jump was so sharp, that the equivalence point could be estimated to the nearest 0.01 ml.

After every titration the silver electrode was rubbed with a clean towel to remove any film that had formed; it was then immersed in a 0.05 *M* potassium cyanide solution for 1 min and rinsed with distilled water.

RESULTS AND DISCUSSION

Standard solutions of silver ranging from 2.00 p.p.m. to 50.0 p.p.m. were prepared by proper dilution of the stock standard silver nitrate solution. Replicate determinations were made on each solution to establish the precision of the method;

TABLE I
PRECISION OF DETERMINATION FOR 2-50 p.p.m. OF SILVER

<i>Silver</i> (p.p.m.)	<i>Dithiooxamide</i> (ml) ^a	<i>Relative standard</i> <i>deviation (%)</i>
2.00 ^b	0.47	0.96
4.00 ^b	0.90	0.50
10.00	2.18	0.46
20.00	4.28	0.35
30.00	6.42	0.44
40.00	8.55	0.26
50.00	10.70	0.03

^a Average of 6 determinations.

^b For these titrations the dithiooxamide solution was diluted ten-fold; the figures shown have been corrected to account for this dilution.

the results (Table I) showed an average relative standard deviation of *ca.* 0.4%, the deviation tending to decrease as the concentration increased. Figure 1a shows representative potentiometric titration curves for each of the silver concentrations tested; the breaks are well-defined and are of the order of 300 mV.

When the average volumes of dithiooxamide consumed at each concentration level in Fig. 1a were plotted against the silver concentrations a linear relationship was obtained. Extrapolation of the graph obtained to zero showed a blank value of

0.08 ml of dithiooxamide, which probably results from traces of heavy metals in the water and reagents and/or from the small amount of dithiooxamide which can exist in solution at the equivalence point.

If all the silver ion reacted to form silver sulfide, then 1 mole of dithiooxamide would react with 4 moles of silver. When this 4 : 1 relationship and the blank correction

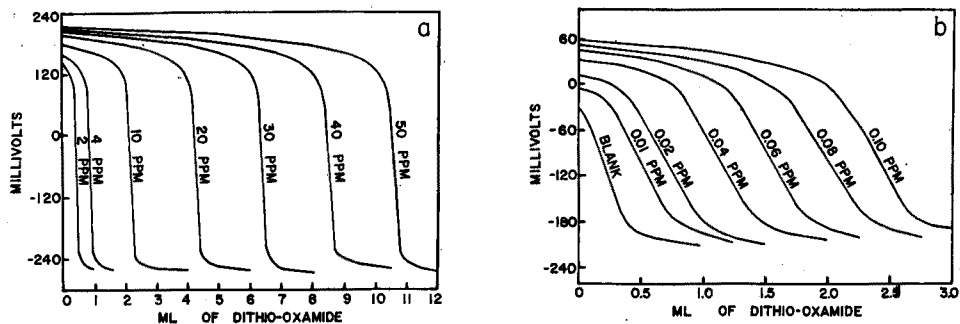


Fig. 1. Representative potentiometric titration curves (a) for 2–50 p.p.m. of silver with $1.091 \cdot 10^{-3}$ M dithiooxamide; (b) for 0.01–0.10 p.p.m. of silver with $1.071 \cdot 10^{-5}$ M dithiooxamide.

were used with the results obtained in the titration of 2–50 p.p.m. of silver, the molarity of the dithiooxamide was calculated to be 0.001091, whereas the molarity calculated from the weight of dithiooxamide in the titrant solution was 0.001044; Thus the molarity was 4.50% stronger than the weight of dithiooxamide taken would indicate. A similar effect was observed in the potentiometric titration of copper with dithiooxamide¹³. Possibly the dithiooxamide may have decomposed before weighing and so contained a greater percentage of sulfide than the formula would indicate. Another possible explanation would be adsorption of silver ions by the silver sulfide. In any case, up to 50 p.p.m. of silver, the plots obtained were linear and reproducible so that no difficulty was found in using dithiooxamide as a titrant.

Lower limits of sensitivity

As the potential change was quite large in the titration of 2.00–50.0 p.p.m. of silver, lower concentrations were examined. Solutions containing 0.0100–0.1000 p.p.m. of silver were prepared and titrated with a dithiooxamide solution diluted 100 fold (*i.e.* on a weight basis, $1.044 \cdot 10^{-5}$ M). For these dilute solutions, it was necessary, near the equivalence point, to wait *ca.* 15 min in order to obtain steady potential readings. The results of replicate determinations over this range (Table II) showed that the method is quite reproducible and applicable down to 0.0100 p.p.m. of silver. Figure 1b shows representative titration curves for each of the 6 different concentrations tested. The potential breaks are well-defined and are of the order of 150 mV. When the average volumes of dithiooxamide used in each of these 6 titrations were plotted *versus* p.p.m. silver, a linear relationship was again found.

Extrapolation of this graph showed that 0.27 ml of dithiooxamide would be required for a blank titration. An actual blank titration gave a result of 0.24 ml. Possible explanations for this blank have already been discussed. With the 0.27-ml.

blank correction and the results obtained from the titrations of silver with dithioamide the molarity of the dithioamide solution was calculated as $1.071 \cdot 10^{-5}$.

Interferences

Previous work on the titration of copper(II) with dithioamide had shown that under the conditions employed, iron(III) up to 1000 p.p.m., cobalt(II) up to 400 p.p.m., and nickel(II) up to 400 p.p.m. did not interfere. These ions were re-examined for the case of silver; the effects of copper and various other ions were also studied.

TABLE II

PRECISION OF DETERMINATION FOR 0.01-0.1 p.p.m. OF SILVER

Silver (p.p.m.)	Dithioamide (ml) ^a	Relative standard deviation (%)
0.0100	0.50	1.26
0.0200	0.70	0.90
0.0400	1.14	0.55
0.0600	1.56	0.50
0.0800	2.00	0.50
0.1000	2.44	0.32

^a Average of 6 determinations.

TABLE III

ANALYSIS OF SYNTHETIC UNKNOWNNS

Sample	True composition (p.p.m.)	Exp. determined Ag (p.p.m.)	Relative error (%)
A	Ag 19.9; Cu 104.0	20.0	+0.50
B	Ag 10.00; Cu 500 ^a	10.05	+0.50
C	Ag 20.0 Pb 250	20.0	0.00
D	Ag 20.0; Pb 620 ^b	20.1	+0.50
E	Ag 10.00; Cd 500	10.05	+0.50
F	Ag 10.00; Zn 500	9.96	-0.40
G	Ag 10.00; Ni 500	10.05	+0.50
H	Ag 10.00; Fe 500 ^a	9.86	-1.40
I	Ag 10.00; Co 60	9.86	-1.40
J	Ag 10.00; Co 100 ^a	10.00	0.00
K	Ag 22.3; Cu 16.5; Zn 13.4; Cd 11.3	22.4	+0.45
L	Ag 30.4; Cu 22.6; Zn 18.3; Ni 3.7	30.3	-0.33

^a 0.50 g of EDTA was added instead of the usual 0.10 g.

^b 0.20 g of EDTA was added.

Mixtures containing different ions at various concentrations were prepared and analyzed (Table III). The results showed that copper, zinc, cadmium, nickel, cobalt and lead caused no apparent difficulties. Zinc, cadmium, cobalt and nickel would not be expected to react with dithioamide in acidic solution. Copper does react at the pH used but was successfully masked with EDTA. Large concentrations of lead (D)

interfered, unless the amount of EDTA was increased. Increased amounts of EDTA were also necessary to prevent interference with other samples containing larger amounts of copper, iron, and cobalt. The presence of iron decreased the magnitude of the potential break, producing slightly low readings when the equivalence point was calculated conventionally; an appropriate correction could be made, but was not done in the results shown.

When mixtures of mercury(II) and silver were titrated in the absence of EDTA, only one potential break was found, which corresponded to the sum of the mercury(II) and silver. When EDTA was added, the mercury(II) did not seem to react, but the silver break was diminished to such an extent that the end-point was difficult to determine.

Comparison with other methods

Potentiometric methods. The commonest potentiometric method for silver is probably by titration with iodide, which has been used for silver solutions down to 0.05 p.p.m.¹⁹. A comparison of the titration curves for 20 p.p.m. of silver with dithiooxamide and potassium iodide showed that the potential break was *ca.* 40 mV greater for dithiooxamide, hence dithiooxamide should yield more precise results for very low silver concentrations. The dithiooxamide reagent has another advantage in that it should be applicable to other metals commonly analyzed with silver. Copper can be determined¹⁹ and preliminary work indicates that mercury(I) and mercury(II) can also be titrated. Exploratory investigations have indicated that simultaneous determinations of mixtures of silver and copper are feasible.

Thioacetamide has been suggested as a reagent for the potentiometric titration of silver²⁰. However, the dithiooxamide potential breaks appear to be greater by a factor of two or three, and the solution preparation is much simpler.

Spectrophotometric methods. Rhodanine is probably the most widely used color reagent for silver, but there are many variables which affect the stability, reproducibility, and absorption characteristics of the silver rhodanate suspension^{1,2,6,21}; it is essential to prepare calibration curves along with each batch of samples. The dithizone method requires very pure solvents, careful pH control, and lengthy extraction procedures to remove interferences^{1,6,8,22}.

The dithiol method is not very sensitive (at the 4-p.p.m. level, the precision is only 5–6%), lengthy and subject to many interferences¹.

The proposed potentiometric method possesses the following advantages over most colorimetric methods: (1) very few interferences, (2) no preliminary separations, (3) rapidity, (4) high sensitivity, and (5) less subject to variables which affect the precision and accuracy.

SUMMARY

Potentiometric titration with dithiooxamide solution can be used to determine silver in the 0.0100–50.0 p.p.m. range with an average accuracy of *ca.* 0.5% and a relative standard deviation ranging from 1.26% to 0.03%. The metals commonly associated with silver can be masked with fluoride and EDTA. The advantages of the method over other potentiometric and common spectrophotometric methods are outlined.

RÉSUMÉ

Le titrage potentiométrique à l'aide de dithioxamide peut être utilisé pour le dosage de l'argent (0.01–50 p.p.m.) avec une précision moyenne de 0.5% et une déviation standard relative de 1.26%–0.03%. Les métaux généralement associés à l'argent sont masqués avec fluorure et EDTA. Les avantages de ce procédé sont décrits.

ZUSAMMENFASSUNG

Silber kann potentiometrisch mit Dithiooxamid-Lösung titriert werden. Im Bereich von 0.01–50 p.p.m. beträgt die mittlere Genauigkeit 0.5%; die Standardabweichung liegt zwischen 1.26% und 0.03%. Die Metalle, die im allgemeinen das Silber begleiten, können mit Fluorid und AeDTE maskiert werden. Die Vorteile der Methode gegenüber anderen potentiometrischen und allgemeinen spektralphotometrischen Verfahren werden aufgezeigt.

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ETUDE THERMOMETRIQUE DE LA FORMATION DES COMPLEXES DU FER(III), DE L'ALUMINIUM ET DU GALLIUM

II. TARTRATES ET CITRATES

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(Reçu le 27 mars, 1967)

COMPLEXES TARTRIQUES

Les complexes tartriques des ions tripositifs sont assez variés et la littérature les concernant déjà abondante. Le Tableau I dans lequel nous avons rassemblé les travaux les plus significatifs sur les tartrates d'aluminium, de fer et de gallium montre nettement que la nature des complexes identifiés dépend de la méthode utilisée et quelquefois de l'expérimentateur.

Bien que la thermométrie ait déjà été appliquée^{1,8} nous n'avons pas cru inutile d'en reprendre l'étude de façon plus systématique car manifestement les auteurs n'en avaient pas tiré le parti maximum. Pour obtenir en effet la série la plus complète des complexes tartriques il importe d'ajouter à la solution de sel métallique légèrement acide au départ, une solution de tartrate à un pH suffisamment élevé pour provoquer une élévation régulière de ce dernier et terminer la réaction en milieu nettement alcalin (principalement dans le cas du fer).

Complexes tartriques de l'aluminium

Conditions opératoires: Dans les bacs thermométriques: solution $\text{Al}(\text{NO}_3)_3$

TABLEAU I

BIBLIOGRAPHIE SUR LES COMPLEXES TARTRIQUES

<i>Cations</i>	<i>Complexes tartriques</i>	<i>Méthodes</i>	<i>Auteurs</i>	<i>Réf.</i>
Al^{3+}	1 : 1, 1 : 4 (supposé)	Thermométrie	Cadariu-Goina	1
	1 : 1, 1 : 2	Spectroscopie	Cadariu-Niac-Oniciu	2
	2 : 1, 1 : 1, 1 : 2, 1 : 3	Conductimétrie	Cadariu-Goina	3
	1 : 1	Potentiométrie	Williams-Wynn	4
	1 : 0.5	Potentiométrie	Shpilev-Ogoleva	5
Fe^{3+}	1 : 1, 1 : 2	Potentiométrie	Piatnisky-Gorbataya	6
	1 : 1	Réfractométrie	Cadariu-Bednar	7
	1 : 1, 1 : 2, 1 : 1.5	Thermométrie	Bobtelsky-Jordan	8
	1 : 1	Potentiométrie	Timberlake	9
Ga^{3+}	1 : 1	Potentiométrie	Savchenko et Goncharov	10
	1 : 2	Conductimétrie		
	1 : 5	Spectroscopie		

0.5025 *M* à pH 4 + KNO_3 . Dans la burette: solution de tartrate diammonique 2.042 *M* amené à pH 10 par NH_4OH . Tension d'alimentation du pont: 2 V. Sensibilité de l'enregistreur: 10 mV.

Les enthalpogrammes enregistrés ont la forme de la Fig. 1 présentant 5 brisures offrant peu d'ambiguïté. Les résultats obtenus pour 3 concentrations sont rassemblés dans le Tableau II. Nous retrouvons ainsi, sur un enregistrement unique les complexes tartriques 1:1, 1:1.5, 1:2 et 1:4 déjà admis par différents auteurs mais, à la place du complexe 1:3 signalé, nous trouvons une composition un peu différente, 4:11 qui nous semble d'autant plus vraisemblable que RONDEAU¹⁷ a mentionné récemment un tel rapport dans le cas des complexes fluorés de l'aluminium.

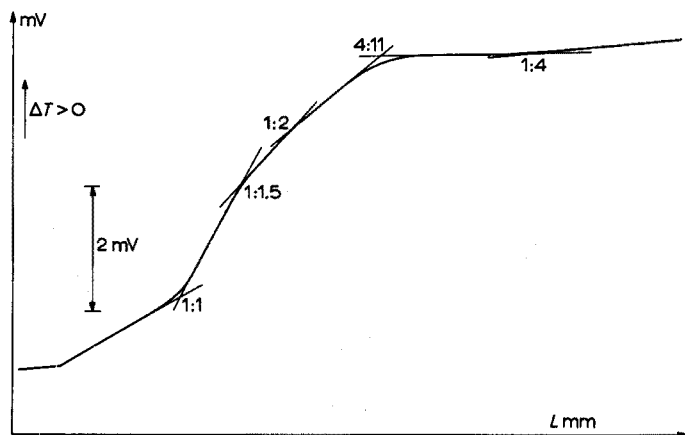


Fig. 1. Tartrates d'aluminium.

TABLEAU II

COMPLEXES TARTRIQUES DE L'ALUMINIUM

<i>r</i>	<i>l</i> (mm)		Vol. prise d'essai								
	3 ml			4 ml			5 ml				
	Théor.	Exp.	Δ (%)	Théor.	Exp.	Δ (%)	Théor.	Exp.	Δ (%)		
1:1	36	36	0	48	47.75	0.5	60	59.5	1		
1:1.5	54	54	0	72	72	0	90	90	0		
1:2	72	72	0	96	94.5	1.5	120	118	2		
4:11	99	98	1	132	129.5	2	164	162.5	1		
1:4	144	145.5	1	192	191.5	0.25	240	239	0.5		

Complexes tartriques du fer (III)

Conditions opératoires: Dans les bacs thermométriques: solution $\text{Fe}(\text{NO}_3)_3$ 0.5002 *M* à pH 1.5 + NH_4NO_3 . Dans la burette: solution de tartrate diammonique 1.267 *M* amené à pH 11.5 par NH_4OH . Tension d'alimentation du pont: 1 V. Sensibilité de l'enregistreur: 10 mV.

Les enthalpogrammes enregistrés ont la forme de la Fig. 2 présentant 5 brisures qui correspondent à la formation successive des 5 complexes 1:0.5, 5:4, 1:1, 1:1.5 et 1:2. Les deux premiers n'avaient pas été signalés à notre connaissance, les autres sont connus mais nous ferons remarquer que la dernière brisure (complexe

1:2) n'apparaît plus lorsque le titrant est à pH trop faible. Les résultats obtenus pour 4 concentrations sont rassemblés dans le Tableau III.

Complexes tartriques du gallium

Conditions opératoires: Dans les bacs thermométriques: solution de GaCl₃

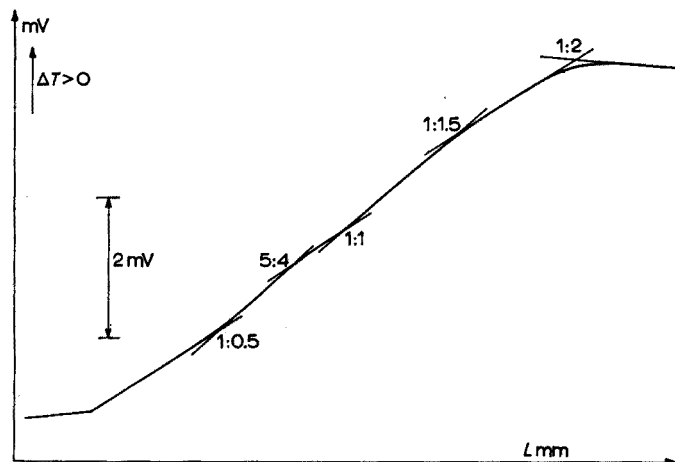


Fig. 2. Tartrates de fer(III).

BLEAU III

PLEXES TARTRIQUES DU FER(III)

l (mm) Vol. prise d'essai

	3 ml			5 ml			7.5 ml			10 ml		
	Théor.	Exp.	Δ (%)	Théor.	Exp.	Δ (%)	Théor.	Exp.	Δ (%)	Théor.	Exp.	Δ (%)
.5	29	29.25	1	48.5	49	1	73	75	2.2	97	99	2
	46.5	46.75	0.5	77.5	78	1.5	118	118.5	0.5	155	155	0
	58	59	2	97	98	1	146	148	0.7	194	195.5	0.7
.5	87	87.5	0.5	145.5	147	1	219	215	2	291	289	0.7
	116	116.5	0.5	194	193.25	0.3	292	286	2	388	379	2.2

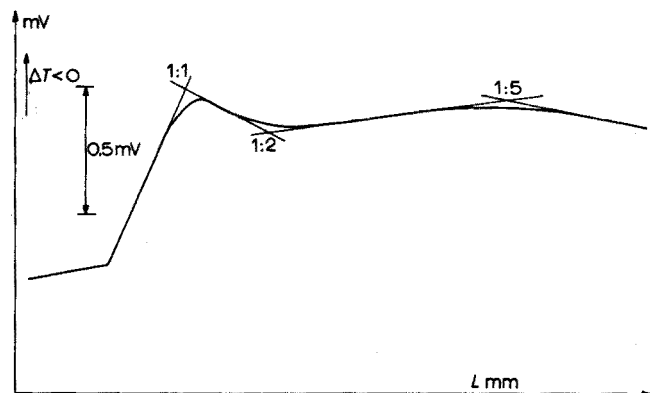


Fig. 3. Tartrates de gallium.

0.3041 *M* à pH 2 + KNO₃. Dans la burette: solution de tartrate disodique 1.482 *M* amené à pH 11 par NaOH. Tension d'alimentation du pont: 2 V. Sensibilité de l'enregistreur: 2.5 mV.

Les enthalpogrammes enregistrés ont la forme de la Fig. 3; on y remarque des brisures très peu nettes et des effets thermiques faibles qui permettent de conclure, avec peu de précision, à la formation des 3 complexes successifs 1:1, 1:2 et 1:5 déjà signalés par SAVCHENKO ET GONCHAROV¹⁰. Les résultats obtenus pour les 3 concentrations utilisées sont rassemblés dans le Tableau IV.

TABLEAU IV

COMPLEXES TARTRIQUES DU GALLIUM

<i>r</i>	<i>l</i> (mm)		Vol. prise d'essai								
	2 ml			3 ml			5 ml				
	Théor.	Exp.	Δ (%)	Théor.	Exp.	Δ (%)	Théor.	Exp.	Δ (%)		
1:1	20.5	20	2.5	30.75	30.5	1	51	50.25	1.5		
1:2	41	41.5	1	61.5	62.25	1.5	102.5	103.5	1		
1:5	102.5	104	1.5	153	154.5	1	255	249	2.5		

TABLEAU V

BIBLIOGRAPHIE SUR LES COMPLEXES CITRIQUES

Cations	Complexes trouvés	Méthodes	Auteurs	Référence
Al ³⁺	1:1	Hétérométrie	Bobtelsky-Goldschmidt	11
		Potentiométrie	Pattnaik-Pani	12
		Thermométrie	Cadariu-Goina	13
Fe ³⁺	3:2, 2:3	Thermométrie	Bobtelsky-Jordan	14
	1:2	Spectroscopie	Swinarski-Adamiak	15
	1:1	Potentiométrie	Zolotukhin	16
	2:3	Hétérométrie	Bobtelsky-Goldschmidt	11

COMPLEXES CITRIQUES

Susceptibles d'applications importantes, les complexes citriques des ions tripositifs ont fait l'objet de nombreuses publications; nous avons résumé dans le Tableau V les principales références concernant ceux du fer(III) et de l'aluminium. Nous n'avons par contre relevé aucun travail concernant ceux du gallium.

Complexes citriques de l'aluminium

Conditions opératoires: Dans les bacs thermométriques: solution Al(NO₃)₃ 0.5021 *M* à pH 4 + KNO₃ et NH₄Cl. Dans la burette: solution de citrate triammonique 1.014 *M* amené à pH 10 par NH₄OH. Tension d'alimentation du pont: 1 V. Sensibilité de l'enregistreur: 2.5 mV.

Les enthalpogrammes enregistrés ont la forme de la Fig. 4 et présentent 4 brisures dont les 3 dernières résultent de l'extrapolation de segments raccordés par des courbures prononcées. Malgré ces courbures, les résultats obtenus pour 3 concentrations,

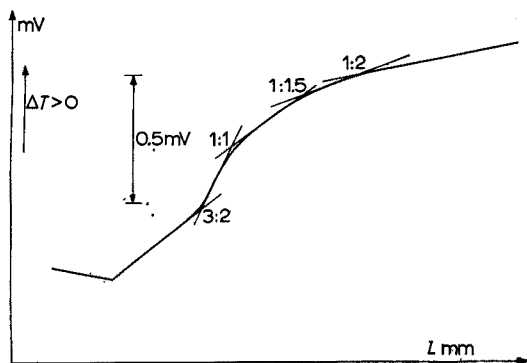


Fig. 4. Citrates d'aluminium.

TABLEAU VI

COMPLEXES CITRIQUES DU FER(III) ET DE L'ALUMINIUM

<i>r</i>	<i>l</i> (mm)		Vol. prise d'essai								
	1 ml			2 ml			3 ml				
	Théor.	Exp.	Δ (%)	Théor.	Exp.	Δ (%)	Théor.	Exp.	Δ (%)		
<i>Fer(III)</i>											
3:2	16.25	16.5	1.5	32.5	32.75	1	48.5	49	1		
1:1	24.25	24.25	0	48.5	48.25	0.5	73	72	1.5		
1:1.5	36.5	36	1.5	73	74.5	2	110.5	112.75	2		
1:2	48.5	49.25	1.5	97	97.5	0.5	146	148.25	1.5		
<i>Aluminium</i>											
3:2	16.5	16.75	1.5	33	33	0	50	50	0		
1:1	25	25.5	2	50	50	0	75	75	0		
1:1.5	37.5	38	1.5	75	76	1.5	112.5	110.5	2		

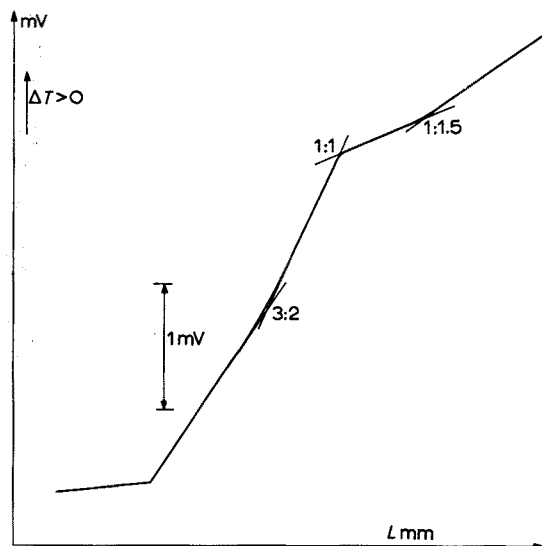


Fig. 5. Citrates de fer(III).

rassemblés dans le Tableau VI montrent que l'on peut, avec une approximation meilleure que 2%, caractériser la formation des 4 complexes suivants: 3:2, 1:1, 1:1.5 et 1:2. Seul le complexe 1:1 avait été signalé antérieurement; les autres n'avaient pas été décelés, malgré la diversité des méthodes employées, vraisemblablement parce que les auteurs n'avaient pas pris soin de faire varier le pH dans les limites suffisantes.

Complexes citriques du fer(III)

Conditions opératoires: Dans les bacs thermométriques: solution $\text{Fe}(\text{NO}_3)_3$ 0.5013 M à pH 2 + KNO_3 . Dans la burette: solution de citrate triammonique 1.017 M amené à pH 10 par NH_4OH . Tension d'alimentation du pont: 1.5 V. Sensibilité de l'enregistreur: 5 mV.

Les enthalpogrammes enregistrés ont la forme de la Fig. 5 et présentent 3 brisures très nettes; les résultats obtenus pour 3 concentrations sont rassemblés dans le Tableau VI. Sur nos enthalpogrammes nous caractérisons donc simultanément les 3 complexes 3:2, 1:1 et 1:1.5 déjà signalés dans la littérature, mais nous ne retrouvons pas le complexe 1:2 que SWINARSKI avait mis en évidence par spectroscopie.

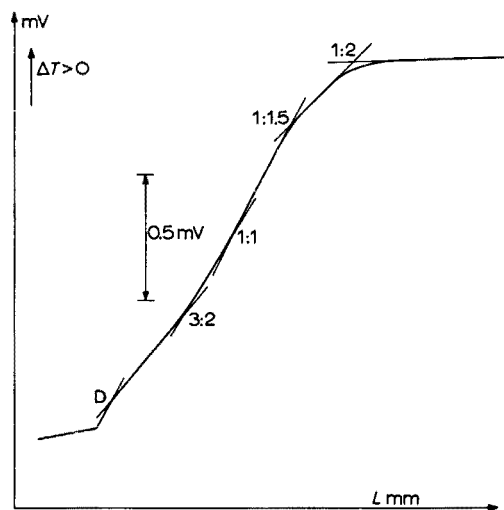


Fig. 6. Citrates de gallium.

TABLEAU VII

COMPLEXES CITRIQUES DU GALLIUM

r	$l(\text{mm})$		Vol. prise d'essai								
	1.5 ml			2 ml			3 ml				
	Théor.	Exp.	Δ (%)	Théor.	Exp.	Δ (%)	Théor.	Exp.	Δ (%)		
3:2	32	32	0	42.5	41.25	2	64	63	1.5		
1:1	48	47	2	64	64	0	96	96	0		
1:1.5	72	70.25	2	96	97	1	144	143	0.75		
1:2	96	95.25	1	128	125.5	2	192	187	2.5		

Complexes citriques du gallium

Conditions opératoires: Dans les bacs thermométriques: solution GaCl_3 0.6731 M à pH 2 + KNO_3 . Dans la burette: solution de citrate triammonique 1.041 M amené à pH 10 par NH_4OH . Tension d'alimentation du pont: 1 V. Sensibilité de l'enregistreur: 2.5 mV.

Les enthalpogrammes enregistrés ont la forme de la Fig. 6 et présentent 4 brisures successives très nettes (à l'exception de la dernière dont la forte courbure n'empêche cependant pas une extrapolation précise). L'écart entre les 2 premières brisures qui dépend de l'acidité initiale montre que dans cette première étape il y a seulement neutralisation partielle de l'excès d'acidité de la solution de gallium, sans formation de complexe. Celui-ci ne se forme qu'à partir de la 1^{re} brisure et cette dernière doit être prise comme point de départ véritable de l'enthalpogramme. Les résultats obtenus pour 3 concentrations sont rassemblés dans le Tableau VII.

Nous pouvons donc conclure, d'après ces résultats, que le gallium se comporte tout à fait comme l'aluminium au point de vue de ses complexes citriques qui correspondent aux rapports 3:2, 1:1, 1:1.5 et 1:2.

CONCLUSIONS

Dans le cas des complexes tartriques et citriques des cations tripositifs étudiés, complexes en général assez nombreux, la méthode thermométrique s'avère extrêmement féconde car un seul enthalpogramme permet de caractériser en général toute la série, à quelques rares exceptions près. Les autres techniques ne mettent souvent en évidence qu'une ou deux espèces seulement mais ces résultats incomplets proviennent généralement aussi du fait que les auteurs ne se sont pas placés dans les conditions optima pour former toute la série des complexes.

RÉSUMÉ

Les auteurs montrent qu'un seul enthalpogramme suffit à mettre en évidence toute la série des complexes tartriques ou citriques des cations tripositifs considérés, à condition de réaliser le gradient de pH convenable pour permettre à ces complexes de se former successivement.

SUMMARY

Thermometric measurements make it possible to detect all tartrate and citrate complexes of iron(III), aluminium and gallium on only one enthalpogram. A suitable gradient of pH must be chosen in order to allow the successive formation of the complexes.

ZUSAMMENFASSUNG

Mit Hilfe von thermometrischen Messungen ist es möglich alle Tartrat- und Zitratkomplexe von Eisen(III), Aluminium und Gallium nachzuweisen. Durch entsprechende Variierung des pH-Wertes wird die stufenweise Bildung dieser Komplexe ermöglicht.

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OXIDATION OF CERIUM(III) TO CERIUM(IV) USING A MIXTURE OF HOT CONCENTRATED PERCHLORIC AND SULFURIC ACIDS

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The oxidizing properties of hot concentrated perchloric acid are well known. From the oxidations performed the reduction potential of the boiling perchloric acid-water azeotrope is estimated to be +2.0 V. As noted by SMITH¹, this suggests the possibility of using this reagent to oxidize cerium to the tetravalent state. However, no suitable procedure has been published. Indeed, cerium is not oxidized to the tetravalent state by boiling with perchloric acid alone, a fact utilized by BANKS AND O'LAUGHLIN² to determine chromium in a chromium-cerium-uranium alloy. Although a faint yellow color appears in cerium solutions during boiling with perchloric acid, the solution becomes colorless when it is cooled and/or diluted with water. However, if a small amount of sulfuric acid is also present, rapid oxidation occurs, indicated by the appearance of the characteristic red-orange color of cerium(IV). This paper presents a satisfactory procedure and optimum conditions for the oxidation of cerium(III) to cerium(IV) using a mixture of hot concentrated perchloric and sulfuric acids. The procedure is potentially useful for the oxidimetric determination of cerium as well as for the preparation of cerium(IV) solutions that are free of foreign cations and of anions other than sulfate and perchlorate.

EXPERIMENTAL

Reagents and equipment

Cerium(IV) sulfate solution, 0.1 N. A stock solution of cerium(IV) sulfate was prepared by slurring 438.6 g of primary standard grade ammonium hexanitratocerate(IV) (G. Frederick Smith Chemical Co., Columbus, Ohio) in 450 ml of concentrated sulfuric acid and slowly diluting with water to 8 l while stirring vigorously. After standing for 2 days a significant amount of precipitate formed, and the solution therefore was decanted. It was standardized against arsenious oxide (Mallinckrodt Chemical Co. primary-standard grade) using osmium tetroxide as a catalyst, and against electrolytic iron (G. Frederick Smith Chemical Co. standard of reference) and found to be 0.1000 N. This value was confirmed by subsequent restandardization at intervals throughout the work.

Iron(II) sulfate solution, 0.1 N. An iron(II) sulfate solution was prepared by dissolving 55.6 g of reagent-grade iron(II) sulfate 7-hydrate and 20 ml of concentrated sulfuric acid in water and diluting to 2 l. The solution was standardized at least once daily against standard ceric sulfate.

Ferroin indicator solution, 0.025 M. This was prepared by dissolving 3.714 g

of 1,10-phenanthroline monohydrate (G. Frederick Smith Chemical Co. reagent grade) and 1.737 g of reagent-grade iron(II) sulfate 7-hydrate in water and diluting to 250 ml. One drop of this solution, used as indicator for each titration, corresponded to 0.014 ml of standard 0.1000 *N* ceric sulfate.

Perchloric acid, reagent grade, 70–72% HClO_4 , and sulfuric acid, reagent grade, s.g. 1.84, 98% H_2SO_4 were used. Cerium metal was obtained from the Lindsay Chemical Division, American Potash and Chemical Corp., West Chicago, Illinois. A sample of mischmetal was supplied by the Mallinckrodt Chemical Co. All other chemicals were of reagent grade.

Oxidations were carried out in 300-ml conical flasks equipped with special condenser heads⁸ to prevent loss of material by spattering and reduce the escape of perchloric acid into the atmosphere by condensing the vapors in the neck of the flask.

Samples containing 4–5 meq of cerium were taken for each oxidation so that subsequent titrations could be carried out using an ordinary 50-ml Normax buret. The same buret was used for both titrations and measuring sample solutions to eliminate errors in glassware calibration.

Optimum conditions for the oxidation of cerium

Place 4–5 meq of cerium(III) solution in a 300-ml conical flask equipped with a condenser head. Add 15 ml of concentrated perchloric acid and evaporate the solution to fumes of perchloric acid; then add 5 ml of concentrated sulfuric acid. Boil the mixture for 15 min after the cerium(III) sulfate (coarse white precipitate) has been oxidized (finely-divided red-orange precipitate). Cool to room temperature, remove the condenser head and pass nitrogen through the solution for 10–15 min or until the escaping vapors no longer give a positive test for chlorine with wetted starch-iodide test paper. Rinse the condenser head into the flask and dilute the solution to 50–75 ml with water. Allow the cerium(IV) sulfate to dissolve completely (15–30 min). This solution can be titrated with standard iron(II) sulfate solution using one drop of 0.025 *M* ferroin indicator.

RESULTS AND DISCUSSION

Samples containing 4–5 meq of the standard ceric sulfate solution were placed in 300-ml conical flasks and the cerium(IV) was reduced to cerium(III) by adding a few drops of 30% hydrogen peroxide solution. The flasks were fitted with condenser heads, and the solutions were boiled to destroy excess of hydrogen peroxide. The samples then were divided into two sets.

In the first set re-oxidation of the cerium was accomplished using the perchloric-sulfuric acid procedure outlined above. In this case, however, the presence of sulfuric acid in the solution from the beginning caused the separation of cerium(III) sulfate (a coarse white precipitate) which resulted in serious bumping if the solution was boiled before the evaporation reached perchloric acid fumes. (To prevent this precipitation and consequent bumping the optimum conditions described above indicate the addition of sulfuric acid *after* the cerium solution containing perchloric acid has been evaporated to fumes of perchloric acid; no precipitate forms until sulfate is added.) After evaporation to perchloric acid fumes the solutions were boiled vigorously for 15 min. During the initial stages of this boiling the white solid became

much more finely divided and turned red-orange in color; the boiling at this stage proceeded smoothly with no bumping.

In the second set of samples re-oxidation of the cerium was accomplished by diluting the sample to about 100 ml with 2 *N* sulfuric acid and adding 4 g of potassium peroxydisulfate and 2 ml of 0.3 *M* silver nitrate as catalyst. After the solutions had stood for an hour or more, they were boiled to complete the oxidation and destroy the excess of peroxydisulfate, cooled and titrated.

The data in Table I summarize the results of these two sets of oxidations. These data are typical of a number of similar runs, and the slightly lower recoveries

TABLE I

OXIDATION OF CERIUM BY PEROXYDISULFATE AND BY A MIXTURE OF HOT CONCENTRATED PERCHLORIC AND SULFURIC ACIDS

Oxidation method	Ce (meq)		% Recovery	Deviation from average
	Taken ^a	Found		
HClO ₄ -H ₂ SO ₄ ^b	4.312	4.334	100.51	-0.04
HClO ₄ -H ₂ SO ₄ ^b	4.378	4.399	100.48	-0.07
HClO ₄ -H ₂ SO ₄ ^b	4.291	4.314	100.55	0.00
HClO ₄ -H ₂ SO ₄ ^b	4.272	4.298	100.60	+0.05
HClO ₄ -H ₂ SO ₄ ^b	4.312	4.337	100.59	+0.04
			Ave. 100.55	0.04
Peroxydisulfate	4.198	4.203	100.12	+0.04
Peroxydisulfate	4.450	4.464	100.31	+0.23
Peroxydisulfate	4.331	4.321	99.76	-0.32
Peroxydisulfate	4.431	4.437	100.14	+0.06
Peroxydisulfate	4.450	4.460	100.22	+0.14
Peroxydisulfate	4.257	4.254	99.92	-0.16
			Ave. 100.08	0.16

^a Does not include any Ce(III) present in the standard Ce(IV) solution from which samples were taken.

^b Following the titration of cerium(IV) each solution was tested for chloride using silver nitrate. In every case the test was negative, indicating that chlorine removal by purging had been complete.

(ca. 0.5%) by the peroxydisulfate method cannot be ascribed to a systematic operative error. The samples oxidized with peroxydisulfate showed a slight turbidity of unknown composition which may be responsible for this small difference. The data demonstrate clearly that the oxidation of cerium(III) to cerium(IV) is quantitative and that the perchloric-sulfuric acid oxidation procedure is capable of high precision under the conditions described. Precision, rather than accuracy, is the significant feature of the data. Recoveries by the perchloric-sulfuric acid method (100.55%) and the peroxydisulfate method (100.08%) should not be interpreted as an indication of accuracy of these two methods. The recoveries of greater than 100% are attributed to the presence, before reduction with hydrogen peroxide, of some cerium(III) in the standard cerium(IV) solution from which samples were taken. The amount is small and could easily have arisen from reduction of cerium(IV) by oxidizable organic impurities in the water used to prepare the standard solution. Therefore, it cannot be inferred that the peroxydisulfate method is more accurate than the perchloric-sulfuric acid method. Indeed, no claim can be made, based on the experimental work reported in this paper, for the accuracy of an oxidimetric analysis using the per-

chloric-sulfuric acid oxidation procedure since no standard samples of known cerium content were analyzed.

The removal of chlorine

A critically important feature of the perchloric-sulfuric acid oxidation procedure is the removal of chlorine, one of the decomposition products of perchloric acid at its boiling point, by purging the concentrated acid solution with nitrogen. The chlorine, if not removed, contributes to the oxidizing capacity of the final cerium(IV) solution. Completeness of chlorine removal was demonstrated by testing the titrated solution for chloride with silver nitrate; in each case the test for chloride was negative.

While no significant amount of chlorine is expected to remain in the boiling concentrated acid, chlorine undoubtedly is produced continually during slow cooling until the temperature drops below the decomposition temperature. The odor of chlorine is easily detectable over the cooled solution. To eliminate or minimize the amount of chlorine remaining in such solutions, SMITH⁴ recommends sudden cooling (quenching) using Vycor glassware to withstand thermal shock. This method was tried but found to be unsatisfactory, partly perhaps because chlorine remains in the vapor above the liquid in the flask. It was expected and subsequently proved that chlorine is not very soluble in cool solutions of *concentrated* perchloric acid (or mixtures of concentrated perchloric and sulfuric acids) and that it can be removed easily and completely by purging the solution with nitrogen for 10–15 min, even if the cooling to room temperature is done slowly. (Other gases, *e.g.*, air, presumably would function similarly.) The easy removal of chlorine may be attributed to an insufficient supply of water to react with chlorine in the disproportionation reaction to form chloride and hypochlorite, any water present being held as perchloric acid dihydrate (the approximate composition of the constant boiling azeotrope of perchloric acid and water).

In addition to the chloride test on the titrated samples described above, the following experiments were performed to verify the effectiveness of the purging technique for the removal of chlorine. Pure perchloric acid and mixtures of perchloric acid and sulfuric acid (containing no cerium) were boiled for 5–10 min during which time chlorine obviously was evolved (odor). These solutions were cooled to room temperature, purged by bubbling nitrogen through them for 10–15 min, diluted with water, and tested for oxidants (chlorine or hypochlorite) by adding potassium iodide and starch solution. In all cases there was no detectable blue color, indicating complete removal of chlorine by the purging technique.

It is important that chlorine be removed by the purging technique *before* the oxidized cerium sample is diluted with water. Chlorine (or hypochlorite) cannot be removed completely *after* dilution of the sample because boiling an aqueous solution of hypochlorite is not effective in destroying this oxidant. In fact, aqueous hypochlorous acid can be concentrated by distillation⁵.

Variation of boiling time

A study was made of the effect of varying the boiling time once the solution had been concentrated and oxidation had begun. If boiling was continued for less than 5 min after the color change, oxidation was frequently incomplete. On the other hand, if boiling was continued for more than 20 minutes, the ceric sulfate apparently

was dehydrated or in some other fashion rendered less readily soluble. The ceric sulfate formed even with only 10–15 min boiling was slow to dissolve on dilution with water, sometimes requiring as long as 45 min to dissolve completely. The longer the precipitate was boiled with the concentrated acid mixture, the slower the subsequent dissolution in water. The optimum time of boiling was 10–15 min.

Variation of sulfuric acid concentration

The role of sulfuric acid in the oxidation of cerium is possibly twofold: (1) it dehydrates the perchloric acid and raises the boiling point of the solution, thereby increasing its reduction potential, and (2) it stabilizes the cerium in the tetravalent state by formation of a sulfatocerate(IV) complex.

The effect of varying the amount of sulfuric acid was investigated. Samples of cerium(IV) were treated as described above, but were re-oxidized using a constant volume (15 ml) of concentrated perchloric acid and varying amounts of sulfuric acid. The results (Table II) showed that the amount of sulfuric acid was not critical between 2 and 22 ml. It should be added, however, that the larger the amount of

TABLE II

VARYING AMOUNTS OF CONCENTRATED SULFURIC ACID ADDED IN THE OXIDATION OF CERIUM WITH HOT CONCENTRATED PERCHLORIC-SULFURIC ACID MIXTURES

72% HClO ₄ present (ml)	98% H ₂ SO ₄ present ^a (ml)	Ce (meq)		% Recovery
		Taken	Found	
15	2	4.228	4.250	100.52
15	4	4.130	4.150	100.54
15	7	4.257	4.279	100.52
15	12	4.134	4.156	100.54
15	22	4.141	4.159	100.45
				Ave. 100.51

^a Includes approximately 2 ml of concentrated sulfuric acid present in the original cerium(IV) solution from which samples were taken.

sulfuric acid, the slower the subsequent dissolution of the ceric sulfate. This apparently is due to the conversion of ceric sulfate to a form which is less easily hydrated, *i.e.* less readily soluble.

Since the oxidation proceeds to completion in the presence of as little as 2 ml of concentrated sulfuric acid, the first role of sulfuric acid mentioned above appears much less important than the second.

Applications and difficulties

Although the perchloric-sulfuric acid oxidation procedure has been applied successfully to the oxidimetric determination of cerium in the recovery experiments described above (with samples prepared from pure ammonium hexanitratocerate(IV)), the author obtained extremely variable, low results when the method was applied to the analysis of mischmetal for cerium. Further study is necessary before these results can be explained, the explanation presumably involving the perchloric acid oxidation-reduction chemistry of the other elements comprising mischmetal. Analysis of the same material using the peroxydisulfate oxidation method yielded higher,

precise, and presumably accurate results. Thus, while the perchloric-sulfuric acid oxidation procedure can be applied conveniently in certain instances, it is clear that it must be applied with caution to the oxidimetric determination of cerium in complex materials.

A second potentially useful application of the perchloric-sulfuric acid oxidation procedure is the preparation of cerium(IV) solutions that are free of foreign cations [including cerium(III)] and anions other than sulfate and perchlorate. A liter of 0.1 *N* cerium(IV) solution was successfully prepared by a scaled-up version of the procedure described above from pure metallic cerium which was dissolved in 1 *N* perchloric acid. Preparation of such a large amount of solution is somewhat difficult owing to the longer time required to heat to boiling and then cool the larger volume of concentrated acid. As indicated previously, boiling for a long time decreases the rate at which the ceric sulfate dissolves upon dilution. Indeed, if boiling is continued too long the solid will not dissolve completely, even on prolonged standing.

It is impossible to summarize and review critically in this short paper all the known procedures for preparing standard cerium(IV) solutions (see LAITINEN⁶) or for oxidizing cerium for oxidimetric determination (see SALUTSKY⁷). However, the perchloric-sulfuric acid procedure, while not without difficulties, deserves consideration along with these other methods which also have their limitations and difficulties.

SUMMARY

The oxidation of cerium(III) to cerium(IV) using a hot concentrated mixture of perchloric and sulfuric acids is shown to be quantitative. Optimum conditions for the oxidation are described. Complete removal of chlorine, an interfering decomposition product of boiling perchloric acid, is achieved by purging the concentrated acid solution with nitrogen *before* dilution with water. The presence of sulfuric acid is essential, the chief role of sulfuric acid apparently being to stabilize the cerium(IV) as a sulfatocerate complex.

RÉSUMÉ

On a examiné l'oxydation du cérium(III) en cérium(IV) à l'aide d'un mélange d'acides perchlorique et sulfurique concentrés, à chaud. Le chlore et les produits de décomposition de l'acide perchlorique bouillant sont chassés par l'azote *avant* de diluer à l'eau. La présence d'acide sulfurique est essentielle, son principal rôle semble de stabiliser le cérium(IV) sous forme d'un complexe sulfatocérate.

ZUSAMMENFASSUNG

Die Oxydation von Cer(III) zur Cer(IV) unter Verwendung einer heissen konzentrierten Mischung von Perchlor- und Schwefelsäure kann quantitativ verlaufen. Die optimalen Bedingungen für die Oxydation werden beschrieben. Die völlige Beseitigung von Chlor und störender Zersetzungsprodukte der siedenden Perchlorsäure gelingt durch Reinigung der konzentrierten Säurelösung mit Stickstoff *vor* der Verdünnung mit Wasser. Die Gegenwart von Schwefelsäure ist wesentlich, da sie anscheinend das Cer(IV) als Sulfatocerat-Komplex stabilisiert.

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QUINOXALINES AS ANALYTICAL REAGENTS

PART I. DERIVATIVES CONTAINING THE COPPER(I)-SPECIFIC GROUPING

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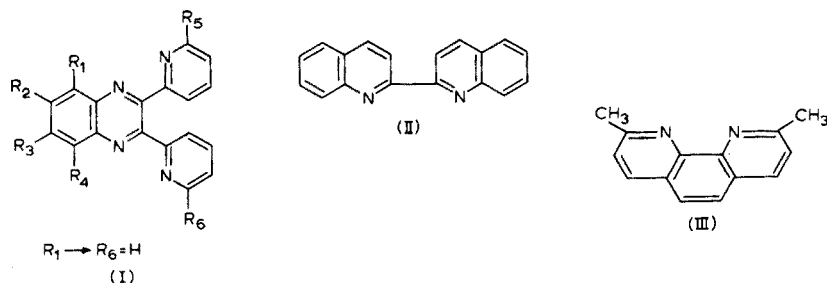
The development of the "ferroine"- and "cuproine"-type compounds as highly selective and sensitive spectrophotometric reagents for the determination of iron(II) and copper(I) is an excellent example of how group action in organic compounds can be modified to provide increased sensitivity and selectivity. The work of HOSTE¹ on 2,2'-diquinolyl (cuproine, itself) and DIEHL AND SMITH^{2,3} on the substituted 1,10-phenanthrolines (ferroines and cuproines) has been summarised by WELCHER⁴ who gives a useful account of the development and properties of these reagents. The "ferroine"

group, used to describe the atomic grouping $=\text{N}-\overset{\parallel}{\text{C}}-\overset{\parallel}{\text{C}}-\text{N}=\text{}$, is responsible for the well-known colour reaction of iron(II) with 1,10-phenanthroline, 2,2'-dipyridyl and related compounds as a result of the formation of coloured octahedral complex ions of the type $[\text{Fe}(\text{ligand})_3]^{2+}$; the molar extinction coefficients of these complexes are favourably influenced particularly by substitution in the 4- and 7-positions of the 1,10-phenanthroline molecule.

The fact that 2,2'-diquinolyl which contains the ferroine group does not react with iron(II) is attributed to the presence of substituents on the ring carbon atoms adjacent to the nitrogen atoms which by steric effects prevent the formation of the octahedral tris-iron(II) complexes. This behaviour is also evident in the 1,10-phenanthrolines substituted in the 2- and 9-positions, which as neo-cuproine (methyl substituents) and bathocuproine (phenyl substituents also in 4- and 7-positions) are valuable reagents for copper(I). This sterically-hindered ferroine grouping which occurs in all these copper-specific reagents can be indicated by $\text{X}-\overset{\parallel}{\text{C}}=\text{N}-\overset{\parallel}{\text{C}}-\overset{\parallel}{\text{C}}-\text{N}=\overset{\parallel}{\text{C}}-\text{X}$; phenanthrolines, dipyridyls and diquinolyls containing this arrangement of atoms readily form stable coloured complex ions of the formula $[\text{Cu}(\text{ligand})_2]^+$. The exact configuration of this type of complex has not been established; DIEHL AND SMITH³ consider that the four C-N bonds are tetrahedrally distributed so that two five-membered chelate rings are produced at right angles to one another, whilst FAYE⁵, arguing from spectroscopic evidence, prefers a trigonal bipyramidal environment for the copper(I) atom. These considerations do not materially affect the use of these reagents for the spectrophotometric determination of copper; their high degree of selectivity makes them most valuable and practically useful reagents. They do, however, suffer from one disadvantage: their preparations are complex and lengthy and thus commercial costs are high.

During the course of certain studies on the oximation of 2,2'-pyridil, it became

evident that a completely new series of compounds containing the copper(I)-specific grouping could be readily synthesised by making use of the quinoxaline ring system. Thus the condensation of the *o*-diketone, 2,2'-pyridil, with *o*-phenylenediamine results in the almost quantitative formation of 2,3-bis(2-pyridyl)quinoxaline (I) whose relationship with diquinolyl (II) is evident from the formulae:



The availability of a number of substituted *o*-phenylenediamines and certain other aromatic *o*-diamines capable of entering into the quinoxaline condensation has provided a series of substituted quinoxalines for study as potential reagents for copper. By the use of 6,6'-dimethyl-2,2'-pyridil as the *o*-diketone, a further series of compounds, derivatives of 2,3-bis[2-(6-methyl)pyridyl]quinoxaline (I, R_5 and $R_6 = CH_3$), in which the relationship with 2,2'-diquinolyl and 2,9-dimethyl-1,10-phenanthroline (III) is more evident, has also been prepared. The behaviour of both series of compounds with a variety of metal ions, but particularly copper(I) ions, has now been studied and their potential as analytical reagents has been assessed.

A search of the literature revealed that GOODWIN AND LIONS⁶ prepared 2,3-bis(2-pyridyl)quinoxaline, and isolated a copper(II) complex of this compound. Certain other pyridyl-substituted quinoxalines were prepared by BUU-HOI AND SAINT-RUF⁷ as part of a major study of possible carcinogenic nitrogen compounds. JENSEN AND PFLAUM⁸ described the preparation of certain pyridyl-substituted pyrazines. None of these workers considered the possibility of a selective reaction for copper(I) with these compounds.

EXPERIMENTAL

Preparation of reagents

2,3-Bis(2-pyridyl)quinoxalines. 2,2'-Pyridil [1,2-dioxo-1,2-di(2-pyridyl)ethane; di(2-pyridyl)-glyoxal] (0.05 mole, 10.6 g) was dissolved in 150 ml of ethanol by heating at reflux temperature and a solution of *o*-phenylenediamine, substituted *o*-phenylenediamine or other aromatic *o*-diamine (0.05 mole) in 50 ml of ethanol was slowly added to the hot solution. The mixture was heated under reflux for 15 min and the hot ethanol solution was gradually diluted with water until a permanent turbidity was apparent in the solution. The mixture was allowed to cool to 3°, and the crystalline product was filtered off under suction, drained well on the filter and dried in air. Recrystallisation was done from ethanol or from benzene-petroleum ether (60–80°) mixtures. Yields of the pure quinoxalines were generally above 80%.

2,3-Bis[2-(6-methyl)pyridyl]quinoxalines. The first step was to prepare 6,6'-

dimethyl-2,2'-pyridil (1,2-dioxo-1,2-di-[2-(6-methyl)pyridyl]ethane; di-[2-(6-methyl)pyridyl]glyoxal). 6,6'-Dimethyl-2,2'-pyridoin (60.5 g, 0.25 mole) was added in amounts of 1–2 g to 500 ml of 6 N nitric acid, with vigorous stirring during the additions. The resultant clear solution was cooled to room temperature and the excess of nitric acid was neutralised by the cautious addition of strong ammonia solution. The bright yellow precipitate of 6,6'-dimethyl-2,2'-pyridil was filtered off, washed well with water and drained on the filter. The crude material was recrystallised from ethanol to give large yellow acicular crystals (m.p. 176°; yield 75%).

The corresponding 2,3-bis[2-(6-methyl)pyridyl]quinoxalines were prepared as described for 2,3-bis(2-pyridyl)quinoxalines, using 0.05 mole (12.0 g) of 6,6'-dimethylpyridil and 0.05 mole of the same *o*-diamines.

Characterisation of compounds prepared

Ultimate analyses of all the compounds were obtained by means of a Perkin-Elmer Model 240 Analyzer and by conventional oxygen-flask methods. Melting points were determined conventionally. The results are shown in Table I.

Determination of copper with 2,3-bis[2-(6-methyl)pyridyl]quinoxaline

To 1 ml of the copper solution, containing 1–100 p.p.m. of copper(II), add 10 ml of acetate buffer pH 4.7 (equal volumes of 0.2 M sodium acetate and 0.2 M acetic acid), 1 ml of aqueous 1% hydroxylamine hydrochloride solution or freshly prepared 1% ascorbic acid solution, and 4 ml of an ethanolic 0.1% (w/v) solution of the reagent. Mix well and transfer to a small separatory funnel. Extract the copper(I)–quinoxaline complex with two 4-ml portions of isoamyl alcohol and collect the extracts in a 10-ml volumetric flask. Dilute to 10 ml with the solvent and measure the absorbance of the solution in a 1-cm cell at 525 nm against a solvent blank.

Prepare a calibration graph in the same way with known amounts of copper(II).

Spectrophotometry

Visible and ultraviolet spectra of the quinoxalines and the copper(I) complexes were measured on a Unicam SP 800 recording spectrophotometer in the range 200–715 nm, with 0.2-cm and 1-cm silica cells. Calibration against standard samples using solvent blanks indicated an accuracy of $\pm 2\%$ in absorbance readings.

Standard absorbance measurements of the copper(I) complexes were made in amyl alcohol solution after extraction from the acetate-buffered (pH 4.7) aqueous formation medium. Ultraviolet spectra of the quinoxalines were measured on ethanolic solutions (Table II). All solvents used were of "AnalaR" grade.

pH measurements

These were made on the aqueous layer after extraction of both chelate and excess of quinoxaline into the organic layer. In the examples where the dependence of colour development on the pH of extraction was followed, a range of Britton-Robinson buffer solutions was used and, after extraction, the pH was measured to ± 0.02 units by a Pye "Dynacap" instrument with a Pye glass electrode and a saturated calomel reference electrode. The presence of phosphate and borate in solution had no effect on colour formation or extraction.

TABLE I
 PREPARATION AND CHARACTERISATION OF THE SUBSTITUTED QUINOXALINES STUDIED
 (A : 2,3-bis(2-pyridyl)-substituted quinoxalines prepared from 2,2'-pyridil;
 B : 2,3-bis[2-(6-methyl)pyridyl]-substituted quinoxalines prepared from 6,6'-dimethyl-2,2'-pyridil)

Quinoxaline A Quinoxaline B	Components Pyridil A } o-diamine Pyridil B }	Molec. formula	M.p. (°)	Ultimate analysis (%)					
				Expected			Found		
				C	H	N	C	H	N
1	A; unsubstituted	A; o-phenylenediamine	184	76.0	4.3	19.7	76.2	4.7	19.7
2	B; unsubstituted	B; o-phenylenediamine	114	76.9	5.2	17.9	77.1	5.3	17.9
3	A; 6,7-benz	A; 2,3-diaminonaphthalene	172	79.0	4.2	16.8	78.8	4.3	16.8
4	B; 6,7-benz	B; 2,3-diaminonaphthalene	177	79.5	5.0	15.5	79.2	5.1	15.3
5	A; 6,7-dimethyl	A; 4,5-dimethyl-o-phenylenediamine	194	79.9	5.2	17.9	76.4	5.3	17.8
6	B; 6,7-dimethyl	B; 4,5-dimethyl-o-phenylenediamine	159	77.6	5.9	16.5	77.8	6.1	16.5
7	A; 6-methyl	A; 3,4-diaminotoluene	138	76.5	4.7	18.8	76.4	4.8	19.0
8	B; 6-methyl	B; 3,4-diaminotoluene	109	77.3	5.6	17.2	77.4	5.6	17.2
9	A; 6-nitro	A; 4-nitro-o-phenylenediamine	184	65.6	3.4	21.3	65.7	3.5	21.0
10	B; 6-nitro	B; 4-nitro-o-phenylenediamine	195	67.2	4.2	19.6	67.2	4.6	19.6
11	A; 5-nitro	A; 3-nitro-o-phenylenediamine	198	65.6	3.4	21.3	65.4	3.3	21.4
12	B; 5-nitro	B; 3-nitro-o-phenylenediamine	159	67.2	4.2	19.6	67.0	4.2	19.8
13	A; 6-methoxy	A; 4-methoxy-o-phenylenediamine	194	72.6	4.5	17.8	72.6	4.6	17.5
14	B; 6-methoxy	B; 4-methoxy-o-phenylenediamine	97	73.7	5.3	16.4	73.4	5.5	16.5
15	A; 6-chloro	A; 4-chloro-o-phenylenediamine	111	67.8	3.5	17.6	67.6	3.6	17.2 ^a
16	B; 6-chloro	B; 4-chloro-o-phenylenediamine	108	69.3	4.4	16.2	69.3	4.4	16.1 ^b
17	A; 6,7-dichloro	A; 4,5-dichloro-o-phenylenediamine	194	61.2	2.9	15.9	61.1	3.1	16.3 ^c
18	B; 6,7-dichloro	B; 4,5-dichloro-o-phenylenediamine	129	63.0	3.7	14.7	63.2	3.7	14.7 ^d
19	A; 6-carboxy	A; 3,4-diaminobenzoic acid	241	69.5	3.7	17.1	69.1	3.7	16.9
20	B; 6-carboxy	B; 3,4-diaminobenzoic acid	236	70.7	4.5	15.7	70.9	4.6	15.4
21	A; 8-aza	A; 2,3-diaminopyridine	138	71.6	3.9	24.6	71.6	4.1	24.8
22	B; 8-aza	B; 2,3-diaminopyridine	142	72.8	4.8	22.3	72.8	4.9	22.4
23	A; 5,6,7,8-dibenzo	A; 9,10-phenanthrenediamine	260	81.4	4.2	14.6	81.5	4.5	14.7
24	B; 6,7-(2',3'-indenylyl)	B; 2,3-diaminofluorene	221	80.6	5.5	13.9	80.3	5.3	14.1
25	A; X ^e	A; 1,8-diaminonaphthalene	150	79.0	4.2	16.8	78.8	4.0	16.9
26	B; Z ^f	B; 3,3'-diaminobenzidine	271	77.2	4.9	18.0	77.0	5.0	17.7

^a Chlorine : expected 11.1%; found 11.3%.

^b Chlorine : expected 10.2%; found 10.5%.

^c Chlorine : expected 20.1%; found 19.8%.

^d Chlorine : expected 18.6%; found 18.6%.

^e X : Naphtho-[1,8-de]-2,3-bis(2-pyridyl)-[1,4]-diazepine.

^f Z : 2,3,2',3'-Tetra-[2-(6-methyl)pyridyl]-6,6'-diquinoxalylyl.

TABLE II

U.V. SPECTRA OF QUINOXALINES IN ETHANOLIC SOLUTION

(Quinoxalines numbered as in Table I)

λ_{max} (nm)	ϵ_{max}	λ_{max} (nm)	ϵ_{max}	λ_{max} (nm)	ϵ_{max}	λ_{max} (nm)	ϵ_{max}	λ_{max} (nm)	ϵ_{max}
<i>Compound 1</i>		<i>Compound 2</i>		<i>Compound 3</i>		<i>Compound 4</i>		<i>Compound 5</i>	
333	10170	336	10550	382	7620	382	9790	344	12200
271	21920	279	18550	295	47020	279	48290	272	27700
246	37170	246	35710	228	36850	229	36850	254	38630
206	27320	208	29480					208	26690
<i>Compound 6</i>		<i>Compound 7</i>		<i>Compound 8</i>		<i>Compound 9</i>		<i>Compound 10</i>	
346	12450	340	10550	341	11690	256	27190	258	28460
279	21600	271	24400	279	20840	210	26430	210	31000
253	36850	250	37870	250	37970				
208	28970	208	26300	209	30245				
<i>Compound 11</i>		<i>Compound 12</i>		<i>Compound 13</i>		<i>Compound 14</i>		<i>Compound 15</i>	
339	10800	342	11310	362	12070	362	12200	340	11560
273	19060	279	17030	275	27450	279	22370	273	22110
240	34310	242	33040	258	29740	256	27960	249	39390
206	25420	208	29480	207	26180	208	28210	212	25420
<i>Compound 16</i>		<i>Compound 17</i>		<i>Compound 18</i>		<i>Compound 19</i>		<i>Compound 20</i>	
343	12200	346	12960	350	13720	340	10290	343	11060
279	19060	273	23640	277	19820	275	24650	281	20840
249	39390	253	44480	252	42950	250	40670	250	41680
212	29990	218	27400	220	29480	208	25160	210	28970
<i>Compound 21</i>		<i>Compound 22</i>		<i>Compound 23</i>		<i>Compound 24</i>		<i>Compound 25</i>	
336	16140	339	16010	375	— ^a	380	23000	444	2030
225	30500	232	24910	319	—	283	42700	348	15760
210	30750	208	37870	257	—	208	35580	334	14360
<i>Compound 26</i>				206	—			274	16520
376	19820							236	42190
290	31000							207	26940
208	27190								

^a Incompletely soluble.

RESULTS AND DISCUSSION

The form of the 2,3-bis(2-pyridyl)quinoxaline molecule (I), indicates a number of possible copper(I) chelate formulations. Where R₅ and R₆ are methyl and R₁–R₄ are hydrogen, two "cuproine" groups are present and thus bidentate chelation under various conditions and at different metal/ligand ratios could give rise to such species as:

- (i) [Cu(lig)₂]⁺; (ii) [Cu(lig)(solvent)₂]⁺
 (iii) [Cu(lig)(solv)Cl]⁰; (iv) [Cu₂(lig)(solvent)₄]²⁺
 or (v) a polymeric form—[Cu(lig)]_n.

When R₅ and R₆ are hydrogen, only one side of each of the two "ferroine" groups is sterically hindered, but the complex formation has characteristics similar to those for a full cuproine structure.

GOODWIN AND LIONS⁶ have argued against the formation of species of the type (iv). They noted that the ability of pyrazine to form only a mono and not a bis quaternary ammonium salt should be reflected in a reduction in any tendency of a second pyrazine nitrogen to function as a donor atom when one has already done so. They offered supporting evidence from analytical data on iron(II) and copper(II) complexes. The results obtained in the present work showed no indication of copper(I) complexes where the ratio of copper to ligand exceeded 1:1. Two chelate species were indicated which are probably of the form (i) and either (ii) or (iii). No evidence for polymeric chelates was found.

Copper-2,3-bis(2-pyridyl)quinoxaline reaction

Addition of a solution of 2,3-bis(2-pyridyl)quinoxaline to a solution of copper(I) produced an orange-yellow complex when the copper was in large excess (*ca.* 10:1), the colour changing progressively through red to purple as quinoxaline was added to excess. Throughout this range all colour was extractable into chloroform giving violet solutions, but with amyl alcohol only partial extraction was achieved to give a violet solution in equilibrium with an orange aqueous layer, the degree of extraction in-

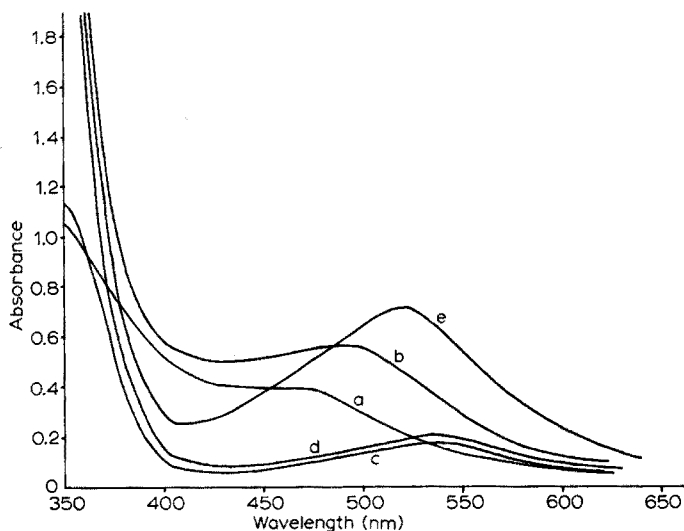


Fig. 1. Visible absorption spectra of copper(I)-2,3-bis(2-pyridyl)quinoxaline complexes formed from various metal-ligand ratios and in different solvents.

- (a) aqueous solution; 10 Cu:1 ligand (40 p.p.m. Cu).
- (b) aqueous solution; 1 Cu:5 ligand (10 p.p.m. Cu).
- (c) chloroform solution; 10 Cu:1 ligand (40 p.p.m. Cu).
- (d) chloroform solution; 1 Cu:10 ligand (2 p.p.m. Cu).
- (e) amyl alcohol solution; 1 Cu:10 ligand (10 p.p.m. Cu).

creasing with excess of quinoxaline until at a ratio of 10:1 no colour remained in the aqueous layer. The indication that two complexes are formed is supported by both spectroscopic and polarographic evidence.

Figure 1 shows visible spectra for the 2,3-bis(2-pyridyl)quinoxaline-copper(I) complexes. In aqueous solution, the complex formed at high copper:ligand ratios (spectrum (a)) has a shoulder on the intense u.v. absorption band at *ca.* 450 nm, im-

parting an orange colour to the complex. When the proportion of ligand is increased, this band moves steadily to a maximum at *ca.* 500 nm (spectrum (b)), remaining broad and indistinct. This gradual shift is attributed to the existence of both $[\text{CuL aq}_2]^+$ and $[\text{CuL}_2]^+$ species in solution.

Extraction of any of these intermediate solutions into chloroform yields similar spectra, (c) and (d), with a maximum at *ca.* 540 nm, the species probably being of the form $[\text{CuL}_2]^+$. Extraction of this form only into amyl alcohol, the $[\text{CuL aq}_2]^+$ species remaining in the aqueous layer, yields a sharper band at *ca.* 520 nm (spectrum(e)). The shift of about 20 nm to a higher wavelength in chloroform compared with amyl alcohol is typical of all the quinoxaline systems studied.

Copper-2,3-bis[2-(6-methyl)pyridyl]quinoxaline reaction

The behaviour of 2,3-bis[2-(6-methyl)pyridyl]quinoxaline (I; $R_5, R_6 = \text{CH}_3$ and $R_1, R_2, R_3, R_4 = \text{H}$) exemplifies the changes in complexing characteristics which occur when the full "double cuproine" grouping is present in this series of quinoxalines. In aqueous solution two distinct complexes are once more observed under conditions parallel to those mentioned above. The major difference is that for the dimethyl derivatives, both forms of complex are fully extractable into amyl alcohol as the $[\text{CuL}_2]^+$ form. Further, in contrast to the unsubstituted quinoxalines, the introduction of the methyl groups inhibits any extraction into chloroform, the colour being destroyed.

Thus any quantitative spectrophotometric comparison of the methyl-substituted and unsubstituted quinoxalines must be made where extraction is carried out into amyl alcohol, in the presence of a sufficient excess of quinoxaline to ensure that only the 1:2 copper-ligand complex is formed.

Spectrophotometric data for copper(I) complexes in amyl alcohol

Values of λ_{max} and ϵ_{max} for amyl alcohol extracts of copper(I) complexes of

TABLE III

PHYSICAL CONSTANTS OF THE COPPER(I) COMPLEX CATIONS OF SUBSTITUTED 2,3-BIS(2-PYRIDYL)-QUINOXALINES AFTER EXTRACTION INTO AMYL ALCOHOL AT PH 4.7

(Quinoxalines numbered as in Table I)

No.	λ_{max} (nm)	ϵ_{max}	No.	λ_{max} (nm)	ϵ_{max}	No.	λ_{max} (nm)	ϵ_{max}
1	519	3250	11	n.e. ^b	—	21	n.e.	—
2	525	6100	12	547	4765	22	568	5400
3	544	3180	13	505	3685	23	— ^a	—
4	562	5460	14	515	5975	24	528	5150
5	513	3750	15	524	3240	25	<i>ca.</i> 510 ^a	—
6	515	5210	16	529	4895	26	538	5150
7	515	3950	17	526	2670	27 ^c	546	6100
8	521	6040	18	550	4190	28 ^d	454	7950
9	549	2035	19	535	3750	29 ^e	474	13700
10	556	5145	20	538	5720			

^a Reagent absorption masks charge-transfer band of complex.

^b n.e.: not extracted.

^c "cuproine". ^d "neocuproine". ^e "bathocuproine".

substituted 2,3-bis(2-pyridyl)quinoxalines are shown in Table III. Comparative values for "cuproine" reagents are also listed. For complete colour development at least a three-fold excess of quinoxaline is required, since, as shown later in the case of 2,3-bis[2-(6-methyl)pyridyl]quinoxaline the stability constant of the reaction $\text{Cu}^+ + 2 \text{L} \rightleftharpoons \text{CuL}_2$ is an order of magnitude smaller than that for 2,2'-diquinolyl.

In all cases, methyl substitution in the pyridine rings gives up to a two-fold increase in molar extinction coefficient, and as all substitution in the quinoxaline ring reduces the value of ϵ_{max} , the most intense charge-transfer band occurs for 2,3-bis[2-(6-methyl)pyridyl]quinoxaline. The decrease caused by substitution in the quinoxaline ring is considerably greater for electron-withdrawing quinoxaline substituents, which induce a bathochromic shift in the charge-transfer band, than for electron-donating groups which give hypsochromic shifts. The extent of these shifts corresponds generally to the inductive effects of the respective group.

Values for ϵ_{max} and λ_{max} for the copper(I) complexes of quinoxaline-substituted 2,3-bis(2-pyridyl)quinoxalines which are fully extractable into chloroform are given in Table IV. As previously noted, in all cases where such extraction takes place, the species $[\text{CuL aq}_2]^+$ and $[\text{CuL}_2]^+$ formed under the appropriate reagent ratios, are considered to be extracted solely as the latter, as in the case 2,3-bis(2-pyridyl)quinoxaline itself. In all cases, maxima are broader, weaker and shifted to lower energies than for extraction into amyl alcohol.

TABLE IV

PHYSICAL CONSTANTS FOR CHLOROFORM EXTRACTS OF COPPER(I)-2,3-BIS(2-PYRIDYL)-QUINOXALINE COMPLEXES

(Quinoxalines numbered as in Table I)

No.	λ_{max} (nm)	ϵ_{max}	No.	λ_{max} (nm)	ϵ_{max}
1	538	2415	13	518	1970
3	571	2540	15	550	2260
5	521	1720	17	556	1240
7	532	2030	19	n.e.	—
9	568	2035	21	n.e.	—

n.e.: not extracted.

The behaviour of two pairs of quinoxaline derivatives is somewhat modified by the presence of acidic or basic substituents. 6-Carboxy-2,3-bis(2-pyridyl)quinoxaline in pH 4.7 acetate buffer formed two copper(I) chelates at high and low ratios of quinoxaline to copper, but neither the orange $[\text{CuL aq}_2]^+$ complex nor the purple $[\text{CuL}_2]^+$ form were extractable into chloroform. The latter only was extracted into amyl alcohol (λ_{max} 535 nm, ϵ_{max} 3750), leaving an orange-yellow aqueous solution, the spectra of which showed a shoulder at 475 nm on the intense U.V. absorption of the quinoxaline system. When the reagents were present in concentrations exceeding 20 p.p.m., this orange solution gradually deposited a flocculent orange-red precipitate. Both chelate forms of 6-carboxy-2,3-bis[2-(6-methyl)pyridyl]quinoxaline were fully extracted into amyl alcohol, but not extracted into chloroform. The insolubility of these complexes in chloroform may be attributed to the increase in polarity imparted by the carboxyl group.

5-Aza-2,3-bis(2-pyridyl)quinoxaline produced copper(I) chelates in aqueous solution (λ_{\max} 518 nm, ϵ_{\max} 2925 for the $[\text{CuL}_2]^+$ form) but no extraction was possible into either chloroform or amyl alcohol over a pH range of 4–11. For 5-aza-2,3-bis[2-(6-methyl)pyridyl]quinoxaline, neither chelate form was extracted into chloroform, but each appeared to be extracted unchanged into amyl alcohol. The spectral data for these amyl alcohol extractions are shown in Table V for different ratios of copper to quinoxaline.

TABLE V

SPECTRAL DATA FOR EXTRACTION OF COPPER(I)-5-AZA-2,3-BIS[2-(6-METHYL)-PYRIDYL]QUINOXALYL COMPLEXES INTO AMYL ALCOHOL

Quin.:Cu ratio*	λ_{\max} (nm)	ϵ_{\max}	Quin.:Cu ratio*	λ_{\max} (nm)	ϵ_{\max}
16	568	5400	2	552	3180
8	568	5350	1	513	1845
6	568	5100	0.4	502	700
4	565	4380	0.1	502	380

* Copper concentration = 10 p.p.m.

The blue colour of this $[\text{CuL}_2]^+$ complex tended to fade in daylight although it was stable in darkness. This might be predicted in view of the fact that the charge-transfer involved is of lower energy than that for the unsubstituted quinoxaline complex. Also noteworthy is that the red 1:1 complex on standing in darkness gradually faded, but also showed a shift in absorption maximum to higher wavelength. Thus after 14 days, ϵ_{\max} for a 1:1 copper to quinoxaline solution dropped from 1845 to 600 while λ_{\max} shifted from 513 to 554 nm. This may be attributed to the gradual formation of a more stable 2:1 complex.

pH dependence of colour development

The copper(I)-quinoxaline chelates resemble their "cuproine" analogues in not being formed in strongly acidic or basic media. With the exception of the 6-carboxy derivative, incipient colour formation was observed between pH 2.1 and 2.5; this reached a maximum and remained constant between pH 4.3 and 7.5 and vanished at pH 12. In the case of 6-carboxy-2,3-bis[2-(6-methyl)pyridyl]quinoxaline, no colour appeared below pH 3.1, and colour development was incomplete up to pH *ca.* 5. Between pH 5 and 6.25 only partial extraction was achieved into amyl alcohol and above pH 6.25 no extraction occurred. Presumably at low pH, the protonated form of the complex is extractable, while in neutral and alkaline solution proton abstraction produces a water-soluble species incorporating the carboxylate ion.

Specificity of reaction with copper(I)

The following cations were tested for colour development with the quinoxaline reagents: NH_4^+ , Group IA, Group IIA, Ti(III), Ti(IV), V(V), Cr(II), Cr(III), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Zn(II), ZrO^{2+} , Nb(V), Ru(IV), Rh(III), Pd(II), Ag(I), In(III), Sn(II), La(III), Ce(III), Ce(IV), Pt(IV), Hg(I), Hg(II), Pb(II), Th(IV), UO_2^{2+} .

The only cation found to give a colour reaction was titanium(III) at pH < 2

in the presence of reducing agents. DIEHL AND SMITH⁸ have noted the formation of a pale green colour between this ion and 2,2-diquinolyl. Addition of aqueous solutions of a number of both 2-pyridyl- and 2-(6-methyl)pyridylquinoxalines to acidic solutions of hexaquoctitanium(III) trichloride in presence of ascorbic acid or other reducing agents, produced deep blue or blue-green solutions. A typical absorption is that with 2,3-bis[2-(6-methyl)pyridyl]quinoxaline at 608 nm. For the 6-nitro and 5-aza derivatives, however, red solutions showing no discrete visible maxima were produced.

The blue colours faded rapidly in air to pale yellow solutions, hence the molar extinction coefficients could be only roughly estimated as being in the range 10-100 (based on a titanium(quinoxaline)₃ species). The colours were restored on adding further titanium ion.

The origin of these absorbing species is obscure. Since they only appear in the presence of reducing agents, it is possible that a transient titanium(II) entity is produced similar to the dark blue TiCl₂ · dipyridyl and TiCl₂ · phenanthroline complexes noted by FOWLES AND LESTER⁹. The great instability and reactivity of these compounds, however, suggests that the formation of quinoxaline analogues in aqueous solution is rather unlikely. An alternative explanation is that the coloured species is an octahedral tris(quinoxaline)titanium(III) complex, the Ti(*d*) → L (π^*) charge-transfer band of which might be expected to lie in the region of 600 nm, by analogy with the bipyridyl complexes of titanium(III) bromide which absorb at *ca.* 550 nm¹⁰. The lower π^* energy levels of the more highly conjugated quinoxaline ring systems would result in the shift of absorption to lower energy. A counter argument (as noted for iron(II)) is that steric hindrance should preclude formation of such an octahedral tris(quinoxaline) complex.

In practice, the presence of titanium(III) does not interfere with the determination of copper because of the different pH of colour formation. Under standard conditions, neither titanium(III) nor iron(II) in a hundred-fold excess gave any diminution in the absorbance of the copper complex.

Assessment of 2,3-bis[2-(6-methyl)pyridyl]quinoxaline as a copper reagent

Standard quinoxaline solutions were prepared on the assumption of a 2:1 ligand:copper(I) ratio in the final extracted complex. On this basis, a quinoxaline solution was prepared so that 1 ml was equivalent to 1 ml of 100 p.p.m. copper solution prepared by dissolving AnalaR copper(II) chloride dihydrate in distilled water. After reduction of 1 ml of copper(II) solution with hydroxylamine hydrochloride or ascorbic acid in pH 4.7 acetate-buffered medium, quinoxaline solution was added. Two 1-min extractions with 4-ml portions of amyl alcohol were sufficient for complete extraction of the copper(I) complex. Final solutions for standard measurements of 10 p.p.m. of copper in 10 ml of extracted solution showed an absorbance of approximately 1.0 for full colour development. Better stability under prolonged exposure to light was observed when the quinoxaline solutions were prepared in AnalaR amyl alcohol or ethanol rather than in slightly acidified (HCl) aqueous media.

Spectrophotometric study of complex formation equilibria

A Job plot on amyl alcohol extracts of the copper(I)-2,3-bis[2-(6-methyl)pyridyl]quinoxaline complex where the total reagent and copper concentration was $3.15 \cdot 10^{-4} M$ showed considerable curvature about the maximum indicating an

appreciable degree of dissociation. Extrapolation of the linear portions of the curve indicated that the quinoxaline:copper ratio lay between 2:1 and 4:1. A mole ratio plot for 10 p.p.m. of copper also gave a considerable degree of curvature, but with 60 p.p.m. of copper, the curve was sharpened so that a quinoxaline-copper ratio of < 2.5 could be estimated. Stability constants calculated from these plots were 9.3 and 9.5 respectively (on the log scale) compared with 10.4 obtained from a comparable treatment of the cuproine system. The absence of inflections on these plots confirmed that only the complex of the form $[\text{CuL}_2]^+$ was present in the amyl alcohol medium. This difference of an order of magnitude in the stability constants of the two systems emphasizes the need for a three-fold or greater excess of quinoxaline over copper. Provided that this criterion is upheld, Beer's law holds over a range from zero to approximately 100 p.p.m. of copper in the final extract with appropriately adjusted cell path-lengths.

As a qualitative test for copper, the detection limit on a spot plate is of the order of one part in $5 \cdot 10^7$, approximately the same as that for cuproine.

Further evidence for the nature of the copper complexes

Both polarography¹¹ and microanalytical data yielded further evidence for the formation of two distinct copper-quinoxaline complexes.

A series of polarograms was obtained in pH 4.7 acetate-buffered media by varying the ratio of quinoxaline to copper, the latter concentration being kept constant at $3 \cdot 10^{-4} M$ in the presence of excess of reducing agent. At a 1:1 ratio of quinoxaline to copper, a decrease was observed in the height of the copper reduction wave to half its value for copper solution alone (in addition to a shift to more negative potentials). Thereafter no further decrease in wave-height occurred as more quinoxaline was added, though the colour of the solution changed gradually from orange to violet. The copper is considered to be fully complexed as copper(I) at the 1:1 ratio by the formation of a $[\text{CuL aq}_2]^+$ complex which is then transformed to the $[\text{CuL}_2]^+$ complex on addition of more quinoxaline.

It proved difficult to obtain pure solid specimens of the various copper(I) complexes themselves, but a preparation of the 1:1 complex with 2,3-bis(2-pyridyl)-quinoxaline was carried out by treating a green aqueous solution of dichloro-2,3-bis(2-pyridyl)quinoxaline-copper(II)⁶ with a large excess of hydroxylamine hydrochloride. A deep red-brown micro-crystalline precipitate was produced; analyses showed that this corresponded to aquo-chloro-bis(2-pyridyl)quinoxaline-copper(I) [Calc. for $\text{C}_{18}\text{H}_{14}\text{N}_4\text{ClO}\text{Cu}$, C 53.9, H 3.5, N 14.0; found C 54.4, H 3.6, N 13.8]. Other preparations yielded complexes which were clearly of two distinct forms, but required further purification.

We are grateful to Professor R. BELCHER for his interest and encouragement.

SUMMARY

2,3-Bis(2-pyridyl)quinoxaline and 25 substituted derivatives were prepared and assessed as spectrophotometric reagents for copper. The compounds contain the copper(I)-specific "cuproine" grouping, but are much more readily prepared than most cuproine-type reagents. The possible formulations of the copper(I) chelates

present under various conditions, and the effect of substituents are discussed. 2,3-Bis[2-(6-methyl)pyridyl]quinoxaline showed the greatest sensitivity for copper and was evaluated quantitatively with respect to ligand : copper ratio, pH effects, interfering ions and Beer's law dependence.

RÉSUMÉ

La 2,3-bis(2-pyridyl)quinoxaline et 25 dérivés substitués ont été préparés et examinés comme réactifs spectrophotométriques du cuivre. Ces composés renferment le groupement spécifique "cuproïne" du cuivre(I); ils se préparent plus facilement que la plupart des réactifs de ce type. La meilleure sensibilité pour le cuivre a été obtenue avec la 2,3-bis[2-(6-méthyl)pyridyl]quinoxaline. Divers facteurs sont examinés: teneur en cuivre, pH, ions étrangers, ainsi que la loi de Beer.

ZUSAMMENFASSUNG

Es wurde 2,3-Bis(2-pyridyl)chinoxalin und 25 substituierte Derivate hergestellt und auf ihre Eignung als spektralphotometrisches Reagenz für Kupfer abgeschätzt. Die Verbindungen enthalten die Kupfer(I)spezifische "Cuproin"-Gruppe, welche sich sehr viel schneller bildet als die meisten Reagenzien des Cuproin-Typs. Mögliche Formulierungen der Kupfer(I)-Chelate, welche unter verschiedenen Bedingungen vorkommen, und der Einfluss von Substituenten werden diskutiert. 2,3-Bis[2-(6-methyl)pyridyl]chinoxalin zeigte die grösste Empfindlichkeit für Kupfer; das Ligand : Kupfer-Verhältnis, der pH-Einfluss, störende Ionen und die Abhängigkeit vom Beerschen Gesetz wurden untersucht.

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OXIMIDOBENZOTETRONIC ACID AS A REAGENT FOR THE SEPARATION AND GRAVIMETRIC DETERMINATION OF PALLADIUM AND COBALT

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BEAMISH¹ has reviewed the use of organic reagents for the gravimetric determination of palladium; most of the reagents mentioned are quite sensitive and accurate, though in most cases, interference is caused by the presence of foreign ions, particularly iron, cobalt, nickel, gold and platinum metals. More recently, other organic reagents have been developed for the gravimetric determination of palladium: 3-methyl-1-phenyl-2-pyrazoline-4,5-dione-4-oxime², for which only interference from platinum was studied; phenanthraquinonemonoxime³, where the interference of platinum and rhodium (the only Pt metals studied) was eliminated by extraction of the palladium complex into an organic phase; and 2-hydroxy-5-methoxy-propiofenoneoxime⁴ which was used for the separation and determination of palladium and nickel. 3,3-Diphenylindane-1,2-dionedioxime⁵ has also been suggested as a gravimetric reagent for palladium, but only preliminary studies have been reported.

Dimethylglyoxime continues to be largely used for the gravimetric estimation of palladium. There are however, a few drawbacks in the use of this reagent^{1,6,7}, and modified procedures have to be adopted when metal ions like platinum, rhodium and iridium are present, while nickel and gold must be absent.

There is thus no satisfactory reagent for the gravimetric determination of palladium in presence of platinum metals, iron, cobalt, nickel and gold. Further, there is no reagent that can be satisfactorily used for the separation of palladium and cobalt and their accurate determination.

Oximidobenzotetronic acid (OBTA) has already been used for the spectrophotometric determination of iron⁸ and cobalt⁹, as well as for the gravimetric determination of the latter¹⁰. In further tests on this reagent, it was found that an ethanolic solution of OBTA precipitated palladium quantitatively from acidic solutions (pH 5.1 to 0.75 *N* acid) as a brownish-red complex, insoluble in most organic solvents. The complex after drying at 140–150° corresponded to the composition Pd(C₉H₄NO₄)₂. The gravimetric determination of palladium was successfully carried out in presence of other platinum metals, iron, nickel, cobalt, silver and gold which are usually associated with palladium, as well as other foreign ions associated with it in group II of qualitative schemes. Complexing ions such as oxalate, fluoride, acetate, tartrate, citrate and phosphate did not interfere. As reported earlier¹⁰, cobalt is precipitated partially at low pH (0.5 *N* acid) but it was shown that palladium can be separated from cobalt by washing the precipitate with hot aqueous alcohol, cobalt being determined in the filtrate by precipitation at higher pH (*ca.* 4).

EXPERIMENTAL

Reagents

Oximidobenzotetronic acid was prepared as described earlier⁸. A 2% solution of the reagent in ethanol was used.

Stock solutions of palladium(II) were prepared by dissolving either palladium nitrate (Johnson Matthey) in nitric acid (B.D.H., AnalaR) or palladium chloride (Arora Matthey, India) in hydrochloric acid (B.D.H., AnalaR), and standardized with dimethylglyoxime⁷.

Among other salts used, chloroplatinic acid, chloroiridic acid, ruthenium chloride, potassium chlorosmate, potassium chlororhodite, chloroauric acid and ammonium titanyl oxalate were obtained from Johnson Matthey; other salts used were generally of analytical-reagent grade. Dilute solutions of hydrochloric acid and potassium hydroxide were used for the adjustment of pH, the pH measurements being made by using a Beckman pH-meter model H-2, with a suitable glass electrode.

Determination of palladium with OBTA

To about 75 ml of a solution of palladium nitrate or palladium chloride, containing 2–16 mg of palladium(II) at pH 1.7 and warmed to about 50°, add the reagent solution slowly with constant stirring until the red-brown complex coagulates leaving a clear yellow supernate. Leave the solution at room temperature (15–20°) for *ca.* 10 min, filter through a weighed sintered glass G-3 crucible, and test the filtrate for complete precipitation. Wash the voluminous complex free from chloride or nitrate ions with hot water, and then wash two or three times with hot 50% aqueous ethanol. Dry at 140–150° and weigh as Pd(C₉H₄NO₄)₂.

TABLE I

DETERMINATION OF PALLADIUM WITH OBTA

<i>Pd(II)</i> taken (mg)	<i>Pd(II)</i> found (mg)	<i>Error found</i> (mg)	(%)
2.113	2.095	-0.0035	-0.17
4.226	4.219	-0.007	-0.17
7.928	7.935	+0.007	+0.09
7.928	7.946	+0.018	+0.23
8.452	8.449	-0.003	-0.04
8.452	8.460	+0.008	+0.10
9.017	9.006	-0.011	-0.12
9.017	9.028	+0.011	+0.12
9.332	9.323	-0.009	-0.10
9.332	9.354	+0.022	+0.23
16.904	16.924	+0.020	+0.12

The results of some of the experiments in which different quantities of palladium(II) were taken, are shown in Table I. Quantities of palladium(II) greater than 17 mg were not determined since the precipitate was very voluminous. The complex was quite stable in the temperature range 110–160°; the temperature range 140–150° for drying the complex was therefore chosen.

The dried complex was insoluble in ethanol, isopropanol, isobutanol, isoamyl alcohol, benzene, ethyl acetate, cyclohexanol, acetone and ether, but slightly soluble in hot chloroform, glacial acetic acid, acetic anhydride, and dioxan. It was soluble in *o*-dichlorobenzene, nitrobenzene and tricresyl phosphate.

Effect of pH on the precipitation of palladium-OBTA complex

Palladium could be accurately determined in solutions which ranged from 0.75 *N* hydrochloric, nitric acid or sulphuric acid, to solutions of pH 5.1 (Table II). At higher pH the complex was unstable and decomposed to give a precipitate of hydrated oxide at pH 10-11.

TABLE II

EFFECT OF pH ON THE PRECIPITATION OF THE PALLADIUM COMPLEX

Acidity or pH	Pd(II) (mg)		pH	Pd(II) (mg)	
	taken	found		taken	found
3.5 <i>N</i>	8.452	0.000	2.55	7.928	7.935
1.5 <i>N</i>	8.452	7.563	3.0	7.928	7.935
1.0 <i>N</i>	8.452	8.188	3.5	7.928	7.935
0.75 <i>N</i>	8.452	8.460	4.1	7.928	7.902
0.50 <i>N</i>	8.452	8.438	4.55	8.452	8.438
1.0	8.452	8.449	5.1	8.452	8.427
1.7	8.452	8.460	6.0	8.452	8.276
2.05	7.928	7.946	6.5	8.452	4.526

Separation of palladium from other ions

It was found that palladium could be successfully separated and determined in presence of even 10-fold amounts of the following ions in 0.1-0.5 *N* nitric or hydrochloric acid solutions (Table III): Pt(IV), Ir(IV), Os(IV), Rh(III), Cu(II), Ni(II), Fe(III), Ag(I), Au(III), Zr(IV), Ti(IV), Pb(II), Bi(III), Cd(II), Hg(II), Sb(III), As(V), Mo(VI), Se(VI), Te(IV), Al(III), Cr(III) and Zn(II). Ruthenium could be tolerated in amounts equal to that of palladium(II); in larger amounts it was absorbed on the complex. When copper(II) or nickel(II) was present, the solution was made 20% in ethanol before precipitation. When iron(III) was present in amounts equal to 4 times that of palladium(II), precipitation from solutions containing 0.5 *N* nitric acid and 60-70% ethanol at room temperature gave a precipitate free from any adsorbed iron(III) complex; when iron(III) was present in 10-fold amounts compared to palladium, there was heavy adsorption of the blue iron complex on palladium precipitate but this could be removed by repeated washings with hot 50% ethanol. Palladium could also be determined at different pH values in the presence of the following anions: acetate, oxalate, tartrate, citrate, phosphate and fluoride (Table IV).

Separation and determination of palladium and cobalt

To about 75 ml of a solution (containing *ca.* 8 mg of palladium and 5-25 mg of cobalt), sufficient nitric or hydrochloric acid was added to give an acidity of 0.1-0.5 *N*. The solution was then warmed to 50-60° and the reagent solution was gradually added until the precipitation of palladium was complete. The precipitate obtained was filtered as described above and washed with hot 50% aqueous ethanol until the

TABLE III

DETERMINATION OF PALLADIUM IN PRESENCE OF FOREIGN IONS

Foreign ion taken	Amount (mg)	Pd taken (mg)	Pd found (mg)	Error (%)
Ag(I) as AgNO ₃	56.74	8.452	8.460	+0.10
	102.7		8.449	-0.04
Au(III)	22.8		8.438	-0.16
	91.2		8.460	+0.10
Fe(III) as sulphate*	8.845		8.427	-0.32
	33.42		8.460	+0.10
	96.44		8.460	+0.10
Pt(IV)	9.130		8.438	-0.16
	27.39		8.460	+0.10
	91.30		8.471	+0.23
Ir(IV)	7.76	9.017	9.006	-0.12
	23.28		9.017	±0.00
	77.60		9.039	+0.22
Rh(III)	12.52		9.039	+0.22
	37.56		9.028	+0.12
	125.2		9.028	+0.12
Ru(III)	2.970	9.017	8.995	-0.24
	8.910	9.332	9.323	-0.10
	14.850		9.400	+0.72
	29.700		9.448	+1.25
Os(IV)	9.015		9.312	-0.22
	27.045		9.365	+0.35
	90.15		9.354	+0.24
Ni(II) as NiSO ₄ ·7H ₂ O ^b	9.374		9.323	-0.10
	28.035		9.312	-0.21
	94.02		9.312	-0.21
Cu(II) as CuSO ₄ ·5H ₂ O ^b	7.886	7.927	7.935	+0.10
	23.64		7.935	+0.10
	79.10		7.913	-0.17
Cd(II) as CdCl ₂ ·2H ₂ O	7.83	7.927	7.935	+0.10
	79.86		7.924	-0.04
Pb(II) as Pb(NO ₃) ₂	28.80		7.946	+0.24
	83.08		7.924	-0.04
Bi(III) as Bi(NO ₃) ₃ ·5H ₂ O	26.19		7.946	+0.24
	86.42		7.924	-0.04
Sb(III) as K·SbO·C ₄ H ₄ O ₆ ^b	15.94		7.946	+0.24
	91.91		7.924	-0.04
Al(III) as KAl(SO ₄) ₂ ·12H ₂ O	15.75		7.935	+0.10
	70.28		7.924	-0.04
Cr(III) as KCr(SO ₄) ₂ ·12H ₂ O	19.96		7.924	-0.04
	82.46		7.935	+0.10
Zn(II) as ZnSO ₄ ·7H ₂ O	16.21		7.924	-0.04
	91.39		7.935	+0.10
Se(VI) as K ₂ SeO ₄	35.72	8.452	8.449	-0.04
	108.2		8.471	+0.23
Te(IV) as K ₂ TeO ₃	12.19		8.460	+0.10
	92.74		8.471	+0.23
Hg(II) as HgCl ₂	41.81		8.449	-0.04
	156.4		8.427	-0.32
As(V) as arsenate	30.23		8.427	-0.32
	81.47		8.449	-0.04
Mo(VI) as (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	24.56		8.427	-0.32
	63.02		8.449	-0.04
Ti(IV)	24.85		8.427	-0.32
	101.6		8.460	+0.10
Zr(IV) as ZrOCl ₂ ·8H ₂ O	31.59		8.427	-0.32
	90.86		8.460	+0.10

* Precipitation done in 70% ethanolic solution; washing with hot 50% ethanol continued until the washings were colourless.

^b Precipitation done in 25% ethanolic solution.

TABLE IV

DETERMINATION OF PALLADIUM IN PRESENCE OF COMPLEXING ANIONS

Foreign ion taken	Amount (mg)	Pd taken (mg)	pH or acidity	Pd found (mg)	Error (%)
Acetate as $\text{CH}_3\text{COONH}_4$	11.57	8.452	1.5	8.438	-0.16
	104.2		4.0	8.460	+0.10
Oxalate as $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	11.42	7.927	3.5	7.935	+0.10
	18.65		0.5 N	7.913	-0.17
	84.72		2.00	7.935	+0.10
Tartrate as $\text{KSB} \cdot \text{C}_4\text{H}_4\text{O}_6$	20.26		0.5 N	7.946	+0.24
Citrate as citric acid (A.R.)	124.5		0.5 N	7.924	-0.03
Phosphate as $(\text{NH}_4)_2\text{HPO}_4$	45.4		0.5 N	7.935	+0.10
	100.1		4.00	7.902	-0.31
	7.365		1.7	7.935	+0.10
Fluoride as NaF	14.95		2.5	7.913	-0.17
	74.26		3.0	7.924	-0.04
	26.48		2.5	7.946	+0.24
	120.5		0.5 N	7.946	+0.24

TABLE V

SEPARATION AND DETERMINATION OF PALLADIUM AND COBALT WITH OBTA

Taken (mg)		Found (mg)		Error (%)	
Pd(II)	Co(II)	Pd(II)	Co(II)	Pd	Co
8.452	9.420	8.460	—	+0.10	—
8.452	18.84	8.471	18.83	+0.23	-0.05
8.452	37.68	8.449	37.65	-0.04	-0.08
8.452	9.420	8.460	9.389	+0.10	-0.33
6.339	18.84	6.317	18.76	-0.34	-0.47
4.226	28.26	4.229	28.19	+0.07	-0.25
3.371	35.80	3.387	35.72	+0.47	-0.22
3.371	15.07	3.376	15.03	+0.15	-0.27

filtrate was free from nitrate or chloride, and sulphate ion. The complex was dried at 140–150° and weighed. The filtrate and washings were collected and diluted to 250 ml. An aliquot containing 5–10 mg of cobalt(II) was taken and made just alkaline to methyl red indicator. The solution was warmed to about 50° and cobalt was determined as reported earlier¹⁰.

Some typical results are given in Table V.

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SUMMARY

Oximidobenzotetronic acid is recommended for the separation and gravimetric determination of palladium and cobalt. An ethanolic solution of the reagent quantitatively precipitates palladium(II) from solutions which are 0.75 N in acid up to pH 5.1; the complex is weighed as $\text{Pd}(\text{C}_9\text{H}_5\text{NO}_4)_2$. Cobalt(II) can be determined in the filtrate after the precipitation of palladium. With 0.5 N acid solutions, no inter-

ference was found from Pt(IV), Ir(IV), Rh(III), Ru(III), Os(IV), Au(III), Ag(I), Cu(II), Fe(III), Ni(II), Hg(II), Pb(II), Bi(III), Cd(II), As(V), Se(VI), Te(IV), Mo(VI), Sb(III), Al(III), Cr(III), Zn(II), Ti(IV), Zr(IV), acetate, oxalate, citrate, tartrate, phosphate and fluoride.

RÉSUMÉ

L'acide oximidobenzotétronique est recommandé pour la séparation et le dosage gravimétrique du palladium et du cobalt. A l'aide de la solution de réactif dans l'éthanol, on précipite quantitativement le palladium dans des solutions 0.75 N en acide jusqu'à pH 5.1. Le complexe est pesé sous forme de $\text{Pd}(\text{C}_9\text{H}_5\text{NO}_4)_2$. Le cobalt est dosé dans le filtrat après séparation du palladium. En solutions acides (0.5 N) les ions suivants ne gênent pas: Pt(IV), Ir(IV), Rh(III), Ru(III), Os(IV), Au(III), Ag(I), Cu(II), Fe(III), Ni(II), Hg(II), Pb(II), Bi(III), Cd(II), As(V), Se(VI), Te(IV), Mo(VI), Sb(III), Al(III), Cr(III), Zn(II), Ti(IV), Zr(IV), acétate, oxalate, citrate, tartrate, phosphate et fluorure.

ZUSAMMENFASSUNG

Oximidobenzotetrone Säure wird zur Trennung und gravimetrischen Bestimmung von Palladium und Cobalt empfohlen. Palladium(II) wird aus saurer Lösung mit einer äthanolischen Lösung des Reagenzes quantitativ gefällt und als $\text{Pd}(\text{C}_9\text{H}_5\text{NO}_4)_2$ gewogen. Cobalt(II) kann im Filtrat bestimmt werden. Es wird für 25 Kationen und 6 Anionen gezeigt, dass diese bei Fällung aus 0.5 N saurer Lösung nicht stören.

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DETERMINATION OF SULPHUR AND SULPHATE BY TITRATION WITH BARIUM PERCHLORATE

COMPARISON OF VARIOUS COLOUR INDICATORS

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Various colour indicators have been recommended for the precipitation titration of sulphate with a solution of barium perchlorate: thorin (1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid)^{1,2}, carboxyarsenazo (3-(*o*-arsonophenylazo)-6-(*o*-carboxyphenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid)³, sulphonazo III (4,5-dihydroxy-3,6-bis(*o*-sulphophenylazo)-2,7-naphthalenedisulphonic acid)⁴, dinitrosulphonazo III (4,5-dihydroxy-3,6-bis(*p*-nitro-*o*-sulphophenylazo)-2,7-naphthalenedisulphonic acid)⁵, dimethylsulphonazo III (4,5-dihydroxy-3,6-bis(*p*-methyl-*o*-sulphophenylazo)-2,7-naphthalenedisulphonic acid)⁶, and dibromosulphonazo III (3,6-bis(*p*-bromo-*o*-sulphophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid)⁶ have been proposed. However, there is no exact information available on how the indication properties of all these substances compare in the given titration. A comparison of the indicators was therefore carried out and the best of the indicators was examined in the determination of organic and inorganic sulphur.

EXPERIMENTAL

Apparatus

All photometric measurements were made with a spectrophotometer SF-63, Prema-Brno (Czechoslovakia), with 0.5-cm glass cells.

The inorganic sulphur was determined by means of an apparatus consisting of a quartz tube, 25 cm in length and 1.2 cm in diameter, with electric heating, for sample decomposition and oxidation; the tube was connected to an absorption vessel, filled with glass beads of 2 mm diameter.

The organic sulphur was determined in a 250-ml Schöniger flask.

Reagents

Aqueous 0.01 *M* solutions of barium perchlorate, potassium sulphate, potassium hydrogen phosphate, sodium hydrogen arsenate, the disodium salt of EDTA and sodium chloride were prepared in the usual manner. A 0.01 *M* solution of barium perchlorate in 80% ethanol was used for the indication with thorin. Aqueous 0.1% (w/v) solutions of the individual indicators were used. The derivatives of 4,5-dihydroxy-2,7-naphthalenedisulphonic acid were prepared as given in the patent literature⁷;

they were obtained as their sodium salts. Since the free acids are the best form for elemental analyses, the sodium salts were converted by passing their aqueous solutions through a column of a strongly acidic cation exchanger, *e.g.* Dowex 50WX8. The results obtained for sulphur and nitrogen are collected in Table I. The purity of the indicators was also checked by paper chromatography on Whatman no. 1 paper with aqueous 2 *M* ammonia saturated with isobutanol as eluant.

All chemicals used were the "pro analysi" products of Lachema (Brno).

TABLE I
QUANTITATIVE ANALYSIS OF REAGENTS

Reagent	Molecular weight	%N		%S	
		Found	Calcd.	Found	Calcd.
Thorin	532.342	5.31	5.26	11.83	12.05
Carboxyarsenazo	696.460	7.87	8.05	9.03	9.21
Sulphonazo III	688.664	8.07	8.14	18.78	18.63
Dinitrosulphonazo III	779.268	10.55	10.79	16.31	16.46
Dimethylsulphonazo III	716.716	7.56	7.82	17.62	17.90
Dibromosulphonazo III	846.478	6.48	6.62	14.87	15.15

TABLE II
DETERMINATION OF POTASSIUM SULPHATE

Indicator	Found(%) ^a	Standard deviation(%)
Thorin	99.4	± 0.15
Carboxyarsenazo	99.6	± 0.14
Sulphonazo III	100.4	± 0.10
Dinitrosulphonazo III	100.5	± 0.12
Dimethylsulphonazo III	99.8	± 0.08
Dibromosulphonazo III	100.2	± 0.10

^a Average values of 10 determinations.

Comparison of indicators

Potassium sulphate (0.01–0.08 mmole) was dissolved in 5 ml of water; 6 ml of acetone and 3 drops of the indicator solution were added and the solution was titrated with 0.01 *M* barium perchlorate. The colour change at the end-point was usually from wine red to blue, but, in the case of dimethylsulphonazo III, from wine red to green-blue. In the case of thorin, 20 ml of ethanol was added instead of acetone, the solution was titrated with 0.01 *M* barium perchlorate in 80% ethanol, and the colour change at the end-point was from orange to red.

The results obtained are given in Table II. In another series of experiments, the same titrations were followed photometrically. The curves obtained are shown in Fig. 1.

With all the indicators, the poorest reversibility of the colour change occurred at the beginning of the titration, because of the precipitation mechanism of the titration; the proper course of the titration requires the formation of precipitation centres in solution. At the end-point, the reversibility was satisfactory. The quality

of the sharpness of the colour change at the end-point was proportional to the standard deviations given in Table II.

The masking effect of phosphate, arsenate, EDTA and sodium chloride

The masking effects of these species were followed by titrating solutions containing 5.40 ml of 0.01 *M* potassium sulphate, *X* ml of 0.01 *M* solutions of masking reagents, 1.2(5 + *X*) ml of acetone and 3 drops of the indicator solution, with 0.01

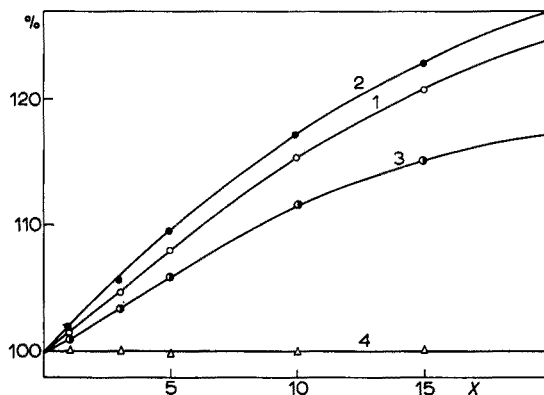
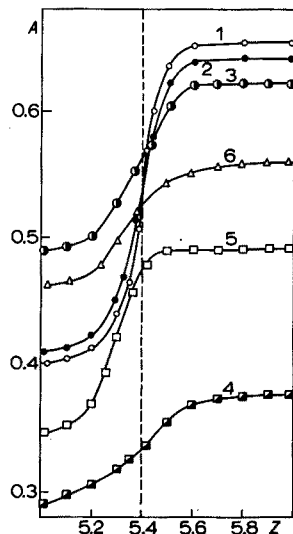


Fig. 1. Photometric titration of potassium sulphate (5.40 ml of 0.01 *M*) with barium perchlorate (*Z* ml of 0.01 *M*). (1) dimethylsulphonazo III, 655 nm; (2) sulphonazo III, 638 nm; (3) dinitrosulphonazo III, 640 nm; (4) dibromosulphonazo III, 640 nm; (5) carboxyarsenazo, 640 nm; (6) thorin, 545 nm. A = absorbance.

Fig. 2. Dimethylsulphonazo III as indicator. Masking effect of phosphate (1), arsenate (2), EDTA (3), and sodium chloride (4) on titration of sulphate with barium perchlorate.

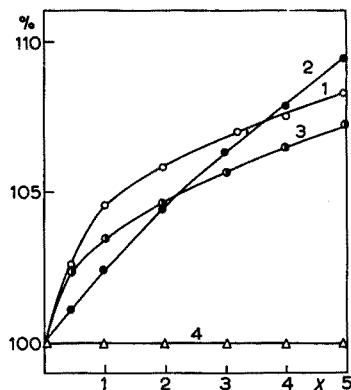


Fig. 3. Sulphonazo as indicator. Masking effects as in Fig. 2.

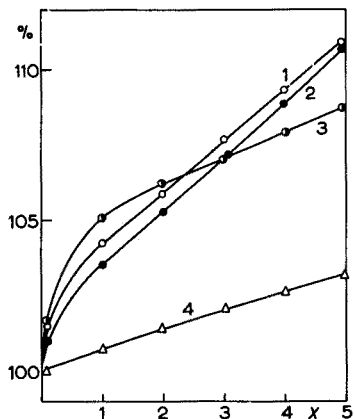


Fig. 4. Dinitrosulphonazo III as indicator. Masking effects as in Fig. 2.

M barium perchlorate. In the case of thorin, 4(5 + *X*) ml of ethanol was used instead of acetone, and the 0.01 *M* barium perchlorate was dissolved in 80% ethanol. The results obtained are shown in Figs. 2–4. The masking effects with dibromosulphonazo III, carboxyarsenazo, and thorin were similar in nature to those shown in Fig. 4.

Determination of inorganic sulphur

A sample containing 0.05–0.08 meq of sulphate or sulphide in a platinum boat was placed into the quartz tube of the apparatus described above (see p. 375). The absorption vessel was filled with 5 ml of water and 0.15 ml of a 30% solution of hydrogen peroxide. Pure oxygen was passed through the apparatus at a rate of 1 l/h and the sample was heated for 60 min at 95°. The absorption solution was transferred to a flask, the absorption vessel was washed with 5 ml of acetone, and 3 drops of dimethylsulphonazo III solution were added. The solution was titrated with 0.01 *M* barium perchlorate to a permanent colour change to green-blue.

Some typical results are given in Table III.

TABLE III
DETERMINATION OF SULPHUR IN SULPHIDES AND SULPHATES
(Dimethylsulphonazo III as indicator)

Sample ^a	%S	
	Found	Calculated
Copper(II) sulphate	19.85	20.09
Copper(II) sulphide	33.25	33.54
Magnesium sulphate	26.72 ^b	26.64
Cadmium sulphate	15.23 ^b	15.38
Aluminium sulphate	28.29 ^b	28.11
Manganese(II) sulphate	21.06	21.24
	21.04 ^b	
Thorium sulphate	15.03	15.12
Thorium sulphide	21.44	21.65
Uranium(IV) sulphide	21.05	21.22
Uranyl sulphate	8.71	8.76
	8.64 ^b	
Chromium(III) sulphate	24.51 ^b	24.53
Nickel sulphate	20.57	20.72

^a All samples were anhydrous.

^b Determination by direct titration without the thermal decomposition; average values of 5 determinations.

This determination of inorganic sulphur is limited by the possibility of sample decomposition and oxidation at 95°. In certain cases (see Table III) direct titration without thermal decomposition is possible. In other cases, the oxidation or decomposition of samples must be carried out at temperatures higher than 95°. Alternatively, oxidation must be done in solution, by adding some oxidant, such as sodium hypochlorite, chloramine T, potassium bromate, etc.; such methods are, however, less convenient for the application of the sulphate titration. Copper(II), nickel, cobalt(II), zinc, iron(II), lead(II), yttrium, lanthanides, palladium(II), and ruthenium(IV) interfere seriously with the titration.

Determination of organic sulphur

Samples (4–7 mg) were burned by SCHÖNIGER's flask method⁸ with a 250-ml flask, the combustion products being absorbed in 4 ml of water and 0.15 ml of 30% hydrogen peroxide solution. The flask was shaken for 15 min to obtain complete absorption; 3 ml of acetone and 3 drops of dimethylsulphonazo III solution were added and the solution was titrated with 0.01 *M* barium perchlorate.

Some typical results are shown in Table IV.

TABLE IV
DETERMINATION OF ORGANIC SULPHUR
(Dimethylsulphonazo III as indicator)

Sample	%S		Standard deviation (%)
	Calcd.	Found ^a	
L-Cysteine	26.47	26.51	± 0.16
Thiosemicarbazide	35.19	35.28	± 0.19
Taurine	25.62	25.54	± 0.15
Chromotropic acid (dihydrate)	18.00	17.87	± 0.15
Thiourea	42.13	41.92	± 0.22
Dimethylsulphonazo III	17.90	17.62	± 0.21
Sulphanilic acid	18.52	18.50	± 0.14
Thiamine	9.51	9.55	± 0.12

^a Average of 5 determinations.

DISCUSSION

Of the six reagents investigated, dimethylsulphonazo III appeared to be the best indicator for determination of sulphate by the precipitation titration with barium perchlorate. This was true for both the visual and photometric titrations.

Phosphate, arsenate, EDTA, and sodium chloride also had the smallest effects when this indicator was used. Thorin, the best known indicator for the sulphate titration, gave clearly less accurate results.

The results obtained are in good agreement with the photometric sensitivity of the reagents investigated (see Table V)^{6,9}.

If the solubility product of barium sulphate is $K_s = [\text{Ba}][\text{SO}_4]$, and the effec-

TABLE V
MOLAR ABSORPTIVITIES^a FOR VARIOUS BARIUM COMPLEXES AT pH 7.0

Reagent	Wavelength (nm)	Aqueous medium	2:3 Acetone-water
Dimethylsulphonazo III	655	13,900	28,800
Sulphonazo III	638	8,700	16,000
Dinitrosulphonazo III	640	7,200	2,800
Dibromosulphonazo III	640	10,500	15,000
Carboxyarsenazo	640	9,200	—
Thorin	545	< 1,000	2,500 ^b

^a In $\text{cm}^2\text{mmole}^{-1}$.

^b In aqueous 80% ethanol medium.

tive stability constant of the complex of indicator In with barium, $K = [\text{BaIn}] / [\text{Ba}][\text{In}]$, then the equivalence point of the sulphate titration is characterized by

$$[\text{Ba}]_{\text{eq}} = \sqrt{K_s}, \quad K = [\text{Ba}]_{\text{eq}}^{-1},$$

i.e. after elimination of $[\text{Ba}]_{\text{eq}}$

$$K = 1/\sqrt{K_s}.$$

This equation gives $K = 9.62 \cdot 10^4$ in aqueous medium at a temperature of 25° ($K_s = 1.08 \cdot 10^{-10}$). This result is also in good agreement with the experimental value. The value of the effective stability constant which is nearest to the theoretical value is obtained⁹ for dimethylsulphonazo III at pH 6.9, the value being $K = 3.8 \cdot 10^4$. Dimethylsulphonazo III was therefore chosen for the determination of inorganic and organic sulphur in this study. The starting material for the synthesis of dimethylsulphonazo III, *p*-toluidine-*m*-sulphonic acid, is much more readily available than the *o*-aminobenzenesulphonic acids used for the other indicator preparations.

The aqueous solutions of all the indicators investigated were stable for several months. The favourable effect of acetone on the photometric sensitivity has been discussed in detail previously⁹.

The reagents of the phosphonazo III type, *i.e.* 4,5-dihydroxy-3,6-bis(*o*-phosphonophenylazo)-2,7-naphthalenedisulphonic acid, give more sensitive photometric reactions with barium ions than the reagents investigated¹⁰; but the barium complexes of these reagents are of higher stability, and they are thus not convenient as indicators for the sulphate titration.

SUMMARY

Thorin, carboxyarsenazo, sulphonazo III, dinitrosulphonazo III, dimethylsulphonazo III and dibromosulphonazo III were compared as indicators for the precipitation titration of sulphate with barium perchlorate solution. Dimethylsulphonazo III was found to be best, and was tested further in determinations of inorganic and organic sulphur.

RÉSUMÉ

Divers indicateurs (thorin, carboxyarsenazo, sulfonazo-III, dinitrosulfonazo-III, diméthylsulfonazo-III et dibromosulfonazo-III) sont examinés et comparés pour le titrage par précipitation des sulfates au moyen d'une solution de perchlorate de baryum. Le diméthylsulfonazo-III s'est révélé le meilleur et est appliqué aux dosages de soufre, inorganique et organique.

ZUSAMMENFASSUNG

Für die massanalytische Bestimmung von Schwefel und Sulfat durch Titration mit Bariumperchlorat wurden folgende Indikatoren untersucht und verglichen: Thorin, Carboxyarsenazo, Sulfonazo III, Dinitrosulfonazo III, Dimethylsulfonazo III und Dibromsulfonazo III. Am besten eignete sich Dimethylsulfonazo III als Indikator.

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EVALUATION OF EFFICIENCIES OF NORMAL FREEZING, COLUMN CRYSTALLIZATION AND ZONE MELTING

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Techniques for the purification of organic materials and for the concentration of impurities based on the solid-liquid phase equilibrium have become more important in recent years¹. Many separations are now possible which hitherto could not have been achieved by other methods. In normal freezing, levels of purity up to 99.99% have been reported^{2,3}. Zone melting has proven itself to be especially applicable to the ultrapurification of metals⁴. Highly purified organic compounds are currently being prepared by this technique on a commercial scale⁵. Column crystallization is still in the development stage, although promising results have already been reported^{1,6}.

For a comparative study of these separations, it would be necessary to have an independent measure of the separating efficiencies of the systems in use. It is obvious that the final degree of purity of a product is no criterion of the effectiveness of the system. Relatively crude techniques give excellent separations if the components are easily separable; the most refined apparatus may barely resolve similar compounds.

There are several excellent papers on the theoretical behavior of these separation techniques. If the fundamental parameters of the system are known, the obtainable separation in a zone melting or normal freezing run can be computed theoretically^{4,7}.

In discussing these experiments it is generally convenient to define an ideal distribution coefficient, k_0 , as the equilibrium ratio between the concentration of the impurities in the solid that has just been deposited and the average impurity concentration in the supernatant liquid. The practical distribution coefficient, k , is defined as this same ratio under practical operating conditions. In general, k , which will be larger than k_0 , will only approach k_0 under ideal conditions. BURTON, PRIM AND SCHLICHTER⁸ have correlated these two coefficients by:

$$k = k_0 / \{k_0 + (1 + k_0) \exp(-f\delta/D)\} \quad (1)$$

The dimensionless quantity $f\delta/D$ may be regarded as a normalized growth velocity, wherein f is the growth rate, D is the diffusivity in the liquid, and δ is the thickness of the boundary layer. For many liquid solutions D lies between 10^{-5} to 10^{-4} cm²/sec, and δ ranges from 10^{-3} cm for vigorous stirring to 10^{-1} cm for quiescent conditions.

Whereas k_0 is the fundamental value which can be derived from the phase diagram of the investigated mixture, the value of k is dependent on several operating variables. The efficiency of the system can be denoted by φ , the ratio between k_0 and k .

In practice, system efficiencies are almost never discussed in experiments described in the literature⁹⁻¹³ possibly because no quantitative data are available

for the quantities given in eqn. (1). It is, therefore, difficult to gage the relative merits or efficiencies of the designated systems.

A known binary system, such as the *n*-hexadecane/*n*-tetradecane system can be used as a test mixture to define the efficiency of these systems. In the 93–100% purity region of hexadecane, both the solidus and liquidus curves are found in the 16–18° range. This is very convenient as these products are liquid at room temperature, while at the same time ice water suffices to yield enough temperature differential to freeze the mixture without difficulties. Sampling of the products during or after a test run can be conveniently carried out without special precautions. Analysis of these mixtures can easily be carried out by conventional gas chromatography.

Construction of phase diagram

Prime data for the construction of this phase diagram were obtained by measuring the melting curves of known mixtures of hexadecane and tetradecane. Figure 1 shows the relationship between the melting curve and the corresponding phase diagram^{14,15}. By measuring the melting curves of samples of different composition, the phase diagram can be constructed.

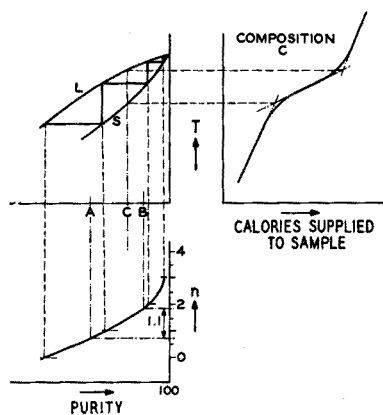


Fig. 1. Phase diagram, melting curve and theoretical plates in the solid-liquid phase diagram.

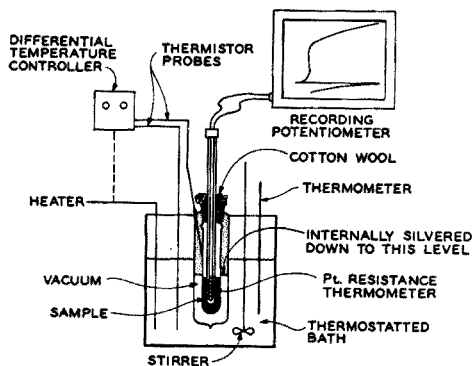


Fig. 2. Measurement of melting curves.

EXPERIMENTAL

Materials

Both *n*-hexadecane and *n*-tetradecane were pure API samples. *n*-Hexadecane was 99.96% pure, and *n*-tetradecane was 99.93% pure. All mixtures were prepared by weighing the components.

Apparatus

A schematic drawing of the apparatus to determine the melting curve is depicted in Fig. 2. The essentials of the apparatus follow closely those of GLASGOW *et al.*⁹ and BARNARD-SMITH AND WHITE¹⁴. Construction of the phase diagram from the curves follows the principle described by MAZEE¹⁵ and GAUMANN¹⁶.

The material to be analyzed is frozen and melted in the double-walled tube,

the rate of heat transfer from the thermostatted bath being controlled by the differential temperature between bath and sample and the vacuum between the walls of the tube. The differential temperature controller maintains the temperature of the bath at a constant difference from the temperature of the sample. A time-proportional temperature-programmed bath is inadequate for this purpose because of the much slower rise in temperature during the melting section of the curve. The platinum resistance thermometer, which senses the temperature of the sample continuously during the experiment has been calibrated by the National Bureau of Standards. It is connected to a Hewlett Packard Null voltmeter Model 413AR, whose output is connected to a Leeds and Northrup Speedomax G recording potentiometer. The setting is regularly checked against the triple point of water. The absolute accuracy of the readings is better than 0.03° and the relative accuracy is *ca.* 0.01° .

The inside diameter of the melting tube is *ca.* 1.5 mm larger than the outside diameter of the bulb of the platinum resistance thermometer. By adjusting the thermometer carefully in the middle of the tube, there is no place where the liquid layer is more than 1 mm thick. In this way the temperature gradient between the wall of the vessel and the thermometer is minimized.

To obtain an insight into the accuracy of the method, use can be made of the approximations derived by SMIT¹⁷. For the difference between the temperature of the outer layer of the liquid, T_0 , and the temperature of the layer adjacent to the thermometer, T_1 , the following equation is approximately valid for that part of the diagram where only one phase is present in the melting tube:

$$\lambda(T_0 - T_1)/h = \frac{1}{2}K(r_0 - r_1)r_0 \quad (2)$$

where λ = thermal conductivity (cal/cm² sec, °/cm); h = specific heat per unit volume (cal/cm³, °); K = rate of heating (°/sec); and r = radius.

For measurements, the temperature of the bath is adjusted to give a heating rate of the sample of *ca.* $0.01^\circ/\text{sec}$. The average value of λ/h for organic substances is $7.5 \cdot 10^{-4}$ cm²/sec. The values of r_0 and r_1 are 0.43 cm and 0.35 cm, respectively, r_1 being at the same time the outer diameter of the platinum resistance thermometer.

Substituting these values in eqn. (2) we obtain:

$$\Delta = T_0 - T_1 \sim 0.2^\circ \quad (3)$$

This temperature difference remains constant until the sample shows a phase transition. The heating curve of the solid part of the melting curve will, therefore, be offset from the real value by 0.2° . The temperature of the intersection is, however, only changed very little by this difference because of the almost horizontal form of the melting curve proper.

The flow of heat to the thermometer decreases at the onset of melting. Melting starts at r_0 ; at that time, the temperature difference between the melting zone and the thermometer is *ca.* 0.2° . This error gradually decreases with time and approaches zero when the curve is continued. To compute the time when the error has decreased to a value less than a given magnitude is a very complicated problem.

By making a few assumptions, WILLIAMSON AND ADAMS¹⁸ derived the following mathematical equation:

$$\frac{T_s - T}{\Delta} = 2 \sum_{m=1}^{m=\infty} \frac{1}{R_m J(R_m)} \exp(\lambda t R_m^2 / r_1^2 h) \quad (4)$$

where T is the temperature of the thermometer, T_s is the melting temperature, and t is the time. The values of R_m are the roots of the Bessel function $J(x) = 0$ where

$$J(x) = 1 - \frac{x^2}{2^2} + \frac{x^4}{2^2 4^2} - \frac{x^6}{2^2 4^2 6^2} + \dots \quad (5)$$

For a number of cases the solution of eqn. (4) is given in tables relating $(T_s - T)\Delta$ to $\lambda t/r_1^2 h$.

For the present purpose, it can be specified that the curve becomes reliable if the temperature differential $T - T_s$ becomes 0.02° or less. Hence:

$$(T - T_s)/\Delta = 0.02/0.2 = 0.1 \quad (6)$$

and from the derived tables¹⁷ the corresponding value of $\lambda t/r_1^2 h$ is *ca.* 0.8. For $\lambda/h = 7.5 \cdot 10^{-4}$ cm²/sec and $r_1 = 0.35$ cm, the corresponding value of t is *ca.* 125 sec. The average time needed for the melting curve proper is about 30 min; thus the curve becomes reliable after *ca.* 7% of the product has melted. To obtain the correct position of the intersections, the first and last 7% of the melting curves are not taken into consideration; extrapolations are carried out based on the straight middle section of the curve. There is a small ambiguity in the exact position of the intersections between the melting curve proper and the heating curves of the solid and liquid phase. The absolute accuracy of each measurement is 0.05° while the relative accuracy is 0.03° .

Results

The results of these measurements are shown in Fig. 3. The value of k_0 is obtained by noting the intersections of a line of constant temperature with the

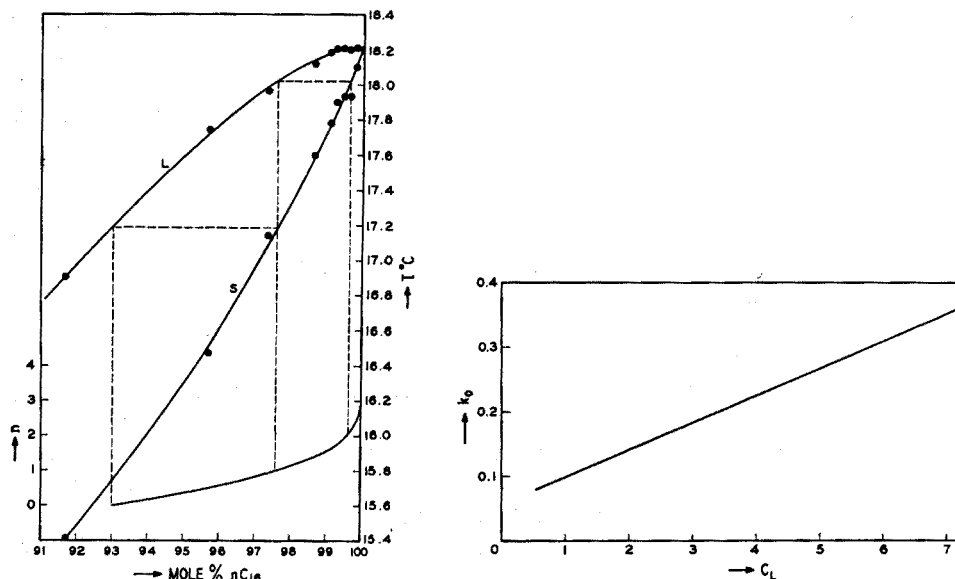


Fig. 3. Phase diagram of *n*-hexadecane-*n*-tetradecane.

Fig. 4. Dependence of the partition coefficient on the impurity concentration.

liquidus and the solidus curves. The ratio of the corresponding tetradecane levels at these points is k_0 , the partition coefficient. Figure 4 shows the dependence of k_0 on the impurity concentration in the liquid. The partition coefficient is not a constant. In the 0.5–7% tetradecane region the value of k_0 proves to be linearly dependent on the C_{14} concentration in the liquid phase.

A regression analysis of these data points yields

$$k_0 = 0.04225 C_L + 0.057 \quad (7)$$

where C_L is the concentration of *n*-tetradecane in mole percent.

EFFICIENCY MEASUREMENTS

Normal freezing

The efficiency, φ , of this system may be expressed as the ratio between the maximum attainable and the attained separation, which is also k_0/k . With the hexadecane–tetradecane system, the value of k_0 is, as the measurements show, dependent on the impurity concentration.

The value of k is obtained from practical measurements. In normal freezing, this measure of the separation efficiency is obtained from the impurity distribution in the ingot after the run, which is described by the equation⁴

$$C_s = C_0 k (1-g)^{k-1} \quad (8)$$

where C_s is the impurity concentration in the most recently deposited solid, C_0 is the initial impurity concentration, and g is the fraction of the liquid solidified.

Equation (8) can also be written as:

$$\log (C_s/C_0) = \log k + (k-1) \log (1-g) \quad (9)$$

By plotting $\log (C_s/C_0)$ against $\log (1-g)$ the value of k can be computed either from the slope or from the intercept. SLOAN¹⁹ determined the effective segregation coefficient of tetracene, anthraquinone, and other impurities in anthracene at different crystallization rates. He noted that different values of k were obtained depending on whether the slope or the intercept of the graphs was taken. This is obviously due to the value of k_0 being dependent on the concentration of the impurities. Equation (8) has been derived assuming k to be constant. As k_0 is dependent on the concentration and assuming the efficiency, $\varphi = k_0/k$ to be more or less a constant, k will, therefore, also be dependent on the impurity concentration. Equation (8) will, therefore, have to be rewritten to take this change into account. In the present case, for the 93–99.5% purity region, the partition coefficient of the impurity between the solid and liquid phases can be described by:

$$k_0 = 0.04225 C_L + 0.057 \quad (7)$$

where C_L is the impurity concentration in the liquid phase. For the general form:

$$k = aC_L + b \quad (10)$$

where a and b are constants, we can derive:

$$C_s = kC_L = (aC_L + b)C_L = aC_L^2 + bC_L \quad (11)$$

Consider a normal freezing tube of unit cross section where a fraction g of the material is frozen, then a total material balance shows:

$$(1-g)C_L = C_0 - \int_0^g C_s dg \quad (12)$$

The relation between C_s and C_L is given by eqn. (11). Substituting this equation in eqn. (12) and differentiating to g yields:

$$\frac{dC_L}{dg} = \frac{-aC_L^2 - bC_L + C_L}{1-g} \quad (13)$$

The solution for this differential equation is:

$$\ln C_L - \ln |(1-b)/a - C_L| = (b-1) \ln(1-g) + \ln A \quad (14)$$

The constant $\ln A$ can be computed from the following boundary condition:

$$\text{for } g = 0, \rightarrow C_L = C_0$$

and this leads to

$$C_L = \frac{1-b}{a + \{(1-b)/C_0 - a\}(1-g)^{(1-b)}} \quad (15)$$

The impurity distribution in the ingots can now be obtained by combining eqns. (7), (11), and (15). Graphs describing this distribution for the ideal case, *i.e.*, for $k = k_0$, are given in Fig. 5 for different values of C_0 .

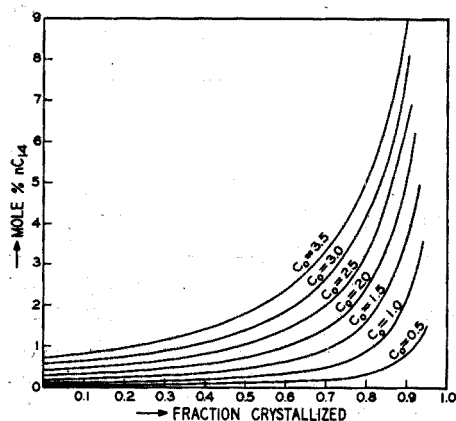


Fig. 5. Ideal impurity distribution after a normal freezing run.

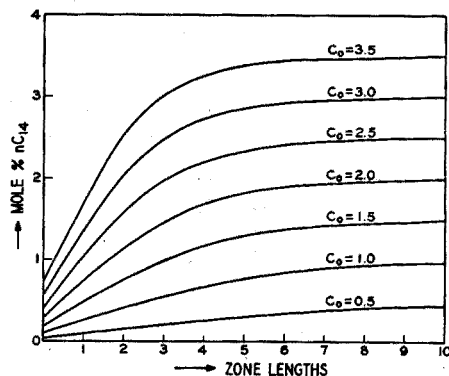


Fig. 6. Ideal impurity distribution after one zone pass.

Results of a test run can now be superimposed on this chart, and the efficiency at any point can be evaluated from the observed impurity concentration and the impurity concentration on the theoretical curve.

A numerical value of the efficiency, φ , can be obtained from the composition of the material at $g = 0$. Practical considerations, however, necessitate the formation of the first crystals under less ideal conditions than during the subsequent part of the run. The value of C_s for $g = 0$ can be obtained by extrapolation from that part of the observed curve which is reliable. The efficiency, φ , is the ratio of the theoretical and the extrapolated impurity concentrations.

Zone melting

The efficiency criterion can be obtained in this system by running one or several passes through the ingot and comparing the obtained impurity distribution with the theoretical one for $k = k_0$.

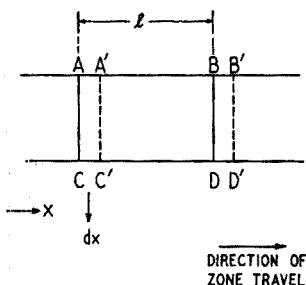
In almost all the studies for organic compounds described in the literature^{8,10,11,20,21}, test systems have been used where the k_0 of the impurity is essentially zero. In a wholly effective system, one zone pass should, therefore, remove all the impurities. The amount of impurity left after one pass, or the number of passes necessary to decrease the impurity level below a certain level, is taken as the criterion of the efficiency of the equipment.

In the choice of substrate, there seems to be a strong preference for naphthalene, but the added impurity varies from one investigator to the other. HERINGTON, HANDLEY AND COOK¹⁰ used 0.03% induline; JONCICH AND BAILEY¹¹ chose 0.1% methyl violet; and RONALD²¹ added 0.1% of 2,4-dinitrophenylhydrazine to test the efficiency of their relative apparatus. In each case, the disappearance of the color, which can be followed visually or spectrophotometrically, is taken as an indication of the efficiency of the process. With anthracene as the added impurity¹⁰, fluorescence can be used to follow the efficiency of a zone refiner. SCHILDKNECHT AND HOPF¹² used 3,4-dimethylphenol as the impurity on a stilbene substrate. Analyses were carried out by cutting the ingot, after subjection to zone melting, into several fractions and determining the melting point of each fraction.

Although the obtained separations appear to be excellent, it is difficult to gage the relative efficiencies of the apparatus from the presented data. Theoretical impurity distributions based on constant, finite values of k have been reported⁴. These curves have been very helpful in elucidating the nature of this separation process. For our case, however, these curves have only qualitative significance because of the dependence of k on the impurity concentration. When k is constant, the impurity distribution after one zone pass is described by:

$$C/C_0 = 1 - (1 - k) \exp(-kx/l) \quad (16)$$

We will now examine the impurity distribution after one zone pass for the case where k follows the general form of eqn. (10).



Assume the bar to have a uniform unit cross section, with C_0 the initial impurity level and l the length of the molten zone. Then melting of the volume dx , $BB'D'D$, adds $C_0 dx$ impurities to the molten volume. At the same time, the volume $AA'C'C$ freezes and decreases the impurity amount in the liquid by $kC_L dx$, where C_L is the impurity concentration in the liquid.

The material balance for this section now becomes:

$$C_L l + C_0 dx = C_s dx + (C_L + dC_L) l \quad (17)$$

where C_s is the impurity concentration in the solid at the solid-liquid boundary, and dC_L is the increase in the impurity concentration in the liquid zone.

Combination with eqn. (10) yields the general equation:

$$-\frac{1}{l} dx = \frac{dC_L}{aC_L^2 + bC_L - C_0} \quad (18)$$

To compute the impurity distribution after one zone pass, eqn. (18) is combined with eqn. (11). For the ideal case (ideal mixing; $C_s = k_0 C_L$) in the *n*-hexadecane/*n*-tetradecane system, these impurity distributions have been plotted for different values of C_0 (Fig. 6). As usual, these curves do not hold for the last zone length because of the phenomenon of normal freezing. To obtain a measure of the efficiency of the zone-melting system under study, the obtained impurity distribution after one pass can be plotted on this diagram and compared with the theoretical distribution.

A numerical value of the efficiency can again be obtained by extrapolation of $x \rightarrow 0$. The efficiency criterion is, therefore, analogous to that obtained for normal freezing.

Column crystallization

In column crystallization, it is very difficult to compute the theoretical separation from the fundamental parameters. In this case, the efficiency of a column can be described in the same way as one would define the efficiency of a distillation or a gas chromatograph column, *i.e.*, by the number of theoretical plates.

For constant k , ANIKIN²² has already derived a mathematical approach:

$$n - 1 = \frac{\log(N_1/N_2)_b / (N_1/N_2)_o}{\log k} \quad (19)$$

where N_1 and N_2 are the concentrations of the impurity and of the main substance, respectively, and n is the number of theoretical plates of the system. The subscripts *b* and *o* refer to the bottom and the overhead products. In the usual setup where a temperature gradient is present in the column with the temperature increasing from top to bottom, and k is less than 1, the purified product comes out as the bottom product and the impurities are concentrated in the top. By means of this equation, the number of theoretical plates can be computed from the observed impurity concentration ratio and from the partition coefficient.

In this case, there is the drawback that the equation was derived on the assumption of a constant k value. This is not always the case, and the following practical approach is suggested. In Fig. 1, L and S are the liquidus and solidus curves of the binary system. The starting composition of the test mixture is C. If, after the run is carried out, the purified product has the composition B and the impure concentrate has the composition A, then the efficiency of the system, as denoted by the number of theoretical plates, can be obtained from this diagram by a McCabe-Thiele type approach. For practical measurements, this number can be easily obtained by the use of the auxiliary diagram below the phase diagram. In this particular example, the system would have a separation efficiency of approximately 1.1 theoretical

plates. This measure gives an evaluation of *effectiveness* of the system in terms of the number of theoretical plates.

SUMMARY

The *n*-hexadecane/*n*-tetradecane solid-liquid phase diagram was determined for low concentrations of tetradecane. It was shown that in the 0.5–7% tetradecane region, the partition coefficient for tetradecane in hexadecane is linearly dependent on the concentration. The results can be applied to the evaluation of separating efficiencies of apparatus for normal freezing, zone melting, and column crystallization.

RÉSUMÉ

Le diagramme *n*-hexadécane-*n*-tétradécane, phase solide-liquide est effectué pour de faibles concentrations de tétradécane. On observe que pour 0.5–7% de tétradécane, le coefficient de partage pour le tétradécane dans l'hexadécane est linéairement dépendant de la concentration. Les résultats permettent d'évaluer les rendements de séparation d'appareils pour congélation normale, zone fondue et cristallisation en colonne.

ZUSAMMENFASSUNG

Das Fest-flüssig-Phasendiagramm von *n*-Hexadekan-*n*-Tetradekan für kleine Konzentrationen von Tetradekan wurde bestimmt. Es wurde gezeigt, dass im Bereich von 0.5–7% Tetradekan der Verteilungskoeffizient des Tetradekans im Hexadekan linear von der Konzentration abhängig ist. Die Ergebnisse können zur Abschätzung der Trenneffekte von Apparaturen für eine normale Erstarrung, zum Zonenschmelzen und zur Kolonnenkristallisation verwendet werden.

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SHORT COMMUNICATIONS

A simple spectrophotometric method for the determination of copper based on the formation of molybdenum blue

Many organic reagents which form coloured chelates with copper have been used for its spectrophotometric determination. Although some of these reagents are highly sensitive, few are highly selective, even under the optimum conditions¹. In many cases, careful pH adjustment is needed¹⁻³. Some reagents and their copper chelates possess excellent stability⁴, but in other cases the reagent and/or the coloured copper chelate are affected by light, pH changes, etc. The best colour reagents for copper tend to be difficult to prepare and expensive.

In the present paper, a very simple spectrophotometric method of adequate precision is described; the reagents are very readily available. The method is based on the formation of molybdenum blue when potassium cyanide and phosphomolybdic acid are added to a copper(II) solution in the presence of dilute hydrochloric acid⁵; reduction of molybdenum(VI) is presumably brought about by the cyanocuprate(I) complex.

Calibration curve

Pipette aliquots (20–300 μg) of copper sulphate solution (a 50-p.p.m. solution prepared by diluting a standardised 1000-p.p.m. solution) into 10-ml standard flasks, and add 1.0 ml each of 1 *M* hydrochloric acid, aqueous 1% potassium cyanide and aqueous 1% phosphomolybdic acid solution. Dilute to 10 ml with twice-distilled water, and after 2 min, measure the absorbance in a 1-cm cell at 725 nm (or by using the red filter No. 70 of a Hilger Biochem absorptiometer).

Effect of experimental variables

Effect of pH. Measurements were made in the pH range 3–9 by adjusting the relative amounts of potassium cyanide and hydrochloric acid. Maximum colour intensity was obtained at pH 7 ± 0.5 .

Effect of temperature. The optimum temperature for maximum colour intensity was at 25°; very slight decreases in colour took place below and above this temperature especially for low copper concentrations (2–3 p.p.m.).

Colour stability. The colour was stable for 24 h. Direct sunlight had no effect on colour intensity.

Precision of the method. The experimental error, within the concentration range used (5–30 p.p.m.), did not exceed 1.5%.

General procedure

Transfer an aliquot of the test solution containing from 50–300 μg of copper, and free from iron or nickel, to a micro-beaker. Add 2 ml of concentrated nitric acid and evaporate to dryness. Take up the residue with 2 ml of water and add 1 ml of 1 *M* hydrochloric acid. If a precipitate is formed, centrifuge and transfer the supernatant liquid to a standard 10-ml flask. Develop the colour as described for the calibration curve.

Effect of foreign ions

Hundred-fold amounts of mercury(II), cadmium, bismuth, aluminium, and zinc did not interfere. Iron(II) increased the colour intensity, but iron(III) decreased it, the simultaneous occurrence of both iron(II) and iron(III) is objectionable because of the formation of the blue iron(III) hexacyanoferrate(II). Both nickel(II) and tin(II) caused an increase in colour intensity; tin(IV) had a much smaller effect. None of the common anions—Cl⁻, SO₄²⁻, PO₄³⁻, SiO₃²⁻, NO₃⁻—interfered; reducing ions should be absent. Lead, silver, and mercury(I) precipitated as chlorides on addition of the acid, and were removed before the colour was developed.

TABLE I
DETERMINATION OF COPPER IN DIFFERENT SOLUTIONS

<i>Solution</i>	<i>Amount of copper found (μg)</i>	<i>Error (%)</i>
100 μg Cu	100	0
30 μg Cu + 500 μg Zn ²⁺	30	0
100 μg Cu + 50 μg Sn ²⁺	104	+4
100 μg Cu + 50 μg Pb ²⁺ + 50 μg Ag ⁺	98	-2
100 μg Cu + 50 μg Fe ²⁺	98	-2
100 μg Cu + 50 μg Fe ²⁺ + 50 μg Ni ²⁺	101	+1

The general procedure was used to determine copper both in pure solutions and in solutions containing copper and foreign ions (Table I). The results show that tin caused a positive error, even after it had been oxidised to tin(IV). When lead and silver were present, the negative error of 2% was probably due to the occlusion of some copper ions in lead and silver chloride. Iron(II) after oxidation to iron(III), caused slightly low results because of its oxidising action which decreases colour intensity; an equal amount of nickel compensated the effect of iron.

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Influence of acid concentration on the atomic fluorescence of cadmium

Recently, in analysis of cadmium by atomic fluorescence flame spectrometry, it was found that the measured signal obtained appeared to depend on the acid content of the stock solutions. This was verified when samples of Johnson-Matthey Pure cadmium gave the same result. To ascertain the magnitude of the acid effect, cadmium samples were dissolved in a small volume of concentrated hydrochloric acid and the excess of acid was distilled off. Solutions were then prepared to give a known volume percent of acid concentration for various cadmium concentrations.

All 1 and 10 p.p.m. cadmium solutions having concentrations (20, 40, 60, 80 volume %) of hydrochloric acid resulted in lower signals than for cadmium solutions with no acid. The fluorescence signal decreased as the acid concentration increased, which may be due to formation of cadmium chloride molecules in the flame gas. At 100 and 500 p.p.m., the signals for cadmium solutions containing acid were greater than for the acid-free solutions. A plot of percent change of the acid solution values from the acid-free values *versus* acid concentrations is given in Fig. 1. Experimental conditions used to obtain the data in Fig. 1 were identical to those used by MANSFIELD, WINEFORDNER AND VEILLON¹. Cadmium solutions containing 20 volume percent of nitric acid gave a working curve which was slightly but nearly uniformly lower than for the acid-free solutions. This indicated a small but uniform nitric acid effect on the fluorescence signal from cadmium. Because of interference from increased solution viscosity, greater nitric acid concentrations gave a large and somewhat drifting blank and could not, therefore, be reliably measured. Blanks were run for all other acid concentrations and all were equal in magnitude to the water blank. Because of the effects of hydrochloric and nitric acids on the signal, it is recommended that all solutions measured by atomic fluorescence flame spectrometry should be carefully prepared with no excess acid or at least prepared to have the same concentration of acid.

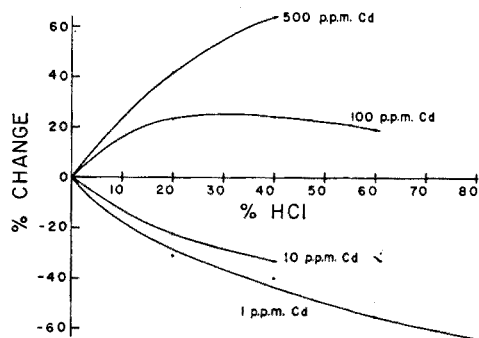


Fig. 1. Influence of HCl concentration on the measured fluorescence signal of Cd 2288 Å line.

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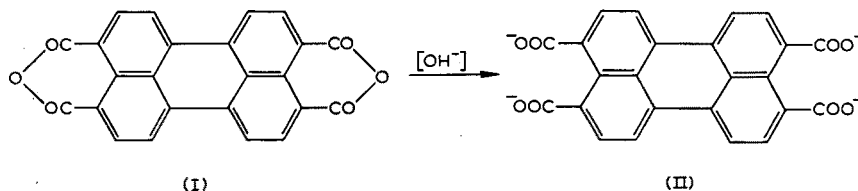
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Determination of small amounts of perylenetetracarboxylic 3,4,9,10-dianhydride in pigments by spectrofluorimetry

Perylenetetracarboxylic 3,4,9,10-dianhydride (PTCD) is used in the preparation of a number of technically important organic pigments¹. Normally the amount of unreacted PTCD retained in the pigment is quite small (<0.1% by weight) but because of technological problems associated with the use of these pigments a method was required for determining their PTCD content. There appears to be no satisfactory method in the literature for determining PTCD directly at these low impurity levels. Attempts to use infrared and mass spectrometry proved unsuccessful. However, by converting the dianhydride (I) by alkaline hydrolysis into its highly fluorescent anionic form (II)²



it was found that the PTCD can readily be extracted from the water-insoluble pigment and the concentration of the anion (II) measured by spectrofluorimetry. By this method quite low concentrations (p.p.m.) of PTCD can be determined, although the

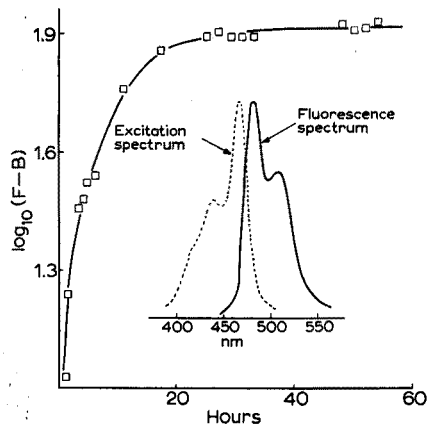


Fig. 1. Development of intensity of anion (II) fluorescence with time. F = relative intensity of solution at 480 nm; B = relative intensity of scattered light from the solvent at 480 nm. Inset shows uncorrected fluorescence and excitation spectrum of anion (II).

accuracy of the method depends on the stability of the pigment itself to alkaline hydrolysis. With suitable modification of the extraction process described here, this method should be applicable to a wide range of PTCD-based pigments.

Method and materials

An Aminco-Bowman Spectrophotofluorimeter with 1-cm cells was used.

Figure 1 (inset) shows the uncorrected fluorescence emission and corresponding excitation spectrum of the anion (II). Hydrolysis of the dianhydride into its fully ionised form proved to be relatively slow at room temperature; it can be seen from Fig. 1 that hydrolysis was not complete until about 24 h after the initial solvation of the dianhydride. Provided that the fully hydrolysed solution was stored in the dark, the concentration of the anion (II) remained constant for about a week after complete hydrolysis was attained.

The working curve was constructed as recommended in the Aminco manual³ using slit arrangement No. 5. The plot of $\log_{10} (F-B)$ against $\log_{10} C$ was linear over the concentration range $1 \cdot 10^{-6}$ to $1 \cdot 10^{-8}$ g of PTCD per ml. During pigment sample determinations, when the concentration of the anion (II) in the extract was reduced 10 times by dilution, the fluorescence intensity was also reduced by this amount. Quenching effects due to the possible presence of further impurities extracted from the pigments were therefore negligible with these solutions.

The PTCD used for preparing the working curve was purified in the following way: 20 g was dissolved in 80 ml of 100% sulphuric acid (monohydrate) over a period of 30 min. Water (12 ml) was added below the surface and this caused the PTCD to separate out as a crystalline precipitate. The precipitate was filtered off, added to water (40 ml), stirred for 1 hour at room temperature, filtered, washed acid-free and dried. The whole process was then repeated. The solvent used for the working curve and for the pigment extraction was de-ionised water containing 10% (by weight) "AnalaR" sodium carbonate.

Results and discussion

Results for 2 different pigments are given in Table I; 0.1 g of the pigment sample, after thorough drying, was refluxed with 200 ml of sodium carbonate solution

TABLE I

AMOUNT OF ANION (II) EXTRACTED FROM PIGMENT SAMPLES
(Results are expressed in p.p.m. (by weight) of PTCD in the pigment)

Pigment ^a	Extraction no.						Estimated PTCD content
	1	2	3	4	5	6	
"A"	191	23	10	3	2	5	210-215
"B"	67	21	42	13	20	31	40-70

^a These pigments are typical members of the range indicated in Ref. 1.

for 5 h and allowed to cool overnight. The insoluble pigment was filtered off and the concentration of the anion (II) in the solvent measured. The result is given in the Table under the column heading *Extraction No. 1*. The residue of partially extracted pigment was then added to a further 200 ml of sodium carbonate solution and a similar extraction carried out. The pigment sample was extracted in this way a total of 6 times and the concentration of anion (II) measured each time.

To check the effect of 5 h refluxing with sodium carbonate on the stability of the anion (II), solutions containing known amounts of PTCD were refluxed for this period. Examination of these solutions after cooling showed an average loss of about 3% anion which is a negligible amount for the method described here.

It is seen from the Table that for pigment "A" a very small and nearly constant amount of PTCD is extracted after the third extraction. Presumably this is mainly due to hydrolysis of the pigment itself. This pigment is therefore reasonably stable to alkaline hydrolysis and its PTCD content is thus determined accurately. In the case of pigment "B" it is seen that, after the first extraction, the amount of PTCD extracted is larger than with pigment "A" and more variable. It is evident that in this case the pigment is less stable to alkaline hydrolysis and only an approximate estimate of its PTCD content is possible.

We thank Dr. P. W. BARKER for preparing the sample of purified PTCD.

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Anal. Chim. Acta, 39 (1967) 395-397

The stability of some lanthanide complexes with 1,3,4,5-tetrahydroxycyclohexanecarboxylate

The influence of alkyl substituents on the α -carbon atom of the glycolate anion upon the stability of the lanthanide complexes with these anions has been examined by many authors¹⁻⁷. SCHURMANS *et al.*⁸ determined the stability of the lanthanide- α -hydroxycyclohexanecarboxylate complexes, which were much lower than other dialkyl substituted glycolates⁵⁻⁷. In order to investigate the influence of substituents in the cyclohexane ring, it was decided to start with the determination of the stepwise stability constants for lanthanide-1,3,4,5-tetrahydroxycyclohexanecarboxylates by potentiometric titrations using quinhydrone electrodes.

Apparatus and reagents

A Keithly 660 guarded differential voltmeter was used. Potentials were measured to 0.01 mV.

Organic acid buffer solution. A 1,3,4,5-tetrahydroxycyclohexanecarboxylic acid (Fluka $\geq 99\%$) solution was partially neutralized with sodium hydroxide. The concentrations of both the acid and its sodium salt were checked by potentiometric titration. The buffer ratio was 0.9269 with $C_L^\circ = 1.0035$ and $C_{HL}^\circ = 0.9301$. All other reagents as well as apparatus were as described previously^{5,8}.

Procedure

The potentiometric titrations were carried out with the CHOPPIN arrangement using 3 half-cell compartments in series. The calculation and the experimental proce-

Anal. Chim. Acta, 39 (1967) 397-400

TABLE I

TITRATION OF Yb^{3+} WITH 1,3,4,5-TETRAHYDROXYCYCLOHEXANECARBOXYLATE($[\text{H}]_{\text{A}} = 5.91 \text{ mM}$; $C_{\text{L}}^{\circ} = 1003.5 \text{ mM}$; $\delta = 0.9269$; $C_{\text{M}}^{\circ} = 20.0 \text{ mM}$; $C_{\text{H}}^{\circ} = 6.33 \text{ mM}$; $V = 20.0 \text{ ml}$ and $k = 1.70$)

Volume (ml)	$E_{\text{AB}}(mV)$	$\Delta E_{\text{AB}}(mV)$	$E_{\text{AC}}(mV)$	$K_{\text{A}\cdot 10^4}$	(L) (mM)	\bar{n}
0.10	-0.17	0.02	67.50	5.56	0.458	0.213
0.20	1.43	0.05	67.18	5.15	0.902	0.424
0.30	2.92	0.07	66.92	5.05	1.398	0.634
0.40	4.62	0.09	66.90	4.98	1.956	0.840
0.50	6.45	0.10	66.88	4.94	2.594	1.042
0.60	8.47	0.12	66.83	4.92	3.341	1.236
0.70	10.74	0.13	66.81	4.90	4.229	1.423
0.80	12.99	0.14	66.75	4.90	5.247	1.604
0.90	15.50	0.15	66.76	4.89	6.461	1.773
1.00	18.10	0.16	66.71	4.88	7.906	1.931
1.20	23.18	0.17	66.74	4.86	11.386	2.218
1.40	27.94	0.18	66.74	4.85	15.758	2.459
1.60	32.10	0.18	66.70	4.85	20.902	2.660
1.80	35.69	0.18	66.68	4.85	26.681	2.826
2.00	38.73	0.19	66.68	4.85	32.913	2.963
2.40	43.43	0.18	66.69	4.84	46.177	3.180
2.80	46.84	0.17	66.67	4.83	60.088	3.337
3.20	49.40	0.17	66.62	4.84	74.307	3.452
3.60	51.40	0.16	66.64	4.83	88.375	3.548
4.00	52.98	0.15	66.65	4.83	102.273	3.627
4.50	54.53	0.15	66.65	4.83	119.271	3.711
5.00	55.73	0.14	66.62	4.83	135.824	3.781
6.00	57.54	0.13	66.62	4.83	167.362	3.898

ture were as described previously^{5,6} as well as the formula for calculating potential corrections due to changes in ionic strength⁷. For 1,3,4,5-tetrahydroxycyclohexanecarboxylate, $k=1.70$ was found, k being the factor relating potential corrections to the change in ionic strength during titrations. All titrations were performed at constant ionic strength ($i=1$) and temperature ($t=25 \pm 0.1^\circ$). To evaluate the stepwise stability constants from the \bar{n} and (L) data with an IBM 1620 computer, a program based upon FRONAEUS' graphical integration method was used.

TABLE II

STABILITY CONSTANTS OF THE LANTHANIDE-1,3,4,5-TETRAHYDROXYCYCLOHEXANECARBOXYLATE COMPLEXES

	Bjerrum					Computer				
	half \bar{n} values									
	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log \beta_4$	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log \beta_4$
La	2.30	1.64	1.15	0.61	5.70	2.08	1.62	1.12	0.80	5.62
Pr	2.50	1.83	1.27	0.67	6.27	2.20	1.96	1.16	0.86	6.18
Sm	2.66	1.99	1.43	0.72	6.80	2.38	2.06	1.44	0.85	6.73
Eu	2.67	2.02	1.46	0.75	6.90	2.375	2.105	1.48	0.87	6.83
Gd	2.64	1.99	1.44	0.73	6.80	2.35	2.06	1.46	0.85	6.72
Tb	2.68	2.05	1.50	0.84	7.07	2.385	2.145	1.48	0.98	6.99
Dy	2.76	2.09	1.53	0.90	7.28	2.47	2.19	1.48	1.06	7.20
Ho	2.79	2.14	1.58	0.94	7.45	2.485	2.26	1.515	1.11	7.37
Er	2.85	2.20	1.63	0.96	7.64	2.56	2.30	1.57	1.14	7.57
Yb	2.97	2.33	1.77	1.08	8.15	2.655	2.465	1.72	1.28	8.10

Results and discussion

Table I gives an example of the experimental data and the calculated values of ΔE_{AB} , K_A , \bar{n} and (L) for the ytterbium-1,3,4,5-tetrahydroxycyclohexanecarboxylate complex system as a function of the added buffer solution.

The formation curves of all the investigated complexes are represented in Fig. 1. The \bar{n} values approaching 4 indicate the existence of ML_4^- complexes. In analogy with previous experiments no polynuclear complexes were formed. From the obtained data the stepwise stability constants were derived once approximately by BJERRUM's half \bar{n} method and once by the computer program. Table II summarizes the results obtained by the two methods. For the Yb^{3+} complex the computer method was

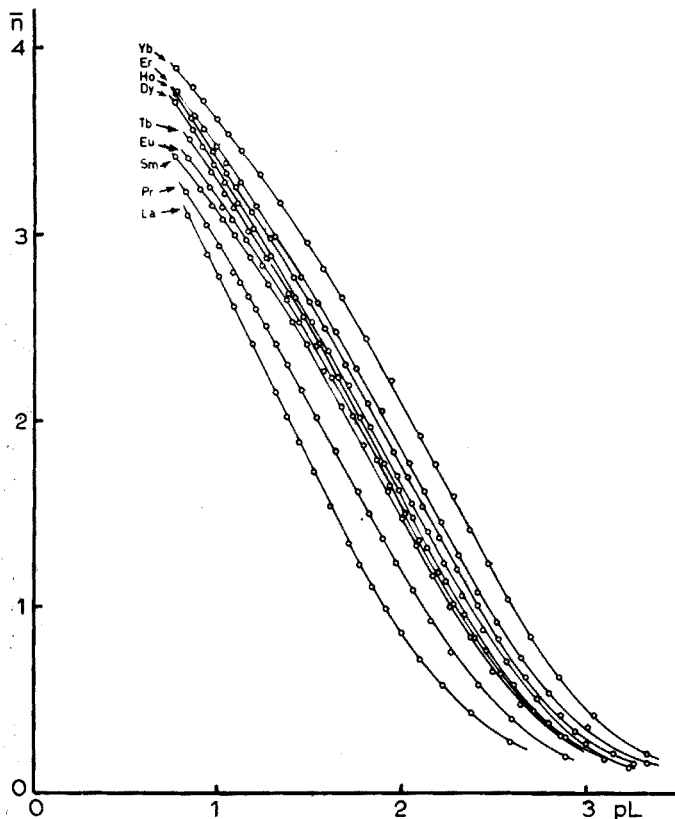


Fig. 1. The formation curves of the lanthanide-1,3,4,5-tetrahydroxycyclohexanecarboxylate complexes.

checked by FRONAEUS' planimetric integration, yielding $\log K_1=2.76$, $\log K_2=2.30$, $\log K_3=1.85$, $\log K_4=1.20$ and $\log \beta_4=8.11$.

In Fig. 2 the $\log \beta_4$ values are plotted vs. the atomic number for the 1,3,4,5-tetrahydroxycyclohexanecarboxylates and also for the α -hydroxyisobutyrate⁹. Although both curves show a similar behaviour (both having the normal Gd break), the tetrahydroxycyclohexanecarboxylate curve is definitely lower (except for La^{3+} and Ce^{3+}) and has a less pronounced slope. For a column separation of lanthanide ions this graph shows the new ligand to be inferior to α -hydroxyisobutyrate.

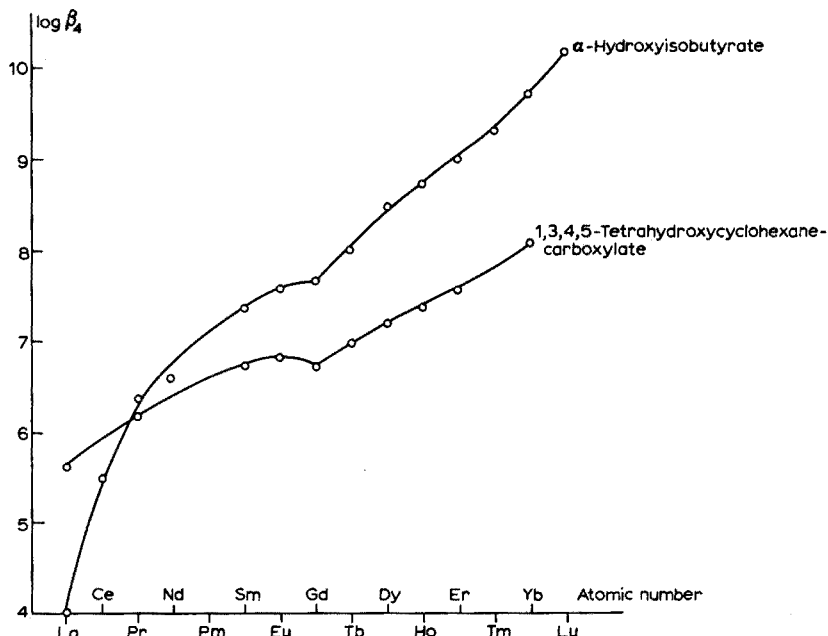


Fig. 2. The $\log \beta_4$ values plotted versus the atomic number of the lanthanide elements.

When the $\log \beta_2$ values of this 1,3,4,5-tetrahydroxycyclohexanecarboxylate are compared with those obtained for α -hydroxycyclohexanecarboxylate⁸, it is obvious that the latter forms less stable complexes. However, the slope in a $\log \beta_2$ -atomic number graph is more pronounced for the α -hydroxy compound, probably because its molecule is less bulky¹⁰.

A further influence of the three additional hydroxy groups is found in the greater solubility of the tetrahydroxycyclohexanecarboxylate complexes, which enabled the determination of all 4 stability constants, whereas for the α -hydroxycyclohexanecarboxylate only $\log \beta_2$ and a few $\log \beta_3$ values could be determined.

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Spectrophotometric end-point detection for determination of magnesium in the presence of calcium and phosphate by titration with CDTA

A recent publication¹ describes the determination of magnesium in the presence of calcium, phosphate, and other metal impurities by titration with CDTA with visual end-point detection. Although the procedure showed sufficient accuracy, additional work has shown a significant improvement in the precision and reproducibility of the procedure in titrations for interfering and total metals for very low concentrations of magnesium with spectrophotometric end-point detection. Spectrophotometric detection utilizes a constant wavelength for each titration, and eliminates variation of color sensitivity associated with the human eye which results in easier and more consistent end-points especially for very low concentrations. Calcium is determined by fluorescence as previously described¹.

Apparatus and reagents

Ultraviolet titration assembly, Fisher Scientific Co. #15-182-600V2; Sargent SE Spectro-Electro titration assembly, E. H. Sargent & Co. #529700; microburet, 10 ml, graduated in 0.01 ml, Ace Glass Co.

All other reagents were as previously described¹.

Calibration of the Model SE Spectro-Electro titrator

All titrations were done in the Spectro-mode of the instrument. Two very critical parameters are the correct filter for the desired wavelength and the lower limit of sensitivity to operate the solenoid valve at the greatest rate of change of the indicator or simply the end-point of the titration. The output signal from the detectors is differentiated to allow a more precise and reproducible end-point. Adjustment of the flow rate proved most critical. A minimum of overshoot with a great enough signal to stop the titration was required. The optimum flow rate with the microburets was found to range from 4.0 to 2.8 ml/min depending on the buret liquid level. Since the burets were not under constant pressure the volume of titration overshoot (blank) varied with the buret liquid level and was determined at various levels throughout the buret calibration. Then the overshoot for each titration for each sample was subtracted from the titration value. This is extremely important for very low concentrations of metals. Standardization was carried out in the same manner.

Procedure

General. Accurately weigh an appropriate sample into a 250-ml pyrex beaker. Add 15–20 ml of 72% perchloric acid and 10–15 ml of water. Digest to strong fumes of perchloric acid, *i.e.*, until the liquid is 5 ml or less. Remove from the heat, partially cool, and dilute to about 50 ml with water, adding the first 10–20 ml cautiously. Heat gently to dissolve all the perchlorates, then filter and wash the residue free of acid with hot water, catching the filtrate and washings in a 250-ml volumetric flask.

Caution. TAKE APPROPRIATE PRECAUTIONS WITH PERCHLORIC ACID.

Total metals. Pipet a 5-ml aliquot into a 250-ml beaker. Add a 4–6 ml excess of 0.05 *M* CDTA and dilute to about 200 ml. Adjust the pH to 10.0 ± 0.03 with ammonium hydroxide and ammonium hydroxide–ammonium chloride buffer. Add 0.5 ml of 0.25% eriochrome black T indicator. With the controls properly set, the wavelength dial at 650 nm, the yellow filter and the Hupp photocell in place, position the beaker in the titration chamber. Titrate the excess of CDTA with 0.05 *M* magnesium sulfate solution by pressing the auto button. At the end-point (indicator change) the differentiated electrical signal actuates the buret solenoid valve and stops the titration and stirrer. Record the ml of 0.05 *M* magnesium sulfate solution used and subtract the overshoot (blank) to obtain the correct titer.

Interfering metals. Pipet a 5-ml aliquot into a 250-ml beaker. Add a 4–6 ml excess of 0.05 *M* CDTA and dilute to about 200 ml. Adjust to pH 5.0 ± 0.1 with 10% sodium hydroxide and sodium acetate buffer (70 g/l sodium acetate adjusted to pH 5.0 with glacial acetic acid). Add 0.5 ml of aqueous 0.4% xylenol orange indicator. With the controls properly set, the wavelength dial at 600 nm and the B2M photocell in place, position the beaker properly and titrate the excess CDTA with 0.05 *M* zinc sulfate solution by pressing the auto button. At the end-point, as before, the titration stops. Record the ml of zinc sulfate solution used and subtract the appropriate overshoot to obtain the correct titer.

Calcium. Titrated as previously described¹.

Calculation

$$\% \text{Mg}^{2+} = \frac{[A - (B + C)] (24.31) (100)}{\text{milligrams sample in aliquot}}$$

where A = net millimoles total metals at pH 10.0; B = net millimoles of calcium; C = net millimoles interfering metals at pH 5.0, and the overshoot is obtained in each case as described in the calibration section above.

Discussion

Conditions for accurate reproducibility described by the manufacturer of the titrimer required marked modification before suitable results were obtained at the low concentrations studied. The delivery rate, and stirring both require delicate adjustment. At the rapid delivery rate described in the literature the overshoot was inconsistent. Often the variation was greater than the titrant required to react with the total metals in solution. With the precise delivery rate adjustment, the overshoot became consistent. However, the electrical signal required to stop the titration was occasionally insufficient and the titration proceeded past the end-point. This was finally corrected by increasing the indicator concentration which effected a pseudo increase in the electrical signal sufficient to stop the buret at a uniform end-point. With all the adjustments properly set, titrations were reproducible to ± 0.005 ml or 0.00025 millimole when 0.05 *M* titrant was used. Since a constant-pressure buret was not used, the titration overshoot had to be determined at the same buret liquid level as the sample end-point. The titration overshoot from the full to empty microburets used varied from 0.24 to 0.11 ml and was consistent at a given level for each buret.

TABLE I

PRECISION TITRATION FOR COMBINED AND INTERFERING METALS IN DIFFERENT SAMPLES USING SPECTROPHOTOMETRIC END-POINT DETECTION

(in millimoles metals)

Sample	No. of replicates	Interfering (pH 5.0)	Rel. dev. (%)	Combined (pH 10.0)	Rel. dev. (%)
1	4	0.02452	±1.07	0.03138	±0.0
2	3	0.02291	0.0	0.02356	±1.10
3	5	0.02189	0.0	0.02586	±1.88
4	4	0.01959	±1.41	0.02280	0.00
5	3	0.01593	±0.46	0.4216	0.00
6	4	0.02188	±2.23	0.02688	0.00
7	7			0.10510	±0.85
8	5	0.4718	±0.07		

Table I shows the precision of titration at pH 5 and pH 10 for both low and high levels of metals in solution. The relative percent deviation ranges from 0 to 2.23% with the practical limit of 0.07% relative at or near the 0.5 millimole level of metals. More important than the relative percent deviation, however, is the absolute magnitude of the difference between replicate titrations. For example, Sample #5 (0.46% rel. dev.) showed a difference of only ± 0.00007 millimoles between replicate titrations. With the burets used, this amounted to less than 0.002 ml. Normally, a difference of 0.004 to 0.005 ml between replicates can be tolerated. Since the buret is graduated in 0.01 ml, these limits are not difficult to obtain. Sample #6 at pH 5 showed the greatest percent relative deviation of 2.23%. This represents a magnitude of only 0.00049 millimoles or about 0.01 ml. Such a difference is ordinarily not acceptable for accurate results, but is shown here to illustrate the great care needed to obtain precise titrations.

Table II describes comparative magnesium results by 3 different methods. It should be noted that the results are generally given to 2 significant figures compared to 5 significant figures for the titrations; however, only 2 significant figures can be justified because of the difference between the very small quantities usually found in the separate titrations. All 3 methods are acceptable, and, in fact, yield essentially the same results. This is not surprising, however, because the difference between the proposed spectrophotometric end-point and visual end-point titration procedures is

TABLE II

COMPARISON OF MAGNESIUM RESULTS BY CLASSICAL, VISUAL END-POINT CHELATION AND PROPOSED SPECTROPHOTOMETRIC END-POINT CHELATION PROCEDURE

Sample	%MgO		
	Classical	Visual	Spectrophotometric
A	0.27	0.28	0.22
B	0.20	0.23	0.24
C	0.38	0.40	0.42
D	0.05	0.02	0.03
E	0.21	0.23	0.21
F	0.53	0.56	0.52

merely a standardization of the end-point by removing the variation of color sensitivity and perception of the human eye from the procedure. The color sensitivity from person to person is not so important at levels of MgO > 0.5%, but becomes increasingly important as the MgO approaches 0.10%. Thus, although we demonstrated the reproducibility and precision of visual titration end-points for MgO from 0.02% and above for high and low calcium and phosphate concentrations, standardization of end-point detection at a constant wavelength spectrophotometrically makes end-point detection much easier and consistent.

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I. D. E. JORDAN AND D. E. MONN, *Anal. Chim. Acta*, 37 (1967) 42.

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Anal. Chim. Acta, 39 (1967) 401-404

Spectrophotometric determination of tin in metals and alloys

From some recent work^{1,2} it appeared that the spectrophotometric MIBK-phenylfluorone method for the determination of tin in steel³ could be greatly simplified by isolating the tin by solvent extraction as the iodide. By using the extraction it is possible to dispense with the sulfide separation, the double carbamate extraction and the use of oxalate and peroxide as complexing agents in the color development with phenylfluorone. Moreover, because of the high specificity of the iodide extraction, the method has proved to be applicable to the analysis of highly alloyed steels and to many of the important nonferrous metals and alloys.

Analysis of steel

Dissolve the sample containing 1-15 μg of tin in 5 ml of hydrochloric acid-nitric acid mixture (4:1), add 2 ml of sulfuric acid and then destroy the nitric acid with a small excess of formic acid³. Boil to a volume of 2.5-3 ml to expel most of the hydrochloric acid. Add about 10 ml of a 42-ml portion of 9 N sulfuric acid¹ and heat to boiling to dissolve all salts. Cool and add the remainder of the 9 N sulfuric acid. Add 5 ml of 5 M sodium iodide solution and then add 7.8% sulfurous acid in small portions until most of the iodine has been reduced. Swirl, allow to stand and add further 0.25-ml portions of sulfurous acid until the reduction is complete.

Transfer the solution to a 75-ml separatory funnel and shake for 1 min with 10 ml of benzene. Drain off and discard the lower layer as completely as possible. (If a clean cut separation of the layers is prevented because of bubbles which collect at the interface, stopper and shake vigorously for a few seconds. In the above and all

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future extractions, wash the stopper free of iron salts under the distilled water tap each time it is removed from the funnel.) Wash down the inside of the mouth of the funnel with 5 ml of a freshly mixed portion of wash solution (10 ml of 9 *N* H₂SO₄ + 1 ml of 5 *M* NaI solution) and shake for 10 sec. Allow the layers to separate, turn the stopcock through 180° 3 or 4 times to wash out iron salts and drain off and discard the lower layer. Repeat the wash once more. Finally wash inside and outside the funnel stem with water. Add about 0.5 ml of nitric acid to the funnel, shake for 10 sec and drain completely to a 100-ml beaker. Close the stopcock, wash down the inside of the funnel with about 4 ml of benzene, shake a few seconds and drain to the beaker.

Place the beaker under an air jet on a low temperature hotplate in a hood and leave until all benzene and iodine has been removed. Add 4 drops of 70% perchloric acid and 4 drops of sulfuric acid and heat on a flame to destroy traces of organic matter. Finally flame carefully to expel all acid. Cool, add 1.0 ml of 1:3 hydrochloric acid, swirl and tilt the beaker to wet all precipitated salts on the wall of the beaker and then determine the tin by the spectrophotometric MIBK-phenylfluorone method³, omitting the addition of ammonium oxalate and hydrogen peroxide in the analysis and in the preparation of the calibration graph.

Discussion

Tests have shown that the iodide extraction provides an elegant separation of tin from large amounts of iron or from 100- μ g quantities of the other 10 metals which interfere in the spectrophotometric phenylfluorone method for tin³. The isolation may not be as complete when larger amounts of these other interfering metals are present. Nevertheless, the separation is good enough for most types of steel. The only common steels that cannot be analyzed are those which contain appreciable amounts of tungsten. Tungstic oxide collects in the benzene layer with the tin; perhaps it would be possible to filter off the oxide before the iodide extraction. Typical data obtained in the analysis of various NBS steels are shown in Table I. It is seen that

TABLE I
ANALYSIS OF NBS SAMPLES OF STEEL

Sample	% Tin	
	Present	Found
11g	0.004	0.004
36a (2Cr-1Mo)	0.011	0.011, 0.012
51a (1C)	0.011	0.011
123b (Cr-Ni-Nb-Ta)	—	0.011
160a (19Cr-14Ni-3Mo)	0.013	0.013
170 (0.2Ti)	0.018	0.018

sample 123b which contains 0.75% of niobium, 0.20% of tantalum and 0.18% of tungsten can be analyzed. In order to prove that the color obtained in the spectrophotometric analysis of this sample was due to tin and not to the 3 metals mentioned above, 0.5 ml of standard tin solution was added to the aqueous extract from the analysis of the sample and the extraction and analysis was repeated. The recovery of the tin was quantitative.

The proposed method can also be used in the analysis of many of the common non-ferrous metals and alloys. The procedure used was as follows. Dissolve the sample in nitric acid or in hydrochloric acid plus, if necessary, a few drops of hydrogen peroxide. Add 13 ml of sulfuric acid and then evaporate to white fumes to expel the volatile acids. If nitric acid has been used, add a little water and take to fumes again. Avoid excessive loss of the sulfuric acid. Cool, add 37 ml of water, heat to boiling to dissolve all salts, cool and add 5 ml of sodium iodide solution. If more than a small amount of iodine is produced, reduce it with sulfurous acid and then proceed to the benzene extraction. In the analysis of aluminum, chromium or their alloys dissolve the sample in hydrochloric acid (or in aqua regia followed by treatment with formic acid) and then take only to incipient fumes of sulfuric acid to avoid precipitation of aluminum or chromium sulfate.

In order to determine which metals can be analyzed by the above method, 0.5-g portions of tin-free metal or the equivalent amount of metal salt plus, in all cases, 0.5 ml of standard tin solution were analyzed. Quantitative recovery of the tin was obtained in the analysis of Ni, Co, Mn, Cd, In, Zn, Al and Mg. For a variety of reasons, the metals Ge, Sb, Se, Te, Pb, Cu, Bi, Ti, U, and Th could not be analyzed. Moreover, difficulty would probably be encountered in the analysis of alloys containing appreciable amounts of one or more of these metals. The extraction of 100- μ g portions of titanium(IV), bismuth and copper is nil in the iodide extraction, but when present in large amounts, appreciable quantities of these metals accompany the tin in the extraction. The copper appears to be collected in the benzene layer as precipitated copper(I) iodide rather than as extracted copper(I) iodide. It is of interest to note, however, that NBS zinc base alloy 94b which contains 1% of copper and 0.005% of tin has been successfully analyzed.

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- 1 E. J. NEWMAN AND P. D. JONES, *Analyst*, 91 (1966) 406.
- 2 K. TANAKA, *Bunseki Kagaku*, 13 (1964) 725.
- 3 C. L. LUKE, *Anal. Chim. Acta*, 37 (1967) 97.

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BOOK REVIEWS

H. H. WILLARD, L. L. MERRITT, JR. AND J. A. DEAN, *Instrumental Methods of Analysis*, 4th Edn., D. Van Nostrand Company, Inc., Princeton, 1965, xviii + 784 pp., price 70 s.

A valuable guide to the popularity and hence the utility of a book is its publishing history; the present volume illustrates this admirably with the third edition, which was published in 1958 and ran to seven reprintings. This new fourth edition follows the pattern of earlier editions but has been suitably revised and brought up to date. Emphasis is still given to optical methods, particularly those useful for structure elucidation, but the wide range of instrumental methods now available to the chemist is covered adequately within the present text. A useful new chapter deals with the instrumentation of process control (on-line analysis) and auto-analyzers.

This is a well-balanced text, essentially for student use but containing much useful information for research and industrial analytical chemists. With the ever-increasing emphasis on rapid instrumental finishes to analytical determinations, students and teachers will find this book a valuable source of useful laboratory exercises, as well as a sound basis for an appreciation of the advantages and limitations of the growing number of physical techniques.

The excellent presentation of this text must ensure its continued success. It can be thoroughly recommended to all students of analytical chemistry as a sound introduction to the intricacies of instrumental chemical analysis.

WILLIAM I. STEPHEN (Birmingham)

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Modern Aspects of Polarography, Edited by T. KIMBARA, Plenum Press, New York, 1966, iii + 245 pp., price \$10.00.

This volume contains 32 collected papers on polarography contributed by internationally known polarographers and dedicated to Professor ISAMU TACHI of Kyoto University, Japan. These papers were originally published in 1963 in *Review of Polarography*, Vol. II, to mark Professor TACHI's retirement in 1962. Accordingly, they are now outdated and their reappearance can be only of sentimental interest to those associated with the preparation of the tribute.

It is difficult to appreciate the reasons for this belated publication of a separate volume. Most of the information is of a specialised nature and is now well-known by interested polarographers. To reproduce published material 3 years on, and in the guise of a volume of general analytical interest smacks of misrepresentation. Such publications do nothing to enhance the reputation of the publisher; the present volume may even do harm to the subject in the eyes of those who do not appreciate it as simply a publisher's venture, however well-intentioned this may have been.

WILLIAM I. STEPHEN (Birmingham)

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W. W. WENDLANDT AND H. G. HECHT, *Reflectance Spectroscopy*, Interscience Publishers—J. Wiley and Sons, Inc., New York, 1966, viii + 298 pp., price 90 s.

The absorption spectrophotometry of dissolved molecules is a well known and thoroughly documented area, but little is known by most analytical chemists about the corresponding reflectance technique, and there is a complete lack of literature except for a few scattered research papers which are not always very easy to find. The authors of this book are thoroughly to be congratulated in producing the first monograph on the topic.

The first instrument capable of yielding precise data on reflected spectra appears to have been devised as early as 1920, but no work of real significance was reported until the introduction of the first spectrophotometers during the 1930–40 decade. Although the technique is used commercially for the testing of many products ranging from dyestuffs to building materials the first analytical application appears to have been made in 1955 by LERMOND AND ROGERS. Since then there has been a steadily increasing flow of papers of more obvious analytical application. The appearance of this book is, therefore, very timely.

Light is reflected from solid surfaces by virtue of 2 processes—*reflectivity* or specular reflection, *i.e.* a mirror-like effect, and by *reflectance* or *diffuse reflectance*, a process involving multiple reflections by individual particle facets at the massive surface of the solid. The theory of the two processes is considered in two separate chapters and there is a very finely illustrated chapter on the instrumentation which is necessary for such studies and which is commercially available for use with a range of absorption spectrophotometers. The chapter on applications to analytical chemistry reveals the real dearth of information available on “analytical” as opposed to “test” methods where there is abundance of application. Internal reflection methods (attenuated total reflectance) of infrared wavelengths is discussed in another chapter. Other topics dealt with in the ensuing chapters are high-temperature reflectance and applications to surface chemistry. It is very probable that the kernel of practicality for the analytical chemist lies in this latter chapter, for the difficulties attached to direct examination of untreated surfaces as reviewed in the earlier chapter on analytical applications and as implied in the initial theoretical treatment appear to be rather prohibitive. It is probable that it is in this direction that reflectance spectrophotometry will find its chief analytical application in the future. The last two chapters are concerned with the measurement of “colour”, its three-dimensional nature, etc. and a theoretical treatment of the behaviour of the integrating sphere, which is an essential feature of most instruments.

This book clearly reveals the lack of true “analytical” as opposed to “test” information that may currently be elucidated by reflectance measurements, but for the first time it presents the case and furnishes a guide for further development where none was formerly available. The authors are to be congratulated on the clarity and excellence of their presentation and for the service they have provided in bringing this interesting and potentially far-reaching technique to the attention of all analytical chemists.

T. S. WEST (London)

F. FEIGL, *Spot Tests in Organic Analysis*, 7th Edn. (completely revised and enlarged), Elsevier Publishing Company, Amsterdam, 1966, xxiii + 772 pp., price Dfl. 85.—.

The value of this type of book should not be measured in terms of how this special form of analysis compares with instrumental methods of analysis, although this point is illustrated where possible in the text. The reader soon realises that the two are complementary, for a number of the listed organic spot tests form the basis of many of the recognised methods in instrumental analysis, *e.g.*, in solution spectrophotometry and spectrofluorimetry. The value of the book is in the wealth of information on chemical reactions that has been gathered and its applicability to many experimental fields. The development of organic spot tests is shown not to be merely an extension of previously developed inorganic spot tests; the two are quite dissimilar and require different methods of approach and solution. Certain syntheses and modes of formation can be used which have attracted little, if any, attention over a long period of years, *e.g.* production of characteristic gaseous fission products when compounds are subjected to dry pyrolysis. Such observations have developed into completely new fields of study, *e.g.* pyrohydrolysis, pyroammonolysis and pyrohydrogenolysis etc. Other observations such as the use of concentrated sulphuric acid in hydrolytic cleavages can completely change the reader's outlook on general chemical reactivity.

In this edition, the use of spot tests in organic analysis is classified under 6 headings: identification of metallic and non-metallic elements, certain reactive groups, characteristic types of compound, individual organic compounds, isomers and homologues and applications of the tests in solving special analytical problems in the testing of materials. Information is given on more than 900 tests, compared to 600 tests in the former edition, and many of the new tests have been recently developed and not published elsewhere.

It would appear that now there are only rare instances of a total lack of information regarding specificity, selectivity and sensitivity of direct and indirect tests for organic compounds or the groups they contain. Also, it is apparent that future developments in this field need not be confined to empirical and time-consuming experimentation since many guide lines are now available. As we have come to expect, Professor FEIGL has once more provided an outstanding service to the chemical community.

T. S. WEST (London)

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F. SZABADVARY, *History of Analytical Chemistry*, International Series of Monographs on Analytical Chemistry, Vol. 26, Pergamon Press, Oxford, 1966, ix + 419 pp., 120 s.

This is the first book to be written about the history of analytical chemistry as a whole and it will be of great interest to all who are concerned with analysis. The development of analytical chemistry is a fascinating tale; indeed, until the 19th century, it was in many respects the development of chemistry itself. It was the means by which the fundamental laws of chemistry were established, and it played a prominent part in the ensuing rapid developments in all branches of chemistry.

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In this book, the origins of analytical chemistry are traced to the Sumerians and Ancient Egyptians. From these roots, progress during the subsequent four millennia is described, including discussions of analysis in the Middle Ages and in the period of Iatrochemistry. The important part played by analytical chemistry in the transition of chemical thought and theory to present-day concepts is described in chapters on the Development of Chemistry in the Phlogiston Period, the Establishment of the Fundamental Laws of Chemistry, and the Period of Berzelius. Because of the subsequent proliferation and diversification of the methods of analysis, the remaining chapters deal with the evolution, to the present decade, of specific types of analytical processes such as volumetric, gravimetric, electrometric, optical and qualitative methods, and the development of analytical theory.

Dr. SZABADVARY has produced a work of considerable scholarship, based on years of extensive and detailed research in a field that has previously received scant attention. The information given is quite remarkable, especially that concerned with the 18th century and before. It ranges from the well-known to the obscure (for example, in 1808 only one platinum crucible existed in Sweden) and includes priceless reminders of days gone by—such as Winterl's procedure for the determination of phlogiston, and the establishment of the end-point of a sodium carbonate-sulphuric acid titration by the disappearance of the "alkali taste".

The text is liberally illustrated and includes concise biographies of hundreds of important contributors to the development of analytical chemistry, many of whom are still alive. There are many proofing errors, including the assignment to Aristotle of a lifespan of 162 years (p. 90) and the establishment of Amenophis as the IVth Egyptian Pharaoh (p. 6); the typesetting is also poor in places. But these are minor faults in a book that is, for a change, worth every penny of its price.

A. TOWNSHEND (Birmingham)

Anal. Chim. Acta, 39 (1967) 409-410

Organometallic Compounds. Vol. I. Compounds of Transition Metals, 2nd Edn., Covering the literature from 1937 to 1964, Edited by M. DUB, Springer-Verlag, Berlin, 1966, xviii + 828 pp., price DM 98.—

This massive book is essentially a source book of information on organometallic compounds of transition metals from Group III (lanthanides and actinides) to Group VIII. It is a non-critical, comprehensive survey of the literature from 1937 to 1964; the publishers hope to produce supplements periodically.

The information covers methods of preparation, properties and chemical reactions — all in summary form and with copious references to the original literature (2335 references in all).

The production, by an off-set process, is good and makes for easy reading. The layout makes it a simple matter to survey any particular area. This is a very worthwhile project, for which we have to thank the indulgence of chemical industry. It is not a book for the individual but should find a place in all reference and departmental libraries.

E. J. FORBES (Birmingham)

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K. B. YATSIMIRSKII, *Kinetic Methods of Analysis*, International Series of Monographs on Analytical Chemistry, Vol. 25, Pergamon Press, Oxford, 1966, xvi+155 pp., price 50 s.

In recent years there has been a growing interest in kinetic methods of analysis and this small monograph should therefore be considered a welcome volume. The book consists of 6 short chapters dealing with theoretical principles, experimental methods, data treatment and different kinetic methods of analysis. The procedures given for 40 different elements and ions should be very useful to chemists involved in trace analysis.

A number of faults can be found in this book. The important topics of differential kinetics and enzyme-catalysed reactions are not discussed; the Western literature is covered inadequately. The translation leaves much to be desired and various typographical errors appear. For example, Figures 7 and 8 on pp. 44 and 47 should be interchanged; ref. 7 is mentioned on p. 51 but does not appear in the list on p. 54; on p. 52 it is stated that the accuracy is increased to 10%, instead of 1%; on p. 71, Fig. 13 does not agree with eqn. (6) on p. 70; on p. 92, it is stated that the concentration of the solution was ten parts of a microgram (?) per millilitre; on p. 126 it is stated that the reaction is accompanied by the formation of metallic silver (correct: nickel), etc. On the whole, however, the book is full of valuable information and should prove a useful aid to those dealing with reaction rate methods.

T. HADJIIOANNOU (Athens)

Anal. Chim. Acta, 39 (1967) 411

F. W. McLAFFERTY, *Interpretation of Mass Spectra*, W. A. Benjamin, Inc., New York, 1966, xvii+229 pp., price \$9.

This is an excellent "Teach Yourself Mass Spectrometry Book". It is well organized and the material is in a logical sequence. The spectra are adequately displayed for interpretation by the reader. The first 4 chapters cover the basic subject matter of interpretative mass spectrometry. The next 5 chapters are natural extensions of the material and the whole book provides a sound basis for the would-be mass spectrometrists—whether he is basically an analytical or an organic chemist. The tenth chapter on *Solutions to Unknowns* is to the point and very understandable.

We have found this book to make a fine text for a graduate course on interpretation of IR, NMR, and MS spectra for organic and analytical chemists. Its only weakness lies in the application to teaching. It would be very advantageous to remove temporarily the *Solutions to Unknowns* chapter to make the book useful for direct classroom application. The student learns to interpret spectra much more quickly by struggling through than by knowing the answers first and then examining the spectra. The temptation to look at that chapter before struggling through is very great.

In summary the book is highly recommended for the analytical chemist and the organic chemist and is also useful as a graduate text.

J. W. ROBINSON (Baton Rouge, La.)

Anal. Chim. Acta, 39 (1967) 411

M. PESEZ, P. POIRIER ET J. BARTOS, *Pratique d'Analyse Organique Colorimétrique*, Masson et Cie, Paris, 1966, 352 pp., prix cartonné 70 F.

Cet ouvrage présente, pour le dosage colorimétrique des substances organiques, ou lorsque le dosage n'est pas possible, pour leur identification, un recueil de réactions colorées dans le visible que donnent, avec les réactifs appropriés, ces substances, soit par un groupement fonctionnel spécifique, soit grâce à la configuration moléculaire. Il s'agit donc d'une chimie analytique de structure, et non d'applications particulières, telles que celles de l'analyse chimique, biochimique ou de la pharmacie. Si les ouvrages traitant du domaine minéral sont nombreux, celui-ci, est, dans le domaine organique, unique en son genre, au moins dans le laps des 10 dernières années; il vient après le tome troisième des *Méthodes et Réactions de l'Analyse organique* de M. PESEZ ET P. POIRIER, et les techniques présentées n'ont en général pas 10 ans d'ancienneté, mais les réactions fondamentales classiques ne sont pas omises.

Toutes les techniques sont vécues, et elles ont assez souvent pour auteurs les signataires du livre; la spécificité et le domaine d'application sont indiqués; elles sont directes, exemptes de séparations préalables.

Sont ainsi passées en revue les fonctions hydroxylées, aminées, carbonylées etc. jusqu'aux composés hétérocycliques et aux stéroïdes.

M. JEAN (Gif-sur-Yvette)

Anal. Chim. Acta, 39 (1967) 412

The Chemistry of Non-aqueous Solvents. Vol. I. Principles and Techniques, Edited by J. J. LAGOWSKI, Academic Press, New York, 1966, xii + 403 pp., price \$ 16.50.

Non-aqueous solvents are becoming increasingly used in quantitative measurements, particularly in physical organic chemistry, electrochemistry and analytical chemistry. Because the relevant information is so widely scattered, the source of information provided by this volume is of great importance.

The general problems discussed in this volume concern Lewis acid-base interactions in polar solvents (D. W. MEEK), solvation of electrolytes and solution equilibria (E. PRICE), and acidity functions in amphiprotic solvents (R. G. BATES). Experimental results are summarized and interpreted in chapters on electrode potential (H. STREHLow) and on solvent extraction of inorganic species (L. I. KATZIN). Experimental techniques are discussed in chapters on handling low-boiling solvents (J. NASSLER) and fused salts (R. A. BAILEY AND G. J. JANZ).

The reviews are well documented and the literature is covered to about 1964. The writing is authoritative and lucid and the editing appears to have been done very well. This book can be recommended to analytical chemists as a valuable source of information.

P. ZUMAN (Prague)

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GAS CHROMATOGRAPHY 1966

Proceedings of the Sixth International Symposium on Gas Chromatography and Associated Techniques held at Rome in September 1966

Edited by A. B. LITTLEWOOD

6½ × 10", xii + 464 pages, 100 tables, 125 illus., 376 lit. refs.
1967, 120s., Dfl. 60.00, US\$16.00

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